

## 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 ( $\text{Rate} = k[\text{A}]^x[\text{B}]^y$ ), 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 Collision Theory - what must happen for a reaction to occur?  
What is  $E_a$ ? How does  $E_a$  correspond to the rate of a reaction? Why?  
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.  
Transition State Theory - what is a transition state? Understand potential energy diagrams, label/determine  $\Delta H$ ,  $E_a$  (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 any 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?  
Why can't you normally write the rate law from a balanced equation?  
 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  $\Delta n$ ? 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  $K^{1/3}$ .)  
 • 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  $\Delta n_{\text{gas}}$ )
- Raise or lower the temperature? (look at the sign of  $\Delta H$ )
- 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  $\Delta n_{\text{gas}}$ )

High or low  $T$ ? (look at the sign of  $\Delta H$ )

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.  $K_w = 1.0 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-]$  at  $25^\circ\text{C}$   
Know how to calculate  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ , 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  $25^\circ\text{C}$ ?)
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 so weak that it has no basic properties in water. Consider it neutral.  
If a base is strong, its conjugate acid is so weak that it has no 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  $[\text{HA}]$  and pH, calculate  $K_a$ : the pH gives the equilibrium  $[\text{H}_3\text{O}^+]$  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  $[\text{HA}]$  and  $K_a$ , find  $[\text{H}_3\text{O}^+]$ ,  $[\text{A}^-]$ , 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  $[\text{HA}]/K_a > 1000$ ). 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 first 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  $[\text{B}]$  and pH, calculate  $K_b$ : the pH gives the equilibrium  $[\text{H}_3\text{O}^+]$ , so you can find  $[\text{OH}^-]$  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  $\times K_b$  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 why 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.

## Chapter 17 Part 1

1.  $SA + SB$ ,  $WA + SB$ ,  $SA + WB$  : all of these types of reactions “go to completion”  
– When mixed, the limiting reactant will be completely consumed.

(For a WA + WB reaction, you must calculate the overall K to determine whether or not it goes to completion. K could be large or small. We usually don't do any problems with these.)

2. Common ion effect: what is it? Explain it. Why do we care?
3. Buffer: What is it? How can you tell if something is a buffer? What does it do? How?
4. Calculating the pH of a buffer (Buffer shortcut equation:
$$K_a = \left[ \text{H}_3\text{O}^+ \right] \frac{(\text{moles A}^-)}{(\text{moles HA})}$$
5. When you mix solutions, you can work in moles first and switch to M later if needed. (If you do use M first, make sure to calculate the M after mixing.)
6. Adding acid to a buffer: it will react with the conjugate base present in the buffer. (It will convert some of the A- to HA.) Two step problem: 1) Complete reaction: chart. 2) What's left? (buffer? WA? WB? SA? SB?) Deal with it appropriately.
7. Adding base to a buffer: it will react with the conjugate acid present in the buffer. (It will convert some of the HA to A-.) Two step problem: 1) Complete reaction: chart. 2) What's left? (buffer? WA? WB? SA? SB?) Deal with it appropriately.
8. Henderson-Hasselbalch equation: (Don't need to use it! Just use the buffer shortcut equation given above.) The pH of a buffer can be within 1 pH unit of the pK<sub>a</sub> of the conjugate acid in the buffer. If [HA] = [A-], the pH = pK<sub>a</sub> of the acid.
9. Making a buffer of a specific pH: 1) Choose system so that the pK<sub>a</sub> of the acid is close to the desired pH. The buffer will contain the chosen acid and its conjugate base. 2) Determine the A-/HA ratio in the buffer that will give you the desired pH. 3) Look at any other constraints in the problem: is the molarity of one of the components specified? You can find the molarity of the other component using the ratio determined in step 2. Is the total volume specified? You can find the number of moles of each using the volume and the molarities. 4) Calculate actual amounts to use.
10. Remember, there are 3 ways of making a buffer:
  1. Add HA and A- in the required ratio.
  2. Start with HA and add some OH- to it in order to convert some of the HA to A-. The number of moles of HA to start with is equal to the sum of the moles of HA and A- needed in the final buffer. The number of moles of OH- to add is the same as the number of moles of A- needed in the final buffer. If moles HA = Y and If moles OH- = Z, then the ratio of A- to HA in the resulting buffer will be (Z)/(Y-Z). WHY?

3. Start with A<sup>-</sup> and add some H<sub>3</sub>O<sup>+</sup> to it in order to convert some of the A<sup>-</sup> to HA. The number of moles of A<sup>-</sup> to start with is equal to the sum of the moles of HA and A<sup>-</sup> needed in the final buffer. The number of moles of H<sub>3</sub>O<sup>+</sup> to add is the same as the number of moles of HA needed in the final buffer. If moles A<sup>-</sup> = Y and if moles H<sub>3</sub>O<sup>+</sup> = Z, then the ratio of A<sup>-</sup> to HA in the resulting buffer will be (Y-Z)/(Z). WHY?

11. Calculate the pH if you mix two solutions: Classify the types of species present, and decide what they will do when placed in the same solution. Will they react? Will it go to completion? What's left after the reaction? Deal with it accordingly.
12. Calculating the pH at the equivalence point of a titration: equal moles of the reacting acid and base have been mixed. (If you know the molarity and volume of one of the reactants, you can determine the volume of the other one used: equal moles!) If you started with a weak acid, at the equivalence point you have a weak base. If you started with a weak base, at the equivalence point you have a weak acid. Steps: 1) Determine volume of each solution and V<sub>total</sub>. 2) Reaction goes to completion. 3) What's left? Calculate new M. 4) Set up an equilibrium chart (K<sub>a</sub> chart if you end up with an acid, K<sub>b</sub> if a base). Solve for x, find pH.
13. Titration curves: know the shape for each of the three types we studied. (SA + SB, WA + SB, SA + WB). What is the significance of the halfway point? What is the pH at the halfway point? What is the equivalence point? How do you calculate the pH at the equivalence point? How do you tell (without doing a calculation) whether the solution will be acidic, basic, or neutral at the equivalence point? Be able to choose an appropriate indicator for the titration. Know what major species are present at each region of the titration curve. What is the shape of the titration curve for a polyprotic acid or base?
14. Be able to calculate the pH at different points in the titration. [Write the overall reaction. Find moles of each reactant to start. Set up a complete reaction chart in moles. LR gets used up. What's left after the complete reaction? Classify it. (Buffer? WA? WB? SA? SB?) If it's a buffer, use the buffer shortcut. If it's a WA, use a K<sub>a</sub> chart. If it's a WB, use a K<sub>b</sub> chart. If there's excess strong acid, find the concentration. If there's excess strong base, find the concentration.]
15. What is an indicator? How does it work? What can it tell you? How do you decide what color it will be in a solution of a given pH? How do you choose an appropriate indicator for a titration?
16. Make sure to work on the extra buffer problems on the handouts. Also see the handout "acid-base, buffer notes" to make sure you know how to deal with all of the types of problems we covered in lecture. (Such as: how much SA or SB or WA or WB is needed to change the pH of the buffer to .....)



## Chapter 17 Part 2

1. “Insoluble” = “slightly soluble”.
2. Be able to use the solubility rules from Chapter 4.
3. Be able to write the  $K_{sp}$  reaction and expression for any salt. (You will need to remember or be able to figure out the ions and charges.)
4. Given solubility, calculate  $K_{sp}$ : convert solubility to M, write  $K_{sp}$  expression. Set up a chart. Solubility in M = x. Solve for  $K_{sp}$ .
5. Given  $K_{sp}$ , calculate solubility (amount that dissolves) in M or g/L: Set up a chart. Solve for x. The solubility will be the x (in units of M). Convert to g/L if needed.
6. Common ion effect – what is it? How will it affect solubility? Explain the underlying reason.  
Be able to calculate the solubility of a substance in the presence of a common ion. (Set up a chart. Check any approximations made.)
7. Will pH affect solubility? Which solid will be affected more? Explain the underlying reason. (Look for basic anions. If the anion is basic, the substance will be more soluble in acid than in water. If the anion is neutral, pH will have no effect on solubility.) Be able to calculate the overall K for dissolving a solid in acid.
8. What is a ligand? How does adding a ligand affect the solubility of a solid? Explain the underlying reason.
9. Complex ions: be able to write the  $K_f$  reaction and expression given the formula of the complex.
10. Be able to calculate the solubility of a solid in the presence of a ligand. [Find overall K (use the  $K_{sp}$  equilibrium and the  $K_f$  equilibrium), then set up an equilibrium chart and find x. Convert x to g/L if needed.]
11. Predicting whether a precipitate will form: calculate  $Q_{sp}$ , compare to  $K_{sp}$ . (Calculate concentrations after mixing.) A ppt will just start to form when  $Q = K_{sp}$ . If  $Q > K_{sp}$ , it will precipitate. If  $Q < K_{sp}$ , it won't.
12. Fractional precipitation: add an ion slowly to a mixture of two or more ions. Which ion/compound will precipitate first? The one that precipitates at a lower concentration of the ion that is being added. (It will start to ppt when  $Q = K_{sp}$ .) What is the concentration of the ion that precipitates first, just before the second compound begins to precipitate? Use the concentration of the ion that is being added in the Q expression for the first compound to calculate the

concentration of the first ion remaining. What % remains in solution? Divide the concentration remaining by the initial concentration and multiply by 100. (No equilibrium charts are needed for this type of problem.)

13. Qualitative Analysis: know the general idea behind it.  
How could you separate specific ions from each other? Refer to the solubility rules,  $K_{sp}$  values, and  $K_f$  values. It may also be possible to separate ions from each other by fractional precipitation. See #12 above.
14. Mix two solutions – calculate all ion concentrations after a precipitate forms  
1) Find all ion concentrations after mixing. 2) What is the net ionic equation? The concentrations of the spectator ions do not change. 3) Which ion is limiting? The precipitation reaction will go to completion. Find ion concentrations after the precipitation. (Set the LR = 0). 4) Consider the  $K_{sp}$  equilibrium. Set up a chart. Solve for x to find the equilibrium concentration of the LR. 5) State all ion concentrations.
15. Be able to do a similar type of problem for complex ion formation when mixing two solutions.  
1) Find all ion concentrations after mixing. 2) What is the net ionic equation? The concentrations of the spectator ions do not change. 3) Which ion is limiting? The formation reaction will go to completion. Find ion concentrations after the formation of the complex. (Set the LR = 0). 4) Consider the reverse of the  $K_f$  equilibrium. Set up a chart. Solve for x to find the equilibrium concentration of the LR. 5) State all ion concentrations.

## Chapter 19

1. Product-favored vs. reactant-favored, spontaneous vs. nonspontaneous. Thermodynamics cannot predict anything about rates of reaction!!!
2. First law of thermo. Sign conventions for q and w.
3. Driving forces for reactions/processes: dispersal of energy, dispersal of matter. (Why? Because it's more probable.) Be able to explain these driving forces.
4. Entropy (S) – disorder units: J/K•mol.
5. Second Law of Thermo (entropy is always increasing!)
6. Be able to calculate  $\Delta S$  for a phase change.
7. Third Law of Thermo (significance – it is possible to calculate absolute entropy values.)
8. Know general trends in entropy values.
9. Be able to predict the sign of  $\Delta S$  for reactions or processes.
10. Calculating  $\Delta S^\circ$  from  $S^\circ$  values (products – reactants)
11. Sign of  $\Delta G$  and spontaneity

12. Gibbs free energy :  $\Delta G = \Delta H - T\Delta S$  **Interpretation of these terms** – see lecture notes! Be able to explain what each of these terms means physically.
13.  $\Delta G^\circ$  - what does the term “standard conditions” imply? What doesn’t it tell you?
14. What is “ $\Delta G_f^\circ$ ”?
15. Calculating  $\Delta G^\circ$ 
  - 1)  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  This can be used at any temperature. Calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  from values in the appendix, and then plug in using the correct temperature. (Why is this OK to do? What are we assuming?)
  - 2) Use  $\Delta G_f^\circ$  values from the appendix to find  $\Delta G^\circ$  at 25°C. This is only valid at 25°C! Why?
16. Under what conditions (signs of  $\Delta H$  and  $\Delta S$ , magnitude of  $T$ ) will a reaction be spontaneous?
17. At what temperature will a reaction be spontaneous under standard conditions?
18. “Enthalpy-driven”, “entropy-driven”: what do these terms mean? Be able to identify reactions that are enthalpy-driven or entropy-driven (or both, or neither).
19. For nonstandard conditions:  $\Delta G = \Delta G^\circ + RT \ln Q$  (nonstandard means  $Q$  is not equal to 1.) You can use this to find out if the reaction is spontaneous under your conditions.
20. What is a thermodynamic  $K$  (or  $Q$ )?
21.  $\Delta G^\circ = -RT \ln K$  : The magnitude of  $K$  can tell you how spontaneous the reaction is under standard conditions. (But watch out – standard conditions rarely correspond to equilibrium conditions.) How does the sign and magnitude of  $\Delta G^\circ$  relate to the sign and magnitude of  $K$ ?
22. What does the value of  $\Delta G^\circ$  or  $K$  tell you? What does the value of  $\Delta G$  or  $Q$  tell you? What is the difference between  $\Delta G^\circ$  and  $\Delta G$ ?
23. Calculating  $K$  for a temperature other than 25°C: 1) get  $\Delta H^\circ$  and  $\Delta S^\circ$  for 25°C. 2) Get  $\Delta G^\circ$  for the desired temperature. 3) Calculate  $K$  for the desired temperature.
24. Estimating the solubility of a solid at a temperature other than 25°C: 1) Use  $\Delta H^\circ$  and  $\Delta S^\circ$  to find  $\Delta G^\circ$  and then  $K$  for the  $K_{sp}$  reaction. 2) Set up an equilibrium chart and use the value of  $K_{sp}$  to determine solubility.
25. Estimating the vapor pressure of a liquid at a given temperature:  $\text{Rxn} = \text{l} \rightarrow \text{g}$ ,  $K = P_{\text{gas}}$ . 1) Get  $\Delta H^\circ$  and  $\Delta S^\circ$  for the vaporization. 2) Find  $\Delta G^\circ$  for the desired temp. 3) Find  $K$  for the desired temp.  $K$  is  $vp$  in atm.

26. Estimating the boiling point of a liquid: Rxn is  $l \rightarrow g$ , normal bp means the temp at which the  $P_{\text{gas}} = 1.00 \text{ atm}$ . If  $K = 1.00 \text{ atm}$ , then  $\Delta G^\circ = 0$  and therefore  $\Delta H^\circ = T\Delta S^\circ$ . Solve for T.
27. Given K's or G's at two different temperatures, calculate  $\Delta H^\circ$  and  $\Delta S^\circ$ : 1) Use  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  to get two equations. Subtract one from the other and solve for  $\Delta S^\circ$ , then substitute  $\Delta S^\circ$  back into one of the equations to find  $\Delta H^\circ$ .
28. Criteria for how T affects how favorable a reaction is: sign of  $\Delta H$ . For an exothermic reaction, higher T means lower K. For an endothermic reaction, higher T means higher K. (To confirm, set  $\Delta H - T\Delta S = -RT\ln K$  and solve for K.)

## Chapter 20 – Things to Know

1. What is oxidation? Reduction? An oxidizing agent? A reducing agent?
2. Know how to find oxidation numbers
3. Balancing redox equations (any method)
4. Be able to sketch and label a voltaic (galvanic) cell. Direction of electron flow, + and – electrodes, anode, cathode, salt bridge, direction of ion flow, etc.
5. Standard cell notation: anode||cathode
6.  $1 \text{ V} = 1 \text{ J/C}$
7. What are standard conditions?
8. Determining  $E^\circ_{\text{cell}}$ : if it's spontaneous,  $E^\circ_{\text{cell}}$  must be positive overall. One substance must be oxidized, the other must be reduced. Find the half-reactions and their corresponding  $E^\circ$ 's, and add them. (Make sure to reverse the anode reaction first.)
9. Comparing the strengths of oxidizing and reducing agents, given a table of reduction potentials: remember, the most positive (or least negative) potential is the easiest or most favorable. For oxidizing agents, look at reductions (oxidizing agents get reduced). For reducing agents, look at oxidations – you have to reverse the reactions and their  $E^\circ$  values.
10.  $\Delta G^\circ = -nFE^\circ$ ,  $\Delta G = -nFE$  (positive overall E means spontaneous)
11. For nonstandard conditions:

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q$$

Understand and be able to explain how changes in concentrations of reactants or products will affect the voltage. (Explain both mathematically and in terms of chemical principles.)

Types of problems using this equation:

- 1) Given actual concentrations, calculate  $E_{\text{cell}}$  (must first get overall reaction, find  $E^\circ$ , get setup of Q, determine n)
- 2) Given actual voltage and some concentrations, calculate the missing concentration (first get overall rxn,  $E^\circ$ , n, Q setup)

3) Given  $K_{sp}$  and certain other concentrations, get actual voltage (use  $K_{sp}$  to calculate the missing concentration, then proceed as above.)  
 4) Given actual voltage and certain other concentrations, calculate  $K_{sp}$  (get rxn,  $E^\circ$ ,  $n$ ,  $Q$ . Calculate missing concentration. Then use  $K_{sp}$  expression to get  $K_{sp}$ ).

12. Also: concentration cells – know how to determine the voltage or one of the concentrations.

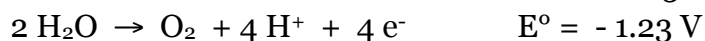
13. Relationship of  $E^\circ$  and  $K$ :

$$E^\circ_{\text{cell}} = \frac{0.0257 \text{ V}}{n} \ln K$$

14. Batteries – what are they? How do they work? What are the electrodes in a car battery? Why is a car battery rechargeable? How is a fuel cell different from a battery? What is the main advantage of fuel cells?

15. How can corrosion be prevented? What is a sacrificial anode? Why doesn't Al corrode?

16. Predict the half reactions that would occur at each electrode in aqueous electrolysis. Remember water can also react. Choose the easiest oxidation and the easiest reduction, and remember that the predicted half reactions aren't always the ones that actually occur. (Why?)



17. Electrolysis stoichiometry – use conversion factors

1) Given current, time, how much will react? (be used up or plate out)

2) Given amount reacted, current, how much time?

3) Given amount, time, how much current? Etc.

For all of these, you need a half-reaction to determine  $n$ . Also use  $1 \text{ A} = 1 \text{ C/sec}$ ,  $1 \text{ F} = 96485 \text{ C/mole e}^-$

18.  $w_{\text{max}} = -nFE$ .

For a nonspontaneous reaction being driven by a power supply,  $w = nFE_{\text{applied}}$ . In this case,  $E$  is the voltage applied by the power supply, and  $w$  is the amount of energy needed in J/mole (for the reaction as written).

## Chapter 21 – Things to Know

1. What are some important differences between nuclear reactions and chemical reactions?
2. Symbols of nuclear particles and types of radiation: alpha, beta, gamma, positron, electron, neutron, proton
3. How to write and/or balance and/or complete a nuclear equation (mass number and atomic number must balance)
4. Writing equations for different types of decay (alpha emission, beta emission, positron emission, electron capture)
5. Band of stability – general characteristics
6. Be able to predict the likely type of decay for a given radioactive nucleus.

7. How are elements artificially produced? What type of transmutations require a particle accelerator? Given the summary notation for a transmutation, be able to write the nuclear reaction. Neutrons are easily absorbed by nuclei, but protons are not. Why?
8. Half-life: definition and use, be able to sketch a graph of how the amount changes as time goes on, be able to reason out conceptually the amount left after a certain number of half lives or a certain amount of time.
9. First order rate equations:

$$\ln\left(\frac{N_t}{N_0}\right) = -kt \qquad \ln\left(\frac{A_t}{A_0}\right) = -kt \qquad t_{\frac{1}{2}} = \frac{0.693}{k}$$

10. Activity – rate of decay    Rate =  $kN_t$     units of activity: dps, dpm, Ci
11. 1 Ci =  $3.70 \times 10^{10}$  dps (nuclei/sec)    Be able to calculate the activity of any radioactive sample, and do variations using Rate =  $kN_t$ . Be able to calculate the amount of radioactive isotope present given the activity and half-life.
12. If you need the molar mass of an isotope in a problem involving activity, estimate it using the mass number of that isotope.
13.  $^{14}\text{C}$  dating: use the first order rate equation.  
 $A_0$  of  $^{14}\text{C}$  = 15.2 dpm/g C,  $t_{1/2}$  = 5715 years, t is how long ago it died.
14. Argon dating – be able to do problems using this. Must interpret the given ratio correctly.
15. Detection: film badge, Geiger counter, scintillation counter (advantages and disadvantages of each)
16.  $\Delta E = (\Delta m)c^2$      $c = 3.00 \times 10^8$  m/sec,     $\Delta m$  in kg or kg/mole, E in J
17. Given the masses of all particles involved in a reaction, calculate  $\Delta m$  and then  $\Delta E_{\text{rxn}}$ .
18. Binding energy – what is it? How do you calculate it? What is mass defect? Use binding energy per nucleon to compare stabilities of different nuclei (higher binding energy/nucleon, more stable). Be able to sketch the graph of binding energy per nucleon vs. number of nucleons and explain the reason for the shape of the graph.
19. Fission: typical reaction, sign of  $\Delta E$ , magnitude, uses, problems  
 What is “critical mass”? What is a chain reaction?
20. Fusion: typical reaction, sign of  $\Delta E$ , magnitude, uses, problems
21. Why do both fission and fusion both give off energy?
22. Biological effects of radiation
23. “ionizing radiation” – what is it? What does it do?
24. What is a “free radical”? What does it do?
25. Background radiation: what is it? sources?)
26. Types of shielding needed for different types of radiation
27. What kinds of things affect the amount of damage done by radiation?
28. What are some uses/applications of radioactivity?

## Chapter 23 – Things to Know

1. Determining electron configurations of transition metal ions. They lose electrons from the outermost s orbital first. Example:  $\text{Fe}^{3+}$   $[\text{Ar}]3d^5$
2. Exceptions to normal filling order: Cr, Cu, etc. Why?
3. Definitions/terms: complex, complex ion, coordination compound, ligand, coordination number, bidentate, polydentate.
4. Symbols, formulas and charges of ligands
5. Experimentally determining formula of complexes – # ions per formula unit, # “free”  $\text{Cl}^-$  ions, etc.
6. How to find the oxidation number of a metal in a complex
7. Geometries of complexes – be able to sketch
8. Chelating agents – why are complexes made with chelating agents stable? What are some uses of  $\text{EDTA}^{4-}$ ?
9. What is a metalloprotein?
10. Naming or writing formulas of coordination compounds or complex ions
11. Structural isomerism (linkage or coordination-sphere isomers) vs. stereoisomerism (geometric or optical isomers): give examples to illustrate the differences between these types of isomerism. Given a complex, what type of isomerism is possible?
12. Geometric isomerism (cis/trans, fac/mer) vs. optical isomerism (chiral)
13. Be able to draw cis/trans and fac/mer isomers and enantiomers
14. Color absorbed = complementary to the color observed. Use color wheel to determine colors (sketch it yourself)  
Low E, long  $\lambda$  ROYGBIV High E, short  $\lambda$
15. Shapes and orientations of d orbitals (and s, p orbitals)
16. Crystal Field theory – what is it?
17. For each geometry (octahedral, tetrahedral, and square planar), know the splitting pattern of the d levels and which d orbital is which in the splitting pattern and why!
18. What is  $\Delta$ ?
19. High spin vs. low spin – what’s the difference? How can you tell whether a complex will be high or low spin? (If it’s octahedral, you can tell by the strength of the ligand. If it’s tetrahedral, it must be high spin. Square planar must be low spin.)
20. Have a general idea of the spectrochemical series – which ligands tend to be strong, weak, medium.
21. Colors – have to do with the magnitude of  $\Delta$ .
22. Higher E of light absorbed  $\rightarrow$  greater splitting, stronger ligand
23. Paramagnetic, diamagnetic, determining # unpaired electrons
24. Why is  $\Delta_o$  always larger than  $\Delta_t$ ?

## Organic Chemistry - Things to Know (Chapter 24)

1. C makes 4 bonds, N makes 3 bonds, O makes 2 bonds, H and halogens make 1 bond.

2. C, N, O, F can **NEVER** have more than an octet!
3. Molecular geometry: under what conditions will the shape be: tetrahedral, trigonal pyramidal, bent, trigonal planar, or linear? (How many groups of electrons, how many lone pairs?) What are the bond angles in each case?
4. What are structural isomers? Give an example of compounds that are structural isomers of each other.
5. Know names of all of the n-alkanes from methane (1 C) to decane (10 C)
6. Be able to draw the structure, the condensed structural formula, and the line structure for all of the n-alkanes.
7. Be able to name and draw structures of alkanes that contain branches and/or halogen atoms (condensed structural formulas and line-bond structures)
8. Be able to identify chiral atoms in a structure (4 different substituents)
9. Cycloalkanes: cyclopentane and cyclohexane are stable, but cyclobutane and cyclopropane are not. Why?
10. Alkenes – How to draw, how to name simple ones. (Start numbering the chain from the end that's closest to the double bond.)
11. There is no rotation around a double bond. Cis and trans isomers are possible. (Why aren't cis and trans isomers possible for alkanes?)
12. Alkynes – How to draw and name simple ones. (Start numbering the chain from the end that's closest to the triple bond.)
13. Be able to identify whether a pair of molecules are isomers of each other.
14. Be able to come up with all isomers of a given molecular formula.
15. Aromatic compounds – recognize and be able to draw a benzene ring. Benzene is "resonance stabilized". What does this mean?
16. Be able to recognize and be able to draw the following types of compounds: alcohols, ethers, aldehydes, ketones, carboxylic acids, esters, amines, amides.
17. Under what conditions will each of them be soluble in water?
18. Know:
  - Rxn of a carboxylic acid with water
  - Rxn of a carboxylic acid with a strong base (products are soluble-why?)
  - Rxn of an amine with water
  - Rxn of an amine with a strong acid (products are soluble-why?)
19. Redox: oxidation corresponds to addition of O and/or removal of H  
Reduction corresponds to addition of H and/or removal of O  
Why?
20. Hybridizations:  $sp^3$ ,  $sp^2$ ,  $sp$   
If an atom is  $sp^2$  hybridized, it also has an unhybridized p orbital. If it is  $sp$  hybridized, it has two unhybridized p orbitals. Understand/be able to draw a picture of how the orbitals are arranged. Understand the difference between a sigma ( $\sigma$ ) and a pi ( $\pi$ ) bond.
21. Be able to rank compounds in order of boiling point and/or solubility and explain, in terms of the types and strengths of intermolecular forces present.



## Chapter 18 – Things to Know

1. Layers of atmosphere. Temp, pressure variations
2. Composition of atmosphere
3. photodissociation, photoionization – difference? examples?
4. How are bombarding energetic particles removed before they get to the surface of the earth?
5. Why is the ozone layer important?
6. What causes depletion of the ozone layer and how?
7. Explain the origin of acid rain. What's bad about acid rain?
8. What's dangerous about CO?
9. What is smog and where does it come from?
10. Explain the greenhouse effect. What are some greenhouse gases?
11. What are some methods of desalination? How does reverse osmosis work?
12. What processes deplete freshwater of dissolved O<sub>2</sub>?
13. How is municipal water treated?
14. What is hard water? What problems can it cause? How is water “softened”? Explain ion-exchange.