Chapter 11 – 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 11.3)?

• Be able to use and identify the **Henderson-Hasselbalch equations** for both acids and bases.

• Be able to calculate the pH of any buffer, acidic or basic.

• What is the **common ion effect**?

• Know the 2 ways to prepare buffers:
  1. Mix the two conjugates with proper molar ratios: e.g. HA and NaA (mentioned on page 412)
  2. Partial neutralization. : e.g. Neutralize a portion of HA with NaOH to MAKE the A⁻ needed. This is what is really going on in Example 11.6 (p 421) in your book - although that don't say so. 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.

• 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⁻, well 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.

• Know how to interpret a pH curve and get the stoichiometric point (aka: equivalence point) and the pK_a (or pK_b) for a weak acid (or base).

• In general, 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.

• 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 10 stuff, Type 1 equations), you titrate a bit and now have a buffer (Chapter 11, 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).

• Know how indicators work and how to chose the correct indicator for a given titration.

• Know the approximate range of an indicator (in general, when given K_a).

• What color will an indicator be at a given pH? (you would know the K_a)

• 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.

MORE Chapter 11 - Solubility Equilibria

Calculations, how to:

• Get molar solubility (x) from K_{sp} (our book uses "s" for molar solubility)

• Get 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}.

• 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.

• I already said this above but I'll say it again, get molar solubility (x) from solubility expressed as grams per liter or in general mass per unit volume like ppm (mg/L) or even g/100 mL..

• Get all final concentrations in saturated solutions. OK, so you can calculate x from K_{sp}. Now tell me what the <u>actual</u> concentration of Mg^{2+} is, or Cl^-, or OH^-, or etc... sometimes it is x, sometimes it's $2x$, or $3x$, and so on.

• Predict whether a precipitation will occur. This is just comparing Q_{sp} to K_{sp}.

• Know what will precipitate 1st, 2nd, etc.. in solutions containing many different ions that can precipitate.

• Fractional precipitation or selective precipitation. What % of the 1st precipitate is precipitated (or % NOT precipitated) when the 2nd precipitate first starts to precipitate?

• How to get certain insoluble compound to dissolve.

• Know what a complex ion is and how they dissociate. 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.

Chapter 12 – Electrochemistry
Sections 1-8

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

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

Know what a redox reaction is. What is being oxidizing 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 the fundamental difference in voltaic (galvanic) vs electrolytic cells

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.

Know how to draw a picture of both a voltaic and an electrolytic cell if given the symbolic cell diagram (or cell "shorthand"). See section 12.5.

generic cell diagram: anode | anodic solution ‖ cathodic solution | cathode

                  where the "|" are phase changes and "‖" is a salt bridge.

Also realize that by writing out that diagram, you have just defined a set of reactants and a set of products in the overall redox reaction. You can write a reaction with a defined forward and reverse once you have the diagram (and vice versa).

What is a salt bridge and what is it used for? bottom of p 451

Which electrode is the anode? the cathode?

What's the sign convention used for the cathode and anode?

What's the significance of the SHE? p 455

What's the difference in an active and an inert electrode? What are the 2 most common inert electrodes?

How do electric current and electron flow relate? they are opposite in direction

How to use a table of standard potentials. What make the best oxidizing and reducing agents?

Calculations, how to get:

• E^0 for any half-reaction (easy, look it up in table - you *might* have to change the sign).

• E^0 for any overall cell reaction. $E^\circ_{cell} = E^\circ_R - E^\circ_L$ or $E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox}$

• Know the formulas (and how to use them) for relating ΔG, $E°$, and K:
    $\Delta G° = -nFE°$ $\Delta G° = -RT\ln K$ $nFE° = RT\ln K$

• How to calculate K (or K_{sp}) for a reaction using electrochemical data.
   The key is to find the 2 half-reactions that add up to equal the overall K or K_{sp} reaction.
   Remember, all K_{sp} reactions are just dissociations: $MX(s)$ → M^+ + X^-