

## Chem 1B – Things to Know for Exam 2

### Chapter 16

1.  $K_a$  of acid  $\times$   $K_b$  of conjugate base =  $K_w$
2. 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<sub>3</sub>COOH)  
Positively charged nitrogen containing ions (NH<sub>4</sub><sup>+</sup>, CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>)  
Metal cations except those in groups I and II (Al<sup>3+</sup>, Fe<sup>3+</sup>)

Bases: Uncharged molecules containing nitrogen (NH<sub>3</sub>, CH<sub>3</sub>NH<sub>2</sub>)  
Anions which are conjugates of weak acids (CN<sup>-</sup>, F<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>)

Amphiprotic species: Anions with an ionizable hydrogen (HCO<sub>3</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>)  
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<sup>+</sup>, Ba<sup>2+</sup>, etc.)  
Anions of strong acids (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, etc.)

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

3. 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)
  - e. carboxylic acidsBe able to explain why in each case (explain the underlying reason, don't just re-state the rule).
4. 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:

$$K_a = [\text{H}_3\text{O}^+] \frac{(\text{moles A}^-)}{(\text{moles HA})}$$

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<sup>-</sup> to it in order to convert some of the HA to A<sup>-</sup>. The number of moles of HA 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 OH<sup>-</sup> to add is the same as the number of moles of A<sup>-</sup> needed in the final buffer. If moles HA = Y and If moles OH<sup>-</sup> = Z, then the ratio of A<sup>-</sup> 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:  $J/K \cdot mol$ .
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:  $Rxn = l \rightarrow g$ ,  $K = P_{gas}$ . 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  $P_{gas} = 1.00$  atm. If  $K = 1.00$  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

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.  $1 V = 1 J/C$
7. What are standard conditions?
8. Determining  $E^\circ_{cell}$ : if it's spontaneous,  $E^\circ_{cell}$  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 qualitatively how changes in concentrations of reactants or products will affect the voltage.

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

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?