

## LEARNING OBJECTIVES – SEPARATION SCIENCE – CHEMICAL EQUILIBRIUM UNIT

Thomas Wenzel, Bates College

### Introductory Material

After the introductory material covered in the text and lecture form, the student will be able to:

1. Describe the concept of activity and its relationship to concentration and rationalize how some chemical species in solution can be thought of as inactive.
2. Identify when the use of concentration instead of activity is a better approximation in an equilibrium calculation.

### *In-class Problem Set #1*

#### *Problem #1*

After completing this problem, the student will be able to:

1. Write the reaction of a weak base with water
2. Identify a chemical that is a weak base
3. Write the equilibrium constant expression for a reaction of a weak base with water
4. Use the expression  $K_a K_b = K_w$  to solve for  $K_a$  if given  $K_b$  (or vice versa)
5. Prove that  $K_a K_b = K_w$  by writing out and multiplying the appropriate equilibrium constant expressions
6. Relate and deploy the concept of a conjugate pair (two species that differ by  $H^+$ )
7. Recall that the conjugate pair of a weak acid is a weak base (and vice versa)
8. Rank the relative strengths of bases or acids
9. Write an expression for the amount of each species present at equilibrium
10. Recall that  $K_w = [H_3O^+][OH^-]$
11. Analyze the value of  $K$  to determine whether approximations can be made in the calculation.
12. Predict whether the change in the concentration of base is negligible compared to the initial concentration
13. Predict whether the amount of hydroxide ion initially in solution will likely be small compared to the amount produced
14. Make any valid approximations and solve the equilibrium constant expression for concentrations
15. Validate any approximations using the 5% criteria
16. Recall typical  $K_a$  (or  $pK_a$ ) and  $K_b$  (or  $pK_b$ ) values for weak acids and bases, respectively
17. Recall that  $pH = -\log[H_3O^+]$ ,  $pK_a = -\log K_a$  and  $pK_b = -\log K_b$

### *Problem #2*

After completing this problem, the student will be able to:

1. Solve the problem using either the  $K_a$  or  $K_b$  expression using procedures established in problem 1
2. Determine whether, for a conjugate pair, the base is a stronger base than the acid is an acid
3. Recall that a solution that has appreciable concentrations of both members of a conjugate pair is a buffer
4. Demonstrate qualitatively using appropriate reactions how a buffer can resist changes in pH
5. Derive the Henderson-Hasselbalch expression for a buffer
6. Use the Henderson-Hasselbalch expression to explain and show quantitatively that a buffer solution resists changes in pH
7. Calculate the pH of a buffer using the Henderson-Hasselbalch expression
8. Relate the criteria that are used in selecting a buffer

### *Problem #3*

After completing this problem, the student will be able to:

1. Relate the common chemical nomenclature that is used to denote cationic and anionic species (Name, using the appropriate suffixes, chemical species that are cationic or anionic)
2. Identify a compound that is a weak acid
3. Identify whether an anion is an anion of a strong acid
4. Identify whether a cation is a cation of a strong base
5. Recall that the conjugate pair of a strong acid or base is produced to an extent of 100% and exists as a spectator ion in solution
6. Solve for the pH of a solution of a weak acid

### *Problem #4 and 5*

After completing these problems, the student will be able to:

1. Determine that a weak acid and a weak base undergo a neutralization reaction
2. Write a neutralization reaction
3. Write the equilibrium constant expression for  $K_n$
4. Prove that  $K_n = K_a K_b / K_w$
5. Determine  $K_n$  for a neutralization reaction
6. Explain why the  $K_n$  value for a neutralization reaction will always be large when either the acid or base is strong
7. Explain when  $K_n$  is expected to be large and when  $K_n$  may be small for a neutralization reaction
8. Determine whether a neutralization reaction goes to completion

9. Be able to solve for the final concentration of all four species present in a neutralization reaction
10. Explain why a neutralization reaction involving a weak acid and a weak base will often lead to the formation of a buffer.
11. Calculate the concentration of species present in a neutralization reaction with a large value of  $K$ .
12. Solve for the final pH of a solution in which a neutralization reaction occurs.

### ***In-class Problem Set #2***

After completing this problem, the student will be able to:

1. Explain why, before the equivalence point, either the molar concentrations or the mole ratio of the conjugate pair can be used to calculate the pH
2. Determine where the equivalence point occurs in an acid-base titration
3. Calculate the pH at any point in an acid-base titration including the equivalence point
4. Calculate the percent of the base has been converted to its conjugate acid at the equivalence point
5. Assess whether the titration is suitable for analytical purposes

### ***In-class Problem Set #3***

#### ***Problem #1***

After completing this problem, the student will be able to:

1. Write the appropriate reactions and equilibrium constant expressions for a solution of a polyprotic acid
2. Write an expression for the concentration of  $\text{H}_3\text{O}^+$  in terms of other species produced by the dissociation of the acid
3. Explain why the first reaction in the sequence is much more significant than any subsequent reactions in the stepwise dissociation of a solution of a polyprotic acid
4. Solve for the pH of the solution of a polyprotic acid

#### ***Problem #2***

After completing this problem, the student will be able to:

1. Write the appropriate reactions and equilibrium constant expressions for a solution of a polybasic compound
2. Determine the  $K_b$  values for each reaction in the series
3. Explain why the first reaction in the sequence is much more significant than any subsequent reactions in the stepwise reaction of a polybasic compound

4. Solve for the pH of the solution of a polybasic compound
5. Name polyprotic acids as well as the other species in the series of reactions that represent the dissociation of a polyprotic acid.

### *Problem #3*

After completing this problem, the student will be able to:

- 1 Determine the concentration of species in a solution of a polybasic compound that has a quantity of strong acid added to it
- 2 Determine the concentration of species in a solution of a polyprotic acid that has a quantity of strong base added to it
- 3 Explain why a polyprotic system can be used to prepare more than one buffer, each of which is centered around the different pK<sub>a</sub> values for the polyprotic acid
- 4 Solve for the pH of the solution prepared by adding a strong acid to a polybasic compound or strong base to a polyprotic acid

### *Problem #4*

After completing this problem, the student will be able to:

- 1 Determine the redistribution of species that occurs when phosphoric acid is mixed with sodium phosphate
- 2 Show that the redistribution of species that occurs in learning objective 1 usually leads to the formation of a buffer
- 3 Solve for the pH when two or more species in a polyprotic acid system are mixed together in solution

### *Problem #5*

After completing this problem, the student will be able to:

- 1 Write an expression for the concentration of H<sub>3</sub>O<sup>+</sup> in terms of other species of a polyprotic acid system when the initial solution is prepared using an intermediate species
- 2 Derive an expression for H<sub>3</sub>O<sup>+</sup> using the appropriate K<sub>a</sub> expressions and the expression written in learning objective #1.
- 3 Show that, in most circumstances, the pH of a solution prepared using only an intermediate species is the average of the two appropriate pK<sub>a</sub> values

## ***In-class Problem Set #4***

### *Problem #1*

After completing this problem, the student will be able to:

1. Write the reaction of a metal ion and ligand to form water-soluble metal complexes.
2. Write the expression for  $K_F$
3. Solve for the concentration of free metal ion, unbound ligand, and metal complex if given the initial concentration of metal and ligand
4. Describe what is meant by a chelating ligand
5. Rationalize why entropy effects account in large part for the high formation constants of chelating ligands with metal ions
6. Describe broad families of ligands (anionic species and nitrogen bases)
7. Write both the neutral and zwitterionic structurew of a ligand such as EDTA

### *Problem #2*

After completing this problem, the student will be able to:

1. Write and evaluate the expression for the fraction of the ligand (weak base) that exists in the fully deprotonated form.
2. Write and evaluate the expression for the fraction of any other form of the ligand (any species in a series of acid or base reactions)
3. Show that these fractions are only dependent on the pH and not the total concentration of the ligand
4. Explain why the  $\alpha$ -value for the fully deprotonated ligand is high at basic pH and low at acidic pH.
5. Explain why the  $\alpha$ -value for the fully protonated ligand is high at acidic pH and low at basic pH.
6. Explain why the  $\alpha$ -value for an intermediate species is low at highly acidic or basic pH values and maximized at an intermediate pH value.
7. Graph the  $\alpha$ -values for all of the species of a polyprotic acid.
8. Evaluate the conditional constant at any pH.
9. Use the conditional constant to determine the final concentrations of unbound metal ion, metal complex, and all forms of the unbound ligand if given the initial concentration of metal and ligand.
10. Explain why the formation of a metal complex with a ligand that is a weak base is more favorable at basic pH.
11. Write and evaluate the expression for the fraction of a metal that exists in solution as its unbound metal ion when in the presence of a competing ligand.
12. Show that this fraction only depends on the concentration of the competing ligand, provided complexation does not lower its value appreciably.
13. Write and evaluate the fraction of all other metal complexes with the competing ligand.

14. Incorporate the  $\alpha$ -value for the unbound metal ion into the  $K_F$  expression and determine the value of the conditional constant.
15. Use the conditional constant to determine the final concentrations of unbound metal ion, desired metal complex, and all forms of the unbound ligand and other metal complexes if given the initial concentration of metal and ligand.

### ***In-class Problem Set #5***

#### ***Problem A***

After completing this problem, the student will be able to:

1. Write the reaction for the dissolution of a slight soluble metal salt.
2. Write the appropriate  $K_{sp}$  expression
3. Write two expressions for the solubility of the complex; one in terms of the concentration of metal cation, the other in terms of the concentration of anion.
4. Substitute the two solubility expressions into  $K_{sp}$  and solve for the solubility of the metal salt.

#### ***Problem B***

After completing this problem, the student will be able to

1. Write two expressions for the solubility of the complex; one in terms of the concentration of metal cation, the other in terms of the concentration of anion and all protonated forms of the anion.
2. Recognize that if the pH is known, the concentration of anion in the  $K_{sp}$  expression can be written as its fraction times the total concentration.
3. Substitute the new expression for the concentration of anion into the  $K_{sp}$  expression and solve for the solubility of the metal salt.

#### ***Problem C***

After completing this problem, the student will be able to

1. Write two expressions for the solubility of the complex; one in terms of the concentration of metal cation and all of its water-soluble complexes, the other in terms of the concentration of anion and all protonated forms of the anion.
2. Recognize that if the pH is known and the concentration of ligand is known, the concentration of anion and cation in the  $K_{sp}$  expression can be written as their fractions times the total concentration.
3. Substitute the new expressions for the concentration of anion and metal cation into the  $K_{sp}$  expression and solve for the solubility of the metal salt.

### *Problem D*

After completing this problem, the student will be able to

1. Recognize that if the pH of a solution is unknown, and if solubilization of a metal salt will alter the pH, that a series of simultaneous equations are needed to solve for the solubility of the metal salt.
2. Write the series of simultaneous equations that are necessary to solve for the solubility
3. Write the expression for the charge balance of a solution.
4. Write the expressions for all mass balances of a solution.

After completing the homework set on precipitation, the student will be able to:

1. Predict whether a precipitate will form in a solution of two ions.
2. Determine whether one ion can be quantitatively precipitated in the presence of another.