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 a possibility now - for buffers and titrations. We used fraction of species for understanding buffer systems it was introduced in Chapter 7 though. 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). Also, we did go back and learn about polyprotic acids and fraction of species.

Fraction of Species
• Know what Fraction of Species is and how to calculate it. Refer to my fraction of species help sheet on our web page. Each fraction of species can be plotted vs pH (see below). Know the way the plot looks and how you would use (interpret) it to answer various questions about what species is the major species at a given pH. Below is a fraction of species plot for a diprotic acid (H2A).

Polyprotic Acids (and Bases)
Be able to write the appropriate stepwise reactions for polyprotic acids and bases. Remember the numbering for polyprotic acids and their conjugates run in opposite directions. The first proton off a diprotic acid (Ka1) is always the LAST proton going ON to the corresponding conjugate base (Kb2).

Know what the dominant species are at various pH’s for any acid or base (mono- or polyprotic). Yes, you do have to know the Ka’s or Kb’s, but those would be given. This task is much easier when you know about fraction of species and the plotting of it versus pH.

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.
• 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:
  1. Mix the two conjugates with proper molar ratios: e.g. HA and NaA
  2. 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 ± 1 pH unit. This is shown on the fraction of species diagram shown below which happen to be for a HA/A⁻ buffer with $pK_a = 5.00$.

![Fraction of Species Diagram](image)

- 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.

![Titration Curve](image)

- 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 $\text{pH} = -\log K_a$ for the indicator. The range is ±1 off the $-\log K_a$ value. There are 2 help sheets on our website 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: ±0.3 is the center and is the “perfect” blend color (like green). Outside of that range and up to ±1 is the “-ish” colors (like bluish-green, or yellowish green). Outside the ±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 ol’ 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-).

• 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\(^{2+} \) is, or Cl\(^{-} \), or OH\(^{-} \), or etc... sometimes it is \( x \), sometimes it’s 2\( x \), or 3\( x \), 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\(^+\) to make Cu(CN)\(_3\)\(^{2-}\) 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\(_3\)) solution.

A good rule here: when you ADD two reactions (say reaction \( x \) and \( y \)) together and create a “new” combination reaction, the new \( K \) for the combo is simply the product of reaction \( x \) and \( y \): \( K_{combo} = K_x \cdot K_y \)