IONIC EQUILIBRIA IN AQUEOUS SYSTEMS Chapter 19 Outline

Text Problems: # 12, 15, 16, 18, 19, 42(C), 50, 56(also calculate S in pure water) + Supplementary Questions (attached)

Text Sample Problems: The text has a number of excellent sample problems (solved in detail) in each section. I would recommend that you study these problems + the "follow up" problems, which have brief solutions at the end of the chapter.

Sect.	Title and Comments	Required ?
1.	Equilibria of Acid-Base Buffers We will also add a section on amino acids/buffers	YES
2.	Acid-Base Titration Curves	YES
3.	Equilibria of Slightly Soluble Ionic Compounds	YES
4.	Equilibria Involving Complex Ions	NO

Chapter 19

Supplementary Homework Questions

Buffers

- S1. In a buffer solution, if $[A^-] > [HA]$, which of the following must be true?
 - a. pH < pK_a
 - b. $pH = pK_a$
 - c. $pH > pK_a$ d. pH < 7.00
 - e. pH > 7.00
- S2. A buffer solution is 0.080 M in lactic acid ($K_a = 1.8 \times 10^{-4}$) and 0.070 M in sodium lactate.
 - The pH of the solution is
 - a. 2.86.
 - b. 3.68.
 - c. 3.80.
 - d. 4.18.
 - e. 4.62.
- S3. Which acid, in combination with its conjugate base, would be the best choice to make a buffer of pH = 4.35?
 - a. acetic acid (K_a = 1.8×10^{-5})
 - b. benzoic acid ($K_a = 6.3 \times 10^{-5}$)
 - c. formic acid (K_a = 1.8×10^{-4})
 - d. hydrofluoric (K_a = 7.2×10^{-4})
 - e. nitrous acid (K_a = 4.5×10^{-4})
- S4. If a buffer is made up using 1.00 mole of a weak acid ($pK_a = 5.00$) and 0.90 mole of its conjugate base, which of the following must be true?
 - a. pH < 5.00 b. pH = 5.00 c. pH > 5.00 d. pH = 7.00 e. pH > 7.00

S5. For each of the solutions below, indicate whether the solution would be a buffer.

- a) A solution prepared by adding 1 L of 0.50 M NaOH to 1 L of 2 L of 0.5 M HAc (acetic acid)
- b) A solution prepared by adding 1 L of 1.0 M HCl to 2 L of 0.80 M NaAc (sodium acetate)
- c) A solution prepared by adding 1 L of 0.50 M H₂CO₃ to 1 L of 0.50 M K₂CO₃
- d) A solution prepared by adding 1 L of 0.50 M HCl to 2 L of 0.50 M K₂CO₃
- e) A solution prepared by adding 3 L of 0.50 M HCl to 2 L of 0.50 M K₂CO₃
- f) A solution prepared by adding 5 L of 0.50 N HCl to 2 L of 0.50 M K_2CO_3

g) A solution prepared by adding 1 L of 0.25 M HNO $_3$ to 1 L of 0.50 M K $_2$ Prop (potassium propanoate)

h) A solution prepared by adding 1 L of 0.25 M NaOH to 1 L of 0.50 M K_2 Prop (potassium propanoate)

- S6. The following **independent** questions are on pH calculations in solutions of Arsenic Acid (H₃AsO₄) and its various anions. H₃AsO₄ is a triprotic acid with Acid Dissociation Constants: $K_a' = 6.0x10^{-3}$, $K_a'' = 1.0x10^{-7}$, $K_a''' = 3.2x10^{-12}$
 - a) Calculate the pH of a solution prepared by mixing 3.0 L of 0.40 M H₃AsO₄ with 1.0 L of 0.80 M KOH.
 - b) Calculate the pH of a solution prepared by mixing 3.0 L of 0.40 M H₃AsO₄ with 2.0 L of 0.80 M KOH.
 - c) Calculate the pH of a solution prepared by mixing 3.0 L of 0.40 M H₃AsO₄ with 4.0 L of 0.80 M KOH.
 - d) Calculate the pH of a solution prepared by mixing 3.0 L of 0.40 M Na₃AsO₄ with 1.0 L of 0.80 M HNO₃.
 - e) Calculate the pH of a solution prepared by mixing 3.0 L of 0.40 M Na₃AsO₄ with 2.0 L of 0.80 M HNO₃.
 - f) Calculate the pH of a solution prepared by mixing 3.0 L of 0.40 M Na₃AsO₄ with 4.0 L of 0.80 M HNO₃.
 - g) What will be the pH of a buffer solution containing $[H_2AsO_4^-] = 0.40 \text{ M}$ and $[HAsO_4^{2-}] = 0.60 \text{ M}$?

- h) What will be the pH of a buffer solution containing $[HAsO_4^{2-}] = 0.40 \text{ M}$ and $[AsO_4^{3-}] = 0.15 \text{ M}$?
- i) What value of the ratio, $[H_2AsO_4^-]/[H_3AsO_4]$, is required to prepare a buffer with pH = 2.60?
- j) What value of the ratio, $[HAsO_4^{2-}]/[AsO_4^{3-}]$, is required to prepare a buffer with pH = 10.90?

Titration

- S7. 138. mL of 0.105 M KOH was required to completely titrate a 25.00 mL sample of H_3PO_4 . Determine the Molarity of the H_3PO_4 sample.
- S8. Consider the weak base, pyridine $[C_5H_5N \equiv Pyr]$, which has $K_b = 1.7 \times 10^{-9}$. Titration of pyridine with a strong acid causes formation of the pyridinium ion $[C_5H_5NH^+ \equiv PyrH^+]$.

(a) Calculate the pH of a solution formed by adding 30.00 mL of 0.20 M HNO₃ to 50.00 mL of 0.20 M pyridine.

(b) Calculate the pH of a solution formed by adding 50.00 mL of 0.20 M HNO₃ to 50.00 mL of 0.20 M pyridine.

- S9. Vitamin C ($C_6H_8O_6$, M = 176.) is a monoprotic acid. To analyze a Vitamin C capsule weighing 0.64 grams by titration, 23.6 mL of 0.120 M NaOH was required. Calculate the mass percent of Vitamin C in the capsule.
- S10. When 6.00 grams of a sample of impure Strontium Hydroxide [Sr(OH)₂, M = 121.6] is titrated with 0.340 M HNO₃, it takes 224. mL of the strong acid to completely titrate the base. Calculate the mass percent of impurity in the Strontium Hydroxide sample.

Solubility Product

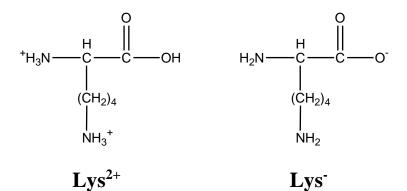
- S11. The solubility product of the slightly soluble salt, Ag_2CO_3 , is $K_{sp} = 6.2 \times 10^{-12}$.
 - a) What is the solubility and the $[Ag^+]$ and $[CO_3^{2-}]$ concentrations in pure water?
 - b) What is the solubility in a solution containing Ag₂CO₃ and 0.20 M AgNO₃?
 - c) What is the concentration of silver ions, [Ag⁺] in a solution containing Ag₂CO₃ and 0.10 M K₂CO₃?

S12. The solubility products of two sparingly soluble Bromide (Br⁻) salts are: AgBr - $K_{sp} = 5.4 \times 10^{-13}$, HgBr₂ - $K_{sp} = 6.2 \times 10^{-20}$ Consider a solution which initially contains 5.0×10^{-5} M Ag⁺(aq) and 5.0×10^{-5} M Hg²⁺(aq). KBr (a strong electrolyte) is added until [Br⁻] = 2.0×10^{-8} M. Which of the above salts (AgBr and HgBr₂) will precipitate? S13. Mercury(I) Sulfate, Hg₂SO₄, is a sparingly soluble salt with $K_{sp} = 6.5 \times 10^{-7}$.

If 1200 mL of 0.010 M K₂SO₄(aq) is mixed with 800 mL of 0.020 M HgNO₃(aq), calculate the concentrations of $[Hg^+]$ and $[SO_4^{2-}]$ in the resulting solution and **determine whether or not** Hg₂SO₄(s) will precipitate.

Amino Acids

S14. Consider the amino acid, Lysine. The most positive and most negative forms are shown below:



The three pKa's are: $pKa'(\alpha$ -COOH) = 2.18 $pKa''(\alpha$ -NH₃⁺) = 8.95 $pKa'''(\epsilon$ -NH₃⁺) = 10.53

- a) What is the isoelectric point?
- b) At what pH does one have 100% Lys⁺.
- c) At what pH does one have 50% Lys and 50% Lys⁻
- d) What is the composition of the solution at pH = 2.18

Answers to the Supplementary Homework Questions are posted on the course web site. Questions about these Problems will be answered in Recitation