REVIEW for EXAM 2

Spring 2010

Textbook Chapters for Exam 2

All of Chapters 6 and 7 PLUS remember Chapter 10 sections 10 and 11. 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 although you should know K_w .

Chemical Equilibrium

• Know how to WRITE the **mass action expression** — same as equilibrium equation

How does this expression change and the value of *K* when a reaction is "flipped", doubled, halved?

When is this expression equal to Q? When is it equal to K?

- What is thermodynamic *K*? How does that relate to K_p and K_c ?
- How does K_p relate to K_c ? When would they be equal?
- What is the relationship between ΔG_{rxn} and Q? (answer: $\Delta G = \Delta G^{\circ} + RT \ln Q$)
- What is the relationship between ΔG⁰_{rxn} and K? (answer: ΔG° = -RTlnK) This is the Chapter 10 stuff in sections 10 and 11 — you might even have to back up a bit and reread section 9.
- What are the units for an equilibrium constant? There are NO units. Why? Zumdahl refers to "apparent" units in places, I prefer to stick with the "true" no-unit version.
- Calculations involving the equilibrium constant, K
- Know how to calculate the equilibrium constant if given equilibrium amounts of reactants and products. This is where you are given the entire bottom row "e" (final equilibrium concentrations) of the equilibrium table (ICE Table) that we use.
- Know how to calculate the equilibrium constant if given initial concentrations and ONE final concentration at equilibrium. This is where you are given only ONE of the bottom row concentrations of your equilibrium table.
- Know how to calculate final (equilibrium) concentrations if given initial concentrations and the value of K_c or K_p . This is the typical type problem where you must set up and solve the equilibrium expression for *x*. Your entire bottom row will be lots of concentration formulas containing *x*.
- Know how to predict the direction of a reaction if given concentrations and a value for *K*. (hint: compare *Q* to *K*)

- Know how to predict how equilibrium shifts (L, R, NC) when a system is stressed. What are stresses? ANYTHING that takes a system OUT of equilibrium. This are typically concentration changes, pressure changes, temperature changes (ΔH is needed), and addition of a catalyst (actually adding a catalyst is a trick question, see next point). This is all a complete understanding of LeChatelier's Principle !!!
- What does a catalyst do for a given reaction? Makes it go faster which is a kinetic issue, not thermodynamic. Does the presence of a catalyst affect the equilibrium? Answer no.
- How does *K* change with temperature? The **Van't Hoff Equa**tion Which looks a lot like the Claussius-Clapeyron equation from exam 1.

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Acid/Base Theory and Aqueous Equilibria

- Know difference in a strong, weak, and non-electrolytes.
- Know your 2 Acid/Base Theories and their definitions. Those are the Arrehenius Theory and the Lowry-Bronsted Theory. We use the latter one for most of our purposes.
- Know how to calculate concentrations of ions for strong electrolyte solutions (strong acids and based fit this criteria).
- Memorize the 7 Strong Acids and 8 Strong Bases listed on my help sheet on our web site.
- Know the autoionization of water. How is it shown? What is the ion product for water? Memorize the value of K_w at 25°C — 1.0 × 10⁻¹⁴
- Know how to calculate ANY "p" function pH, pOH, pK_a, pK_b, pK_w, and in general, pX. Of course know how to do the opposite too. Given pH, what is the H⁺ or H₃O⁺ concentration?
- What's the definition of a neutral solution? What is an acidic pH? basic? neutral? How does the pH scale work? What's the relationship between pH and pOH?
- Know acid/base strength trends that is know how a conjugate strength is related to the parent acid or base strength. I spend almost an entire lecture on this. I pointed out that "opposite" in strength is really a multitude of possibilities. Strength is quantitatively shown by knowing K_a or K_b. Those two values are linked mathematically via K_w.
- Know how to write and use the mass action expressions for weak acids (*K*_a) and weak bases (*K*_b). This also includes the conjugates of each type which would be
 - salts of a weak acid/strong base (Generic: NaA)
 - salts of a weak base/strong acid (Generic: BHCl) (these last 2 points are in section 8)
- Be able to calculate the pH of a solution if only given the percent ionization of the acid or base.
 - Also be able to then calculate what the value of K_a or K_b is from the percent ionization and concentration information.
- Know when TO USE and when NOT TO USE the approximation for solving quadratics in acid/base equilibria. What is a reasonable concentration?

Polyprotic Acids (and Bases)

- Be able to write the appropriate stepwise reactions for polyprotic acids and bases. Know how to calculate the concentrations of various deprotonated species 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 (K_{a1}) is always the LAST proton going ON to the corresponding conjugate base (K_{b2}).

For a triprotic acid: $H_3A \rightleftharpoons H^+ + H_2A^-$ matches up with K_{a1}

The conjugate reaction is $H_2A^- + H_2O \rightleftharpoons H_3A + OH^-$ and matches up with K_{b3} .

The relationship between the two is $K_{a1} \cdot K_{b3} = K_w$.

• 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 K_a 's or K_b '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.

Systematic Treatment of Equilibrium

- You need as many unique equations as you have unknowns in your system. This is taken all the way to an answer in section 7.9 in your book. I don't expect you to memorize that equation but you should understand the WAY in which they went about getting there. The 2 NEW equations in that section are the material balance and the charge balance.
- Know how to write a proper *material balance* for any given aqueous system.
- Know how to write a proper *charge balance* for any given aqueous system.

Very Dilute Solutions of Acid

• This is typically answered via the charge balance equation. See section 7.10 in your book. Remember, the more dilute you make a solution, the more you approach a pH of 7.

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• 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.



• Know how to calculate the pH (and pOH) for any solution. You should refer to my Acid/Base pdf's that are available on our web page. There are a total of 6 versions of 2 Types of problems...

Chapter 7 problems are "Type 1" problems (EXAM 2) – ONE species put into solution.

Type 1 : only HA in solution (plain neutral acid)

Type 1 : only B in solution (plain neutral base)

Type 1 : only A⁻ put in solution (the SALT of a weak acid - works the same as B in solution)

Type 1 : only BH⁺ put in solution (the SALT of a weak base - works the same as HA in solution)

• Note these could also be polyprotic acids and bases

Also note that all these cases are summarized in Table 7.6 of your textbook.

HOW do you do all this? THINK! READ section 7.11 for a nice summary of your thinking.

 Know what happens with salts that contain small, highly charged cations like Al³⁺. You treat these EXACTLY like you do any weak acid, HA. However, do know HOW/WHY these things behave this way. Read the paragraph in your textbook right before Example 7.13.

NOTE: Chapter 8 problems are "Type 2" problems (EXAM 3) where TWO species put into solution (Buffers). These are listed as a point of reference only on this review sheet. Buffers will be on Exam 3, not Exam 2. Type 2 : both HA and A⁻ put in solution (acidic buffer) Type 2 : both B and BH⁺ put in solution (basic buffer) I talked about this mainly in understanding the "crossover" points on the fraction of species diagram. Those crossovers are the special points where the conjugates are equal in concentration and the pH must therefore equal pK_a .

Now your turn

- Now you start writing about all this stuff. Read your book. Over and over. Read other books if you need more help and insight. The more you expose yourself to the concepts the more things will make sense.
- Remember, I didn't purposely leave anything out here to trick you on the exam. If I talked about it in class it is fair game on the exam. Practice working problems in the book and on the homework.
- Don't forget that the questions in your book are an excellent resource for learning. You just have to make yourself do them.