## 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

1. Equilibria of Acid-Base Buffers

## Required?

We will also add a section on amino acids/buffers
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 $\left[\mathrm{A}^{-}\right]>[\mathrm{HA}]$, which of the following must be true?
a. $\mathrm{pH}<\mathrm{pK}_{\mathrm{a}}$
b. $\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}$
c. $\mathrm{pH}>\mathrm{pK}_{\mathrm{a}}$
d. $\mathrm{pH}<7.00$
e. $\mathrm{pH}>7.00$

S2. A buffer solution is 0.080 M in lactic acid $\left(\mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-4}\right)$ 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 $\mathrm{pH}=4.35$ ?
a. acetic acid $\left(\mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5}\right)$
b. benzoic acid $\left(\mathrm{K}_{\mathrm{a}}=6.3 \times 10^{-5}\right)$
c. formic acid $\left(\mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-4}\right)$
d. hydrofluoric $\left(\mathrm{K}_{\mathrm{a}}=7.2 \times 10^{-4}\right)$
e. nitrous acid $\left(\mathrm{K}_{\mathrm{a}}=4.5 \times 10^{-4}\right)$

S4. If a buffer is made up using 1.00 mole of a weak acid $\left(\mathrm{pK}_{\mathrm{a}}=5.00\right)$ and 0.90 mole of its conjugate base, which of the following must be true?
a. $\mathrm{pH}<5.00$
b. $\mathrm{pH}=5.00$
c. $\mathrm{pH}>5.00$
d. $\mathrm{pH}=7.00$
e. $\mathrm{pH}>7.00$

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 $0.50 \mathrm{M} \mathrm{H}_{2} \mathrm{CO}_{3}$ to 1 L of $0.50 \mathrm{M} \mathrm{K}_{2} \mathrm{CO}_{3}$
d) A solution prepared by adding 1 L of 0.50 M HCl to 2 L of $0.50 \mathrm{M} \mathrm{K}_{2} \mathrm{CO}_{3}$
e) A solution prepared by adding 3 L of 0.50 M HCl to 2 L of $0.50 \mathrm{M} \mathrm{K}_{2} \mathrm{CO}_{3}$
f) A solution prepared by adding 5 L of 0.50 N HCl to 2 L of $0.50 \mathrm{M} \mathrm{K}_{2} \mathrm{CO}_{3}$
g) A solution prepared by adding 1 L of $0.25 \mathrm{M} \mathrm{HNO}_{3}$ to 1 L of $0.50 \mathrm{M} \mathrm{K}_{2} \operatorname{Prop}$ (potassium propanoate)
h) A solution prepared by adding 1 L of 0.25 M NaOH to 1 L of $0.50 \mathrm{M} \mathrm{K}_{2} \operatorname{Prop}$ (potassium propanoate)

S6. The following independent questions are on pH calculations in solutions of Arsenic Acid $\left(\mathrm{H}_{3} \mathrm{AsO}_{4}\right)$ and its various anions. $\mathrm{H}_{3} \mathrm{AsO}_{4}$ is a triprotic acid with Acid Dissociation Constants: $\mathrm{K}_{\mathrm{a}}{ }^{\prime}=6.0 \times 10^{-3}, \mathrm{~K}_{\mathrm{a}}{ }^{\prime \prime}=1.0 \times 10^{-7}, \mathrm{~K}_{\mathrm{a}}{ }^{\prime \prime \prime}=3.2 \times 10^{-12}$
a) Calculate the pH of a solution prepared by mixing 3.0 L of $0.40 \mathrm{M} \mathrm{H}_{3} \mathrm{AsO}_{4}$ with 1.0 L of 0.80 M KOH .
b) Calculate the pH of a solution prepared by mixing 3.0 L of $0.40 \mathrm{M} \mathrm{H}_{3} \mathrm{AsO}_{4}$ with 2.0 L of 0.80 M KOH .
c) Calculate the pH of a solution prepared by mixing 3.0 L of $0.40 \mathrm{M} \mathrm{H}_{3} \mathrm{AsO}_{4}$ with 4.0 L of 0.80 M KOH .
d) Calculate the pH of a solution prepared by mixing 3.0 L of $0.40 \mathrm{M} \mathrm{Na}_{3} \mathrm{AsO}_{4}$ with 1.0 L of $0.80 \mathrm{M} \mathrm{HNO}_{3}$.
e) Calculate the pH of a solution prepared by mixing 3.0 L of $0.40 \mathrm{M} \mathrm{Na}_{3} \mathrm{AsO}_{4}$ with $2.0 \mathrm{~L}^{\text {of }} 0.80 \mathrm{M} \mathrm{HNO}_{3}$.
f) Calculate the pH of a solution prepared by mixing 3.0 L of $0.40 \mathrm{M} \mathrm{Na}_{3} \mathrm{AsO}_{4}$ with $4.0 \mathrm{~L}^{\text {of }} 0.80 \mathrm{M} \mathrm{HNO}_{3}$.
g) What will be the pH of a buffer solution containing $\left[\mathrm{H}_{2} \mathrm{AsO}_{4}^{-}\right]=0.40 \mathrm{M}$ and $\left[\mathrm{HAsO}_{4}{ }^{2-}\right]=0.60 \mathrm{M}$ ?
h) What will be the pH of a buffer solution containing $\left[\mathrm{HAsO}_{4}{ }^{2-}\right]=0.40 \mathrm{M}$ and $\left[\mathrm{AsO}_{4}{ }^{3-}\right]=0.15 \mathrm{M}$ ?
i) What value of the ratio, $\left[\mathrm{H}_{2} \mathrm{AsO}_{4}^{-}\right] /\left[\mathrm{H}_{3} \mathrm{AsO}_{4}\right]$, is required to prepare a buffer with $\mathrm{pH}=2.60$ ?
j) What value of the ratio, $\left[\mathrm{HAsO}_{4}{ }^{2-}\right] /\left[\mathrm{AsO}_{4}{ }^{3-}\right]$, is required to prepare a buffer with $\mathrm{pH}=10.90$ ?

## Titration

S7. 138. mL of 0.105 M KOH was required to completely titrate a 25.00 mL sample of $\mathrm{H}_{3} \mathrm{PO}_{4}$. Determine the Molarity of the $\mathrm{H}_{3} \mathrm{PO}_{4}$ sample.

S8. Consider the weak base, pyridine $\left[\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N} \equiv \mathrm{Pyr}\right]$, which has $\mathrm{K}_{\mathrm{b}}=1.7 \mathrm{x} 10^{-9}$. Titration of pyridine with a strong acid causes formation of the pyridinium ion $\left[\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{NH}^{+} \equiv \mathrm{PyrH}^{+}\right]$.
(a) Calculate the pH of a solution formed by adding 30.00 mL of $0.20 \mathrm{M} \mathrm{HNO}_{3}$ to 50.00 mL of 0.20 M pyridine.
(b) Calculate the pH of a solution formed by adding 50.00 mL of $0.20 \mathrm{M} \mathrm{HNO}_{3}$ to 50.00 mL of 0.20 M pyridine.

S9. Vitamin $\mathrm{C}\left(\mathrm{C}_{6} \mathrm{H}_{8} \mathrm{O}_{6}, \mathrm{M}=176\right.$. $)$ 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 $\left[\operatorname{Sr}(\mathrm{OH})_{2}, \mathrm{M}=121.6\right]$ is titrated with $0.340 \mathrm{M} \mathrm{HNO}_{3}$, 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, $\mathrm{Ag}_{2} \mathrm{CO}_{3}$, is $\mathrm{K}_{\mathrm{sp}}=6.2 \times 10^{-12}$.
a) What is the solubility and the $\left[\mathrm{Ag}^{+}\right]$and $\left[\mathrm{CO}_{3}{ }^{2-}\right]$ concentrations in pure water?
b) What is the solubility in a solution containing $\mathrm{Ag}_{2} \mathrm{CO}_{3}$ and $0.20 \mathrm{M} \mathrm{AgNO}_{3}$ ?
c) What is the concentration of silver ions, $\left[\mathrm{Ag}^{+}\right]$in a solution containing $\mathrm{Ag}_{2} \mathrm{CO}_{3}$ and $0.10 \mathrm{M} \mathrm{K}_{2} \mathrm{CO}_{3}$ ?

S12. The solubility products of two sparingly soluble Bromide ( $\mathrm{Br}^{-}$) salts are:

$$
\mathrm{AgBr}-\mathrm{K}_{\mathrm{sp}}=5.4 \times 10^{-13}, \mathrm{HgBr}_{2}-\mathrm{K}_{\mathrm{sp}}=6.2 \times 10^{-20}
$$

Consider a solution which initially contains $5.0 \times 10^{-5} \mathrm{M} \mathrm{Ag}^{+}(\mathrm{aq})$ and $5.0 \times 10^{-5} \mathrm{M} \mathrm{Hg}^{2+}(\mathrm{aq}) . \mathrm{KBr}(\mathrm{a}$ strong electrolyte) is added until $\left[\mathrm{Br}^{-}\right]=2.0 \times 10^{-8} \mathrm{M}$. Which of the above salts $\left(\mathrm{AgBr}\right.$ and $\left.\mathrm{HgBr}_{2}\right)$ will precipitate?

S13. Mercury(I) Sulfate, $\mathrm{Hg}_{2} \mathrm{SO}_{4}$, is a sparingly soluble salt with $\mathrm{K}_{\mathrm{sp}}=6.5 \times 10^{-7}$.
If 1200 mL of $0.010 \mathrm{M} \mathrm{K}_{2} \mathrm{SO}_{4}(\mathrm{aq})$ is mixed with 800 mL of $0.020 \mathrm{M} \mathrm{HgNO}_{3}(\mathrm{aq})$, calculate the concentrations of $\left[\mathrm{Hg}^{+}\right]$and $\left[\mathrm{SO}_{4}{ }^{2-}\right]$ in the resulting solution and determine whether or not $\mathrm{Hg}_{2} \mathrm{SO}_{4}(\mathrm{~s})$ will precipitate.

## Amino Acids

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


Lys ${ }^{2+}$


Lys ${ }^{-}$

The three pKa 's are: $\mathrm{pKa}^{\prime}(\alpha-\mathrm{COOH})=2.18 \quad \mathrm{pKa}^{\prime}{ }^{\prime}\left(\alpha-\mathrm{NH}_{3}{ }^{+}\right)=8.95 \quad \mathrm{pKa}{ }^{\prime}{ }^{\prime}\left(\varepsilon-\mathrm{NH}_{3}{ }^{+}\right)=10.53$
a) What is the isoelectric point?
b) At what pH does one have $100 \% \mathrm{Lys}^{+}$.
c) At what pH does one have $50 \%$ Lys and $50 \%$ Lys $^{-}$
d) What is the composition of the solution at $\mathrm{pH}=2.18$

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

