

## Textbook Chapters for Exam 3

You still need to know many of the concepts and calculations from Chapter 7 (type 1 problems). Polyprotic acids are still fair game here and could be part of a buffer. And fraction of species is very useful for buffer systems too. All of Chapter 8 (although you can skip section 3 - I did not cover that) is valid for exam 3. You're responsible for any material covered in class whether it was on the homework or not. This review sheet covers most everything we have done. Also remember that **no equations** are given on the exams. Values for equilibrium constants are given where needed.

## Chapter 7 – Type 1 problems

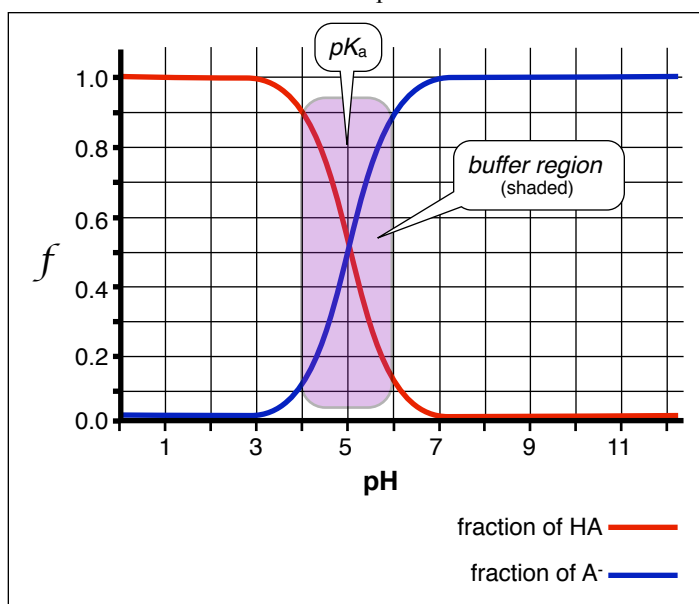
- You STILL have to be able to solve type 1 problems (like on exam 2). Type 1 problems are the starting point and the equivalence point on pH curves (titrations).

## Chapter 8 – Buffers, pH curves, Titrations, and Indicators

- Know the basic premise for making a **buffer solution**. These are “type 2” problems according to Dr. McCord (see acid/base help sheets on our web site)
- Know HOW a good buffer will neutralize both acid and/or base. Yes, this means know the actual reactions that do the neutralizing.
- What is buffer capacity (section 8.4)? remember, the amounts (concentrations) determine buffer capacity and the ratio of conjugates determines the actual pH of the buffer.
- Be able to use and identify the **Henderson-Hasselbalch equations** for both acids and bases. There are help sheets for both of these cases available on our web site.
- Be able to calculate the pH of any buffer, acidic or basic.
- What is the **common ion effect**? Where an ion has more than one source.  $A^-$  comes a little bit from HA and a lot from NaA, so  $A^-$  is a common ion.
- Know the 2 ways to prepare buffers:
  - Mix the two conjugates with proper molar ratios: e.g. HA and NaA
  - Partial neutralization. : e.g. Neutralize a portion of HA with NaOH to MAKE the  $A^-$  needed. You are essentially doing a titration but stopping somewhere in the middle. After all, that IS where you will have a nice mixture of BOTH acid and conjugate base.

## Fraction of Species

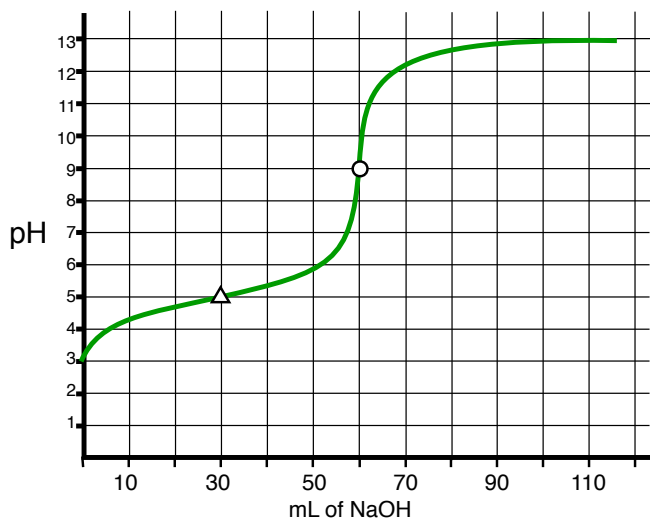
- Fraction of species still comes in very handy when it comes to understanding buffers. The buffer region is always centered about the pH that equals  $pK_a$  for the species. The useful region surrounding that pH is  $\pm 1$  pH unit. This is shown on the fraction of species diagram shown below which happen to be for a HA/ $A^-$  buffer with  $pK_a = 5.00$ .



- Be able to calculate the new pH of a buffer AFTER the addition of strong acid or strong base. Remember that you will always be subtracting from one species and adding to the other in this calculation. For example, if my acid/conjugate base ratio is 50 mmol HA and 50 mmol  $A^-$  and I add 15 mmol of  $OH^-$ . After the addition the HA is now  $50 - 15 = 35$  mmol, and the  $A^-$  is now  $50 + 15 = 65$  mmol. That 65/35 ratio is the new ratio that governs the buffer pH.

## Titration Curves

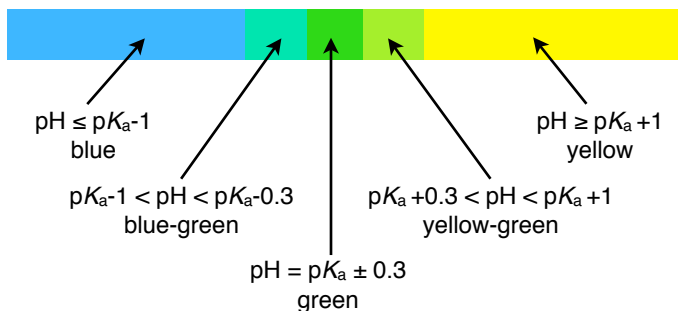
- Know how to interpret a pH (titration) curve and get the stoichiometric point (aka: equivalence point) and the  $pK_a$  (or  $pK_b$ ) for a weak acid (or base). Here is a titration curve of a weak acid ( $K_a = 1.0 \times 10^{-5}$ ) titrated with strong base.



- What's the pH at the stoichiometric point of a titration of a strong acid with strong base? a weak acid with a strong base? a weak base with a strong acid? Know the answer to this in general first - is the pH equal to, greater than, or less than 7.00 (no calculation necessary). Then know the answer exactly which means you'd have to actually calculate the answer.
- Note that on the curve given above the stoichiometric point is where the circle is on the plot (at 60 mL and a pH = 9). Also important is the pH at the halfway point which is shown by the triangle on the curve (30 mL and pH = 5). This point is important because the pH here is equal to the  $pK_a$  of the acid.
- Be able to calculate all the points on a titration curve (pH curve). This really means you now have a full knowledge of acid/base theory from start to finish. You start with only HA (chapter 7 stuff, Type 1 equations), you titrate a bit and now have a buffer (Chapter 8, buffer stuff, Type 2 equations), you then reach the stoichiometric point (back to Type 1 equations - now the conjugate of what you started with), and finally you keep going and overshoot the end point (governed only by excess titrant).

## Indicators

- Know how indicators work and how to choose the correct indicator for a given titration.
- Know the approximate range of an indicator (in general, when given  $K_a$ ). Remember, the center of its range is where  $pH = pK_a$  for the indicator. The range is  $\pm 1$  off the  $pK_a$  value. There are 2 help sheets on our web site about indicators.
- What color will an indicator be at a given pH? (you would know the  $K_a$ ). Is it red? yellow? orange? yellowish orange? bluish green? reddish purple? ... you get the idea. Remember to split the 2-pH range into 3 regions:  $\pm 0.3$  is the center and is the "perfect" blend color (like green). Outside of that range and up to  $\pm 1$  is the "-ish" colors (like bluish-green, or yellowish green). Outside the  $\pm 1$  are the straight colors (blue and yellow). Here is a figure illustrating this concept:



- Realize that you can have polyprotic acids in the mix for all of the above information. If you make a buffer with a polyprotic acid/base you need to know WHICH  $K_a$  to use. Answer, look at which conjugate pairs are the dominant species. Once you know which pair, you know which  $K_a$  to use.
- No exam questions on the "Exact Treatment of Buffered Solutions" which is section 3 of Chapter 8. SKIP this section.
- I also pointed out in class how useful a fraction of species diagram is for a titration (and buffer formation). I pointed out equivalent points on both the fraction of species diagram and a pH curve. Fraction of species plots are really very helpful in helping you visualize the various species and their various amounts at different pHs. This was mentioned previously in this review sheet.

**REMINDER:** It should go without saying but I'll say it anyway. You still have to know Chapter 7 stuff in order for Chapter 8 to make sense. Chapter 8 concepts and principles are *built* on Chapter 7 ones.

## MORE Chapter 8 - Solubility Equilibria

- Know how to calculate the molar solubility ( $x$ ) from  $K_{sp}$
- Know how to calculate  $K_{sp}$  from molar solubility. Do realize that for many problems you must first *convert* the plain old solubility (g/L, mg/L, g/100mL, ppm, ppb, etc...) into molar solubility first, then convert that to  $K_{sp}$ .
- Know also how to calculate the apparent solubility in the presence of a common ion. This is where one of the ions concentrations is already SET in the solubility product expression. My example in class was dissolving AgCl into water (no common ion) or into 0.001 M NaCl (common ion of Cl<sup>-</sup>).
- I already said this above but I'll say it again: be able to calculate molar solubility ( $x$ ) from "plain" solubility which can be expressed as grams per liter or, in general, mass per unit volume like ppm (mg/L) or even g/100 mL..
- Know how to calculate all final concentrations in saturated solutions. OK, so you can calculate  $x$  from  $K_{sp}$ . Now tell me what the actual concentration of Mg<sup>2+</sup> is, or Cl<sup>-</sup>, or OH<sup>-</sup>, or etc... sometimes it is  $x$ , sometimes it's  $2x$ , or  $3x$ , and so on. Remember,  $x$  isn't always the answer.
- REMEMBER: Not all salts have the same solution for  $x$  from  $K_{sp}$ . There are 1:1 salts, 1:2 salts, 1:3 salts, 2:3 salts and so on. Also remember that  $3^3 = 27$  and not 9.
- Be able to predict whether a precipitation will occur. This is just comparing  $Q_{sp}$  to  $K_{sp}$ . If a precipitation does occur, how much does precipitate? What are the concentrations of the ions in solution after the precipitation?

## Fractional or Selective Precipitation

- Know what will precipitate 1st, 2nd, etc.. in solutions containing many different ions that can precipitate. Remember that to do this you must calculate the minimum concentration of the added ion in order to reach the saturation point (solve the  $K_{sp}$  expression). The one that precipitates first is the one with the *lowest* concentration needed of the added ion.
- Know how to solve questions about fractional precipitation or selective precipitation. What % of the 1st precipitate is precipitated (or % NOT precipitated) when the 2nd precipitate first starts to precipitate?

## Dissolving Precipitates

- What do you add/use to get certain insoluble compounds to dissolve? Usually this involves some sort of chemical reaction with one of the ions of the salt. As the ion from the salt reacts, its concentration starts to drop and Le Chatlier's Principle takes over shifting the reaction to the right thus dissolving more salt.

## Complex Ions

- Know what a complex ion is (metal cation + ligands) and how they dissociate. Know how to write a  $K_f$  or  $K_d$  expression and how to SOLVE it. Remember that  $K_f$  is a formation constant and  $K_d$  is a dissociation constant and they have an inverse relationship.

## Combining Reactions

- When dissolving precipitates we often combine the  $K_{sp}$  reaction and the "other" reaction - like the formation of a complex ion. I illustrated this in class with CuBr dissolved it in a solution of 1.0 M NaCN (#137 in your book). The cyanide ion complexes the Cu<sup>+</sup> to make Cu(CN)<sub>3</sub><sup>2-</sup> and "pulls" the overall reaction forward. The new  $K$  is a combination (the product) of the other two  $K$ 's. Another good example of this is in your book in section 8.10 under a heading titled "Complex Ions and Solubility". This example uses AgCl in an ammonia (NH<sub>3</sub>) solution.

## Chapter 11 - Electrochemistry

Remember your redox chemistry - Chapter 4. Know the basic concepts that were presented on homework 11 (Redox Reactions).

Know how to assign oxidation numbers to all the elements in a given formula.

Know how to balance a redox equation in acid.

What is the difference in oxidation and reduction. KNOW your definitions here!

Know what a redox reaction is. What is being oxidized and what is being reduced? What is the oxidizing agent and what is the reducing agent?

What is a half-reaction? Why is it so useful? Know how to write half-reactions for both oxidations and reductions.

Know how to combine 2 half-reactions to give an overall cell reaction. (electron balance?) This is essentially the same as what was stated above except that in electrochemical cells we run the 2 half-reactions in 2 different locations - that is we have them physically separated.