Chapter 17: Additional Aspects of Aqueous Equilibria

- Buffer Problems
- Titrations
- Precipitation Rx

**Common Ion Effect** - The effect that a common ion (from two different sources) has on an equilibrium. (LeChatelier's Principle)

**Buffer** - a solution that has appreciable concentrations of a conjugate acid (weak) and
its conjugate base (weak). A buffer is prepared by adding a conjugate base (as a salt) to a solution of the conjugate acid (or the reverse). **A buffer is resistant to changes in pH.**

Which of the following solutions is buffered
a) HCl/NaCl
b) HF/NaF
c) HF/NaCl
d) NH₃/NH₄Cl
e) HOAc/NaOAc
A buffer neutralizes acid by:
\[
\begin{align*}
H^+ + \text{con. base} & \rightarrow \text{con. acid} \\
H^+ + A^- & \rightarrow HA
\end{align*}
\]

A buffer neutralizes base by:
\[
\begin{align*}
\text{OH}^- + \text{con. acid} & \rightarrow \text{con. base} \\
\text{OH}^- + HA & \rightarrow A^- + H_2O
\end{align*}
\]
Calculate the pH of a) .10M HOAc b) a solution .10M in HOAc and .050M in NaOAc
and c) .10M in HOAc and .10M in NaOAc d) a solution .10M in HOAc and .15M in NaOAc.
\[ K_a = 1.8 \times 10^{-5} \]

**Henderson Hasselbalch Equation** - an equation that gives the pH of a buffer solution in terms of the ratio of concentrations of the conjugate acid and base and the pK$_a$.

\[ pH = pK_a + \log \frac{[A^-]}{[HA]} \]
Calculate the pH after the addition of 10.0 ml of .100M HCl and 10.0ml of .100M NaOH to a) 100. ml of pure water and b) 100. ml of a solution that is .100M in HOAc ($K_a=1.8\times10^{-5}$, $pK_a=4.74$) and .100 M in NaOAc.
pH

water buffer
<table>
<thead>
<tr>
<th>Reaction</th>
<th>pH</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}^+$</td>
<td>7.00</td>
<td>10.0 ml</td>
</tr>
<tr>
<td>$\text{OH}^-$</td>
<td>2.04</td>
<td>4.74</td>
</tr>
<tr>
<td>$\text{H}^+$</td>
<td>11.96</td>
<td>4.65</td>
</tr>
</tbody>
</table>

**Titration Curve** - a plot of pH vs volume of added base (or acid) in a neutralization reaction (acid base rx).
Equivalence Point - the point in a titration when moles of one reactant have been exactly consumed by the addition of the other reactant. (moles of acid and base are equal for a 1:1 Rx)
**Indicator** - a species which is added to a reaction mixture to visually indicate the passage of the equivalence point. Acid base indicators are organic dyes which are different colors in solutions of different pH's.

**End Point** - the point in a titration when the indicator has indicated that the reaction is complete. Ideally this must occur at or very near the equivalence point.
Calculate the volume of base at the eq. point in titration of 50.0 ml of a) .150M HCl, b) .785M HOAc, and c) .200M H₂SO₄ with .100M NaOH

Acid-Base titration reactions go to completion

**Points of difference between SA-SB and WA-SB titrations**
- SA has lower initial pH
- WA rises faster initially
- SA has greater pH jump at equiv. point
- pH at Equilance point
SA vs SB 7.00
WA vs SB >7.00
SA vs WB <7.00
WA vs WB depends (not done)
pH at equiv. point in titration of WA vs SB is determined by the $K_b$ of the conjugate base of the parent weak acid.
.2140g of an unknown monoprotic acid in 25.00 ml of water required 27.4 ml of .0950M NaOH to reach the eq pt. Calculate the MW. What is the pKa if after 15.0 ml of base the pH was 6.50

For the titration of 25.0ml of 0.239M hypochlorous acid with 0.125M NaOH.
HOCl + NaOH → NaOCl + H2O
Calculate a) the volume of NaOH required to reach the
equivalence point b) the initial pH of the HOCl, $K_a=3.5 \times 10^{-8}$ c) the pH after the addition of 5.0 ml of base d) the pH at half neutralization e) the pH at the equivalence point and f) the pH at 50.0 ml of NaOH.

**Molar Solubility, $s$** is the maximum number of moles of a solute that will dissolve in a L of solvent

$s>.01$ mol/L soluble
$s<.01$ mol/L insoluble

**SOLUBILITY RULES** (Table
4.1) 
- All IA and NH$_4^+$ salts soluble 
- All NO$_3^-$, ClO$_4^-$, C$_2$H$_3$O$_2^-$ sol. 
- All Ag$^+$, Hg$^+$, Pb$^{2+}$ salts insol. 
- All Cl$^-$, Br$^-$, I$^-$ soluble 
- SO$_4^{2-}$ soluble ex. Ca, Sr, Ba 
- CO$_3^{2-}$, PO$_4^{3-}$, S$^{2-}$, O$^{2-}$, OH$^-$ insol. 
(PRIORITY)

**Solubility Product Constant, $K_{sp}$** - A equilibrium expression governing the solubility of sparingly soluble compounds, solubility $< .01$mol/L. 

$M_aX_b \rightleftharpoons aM^{+m} + bX^{-x}$
\[ K_{sp} = [M^{+m}]^a[X^{-x}]^b \]

Write \( K_{sp} \) expressions for the following salts:

- AgCl
- Pb(IO_3)_2
- Fe(OH)_3
- Mn_3(AsO_4)_2

Evaluate the \( K_{sp} \) expressions of the above in terms of the molar solubility.

**Types of calculations:**
- Evaluate \( K_{sp} \) from molar
solubility
-Evaluate molar solubility from $K_{sp}$

Evaluate the $K_{sp}$ of Pb(IO$_3$)$_2$ (557g/mol) if its solubility is 0.00224g/L

Evaluate the molar solubility of Mn$_3$(AsO$_4$)$_2$ if its $K_{sp}$=1.9x10$^{-11}$

**Common Ion Effect** - The effect that an ion from two different sources has on an equilibrium. (LeChatelier's
Principle)

Calculate the \([\text{Ca}^{2+}]\) in water 0.10 M NaF and 0.20 M NaF. 
\[
K_{sp}(\text{CaF}_2) = 3.9 \times 10^{-11}
\]

Simultaneous Equilibria
Consider the effects of hydrolysis, pH and complex formation on solubility.

PbS, CaF$_2$ hydrolysis
Fe(OH)$_3$, sol. at pH 1.0 vs 7.0
AgCl, complexation by NH$_3$

The solubility of a salt containing the anion of a weak acid is affected by hydrolysis and pH.
Calculate the $[\text{Fe}^{3+}]$ from $\text{Fe(OH)}_3$ ($K_{sp} = 2.6 \times 10^{-39}$) in pH 1.0 and 7.0 buffers.

Calculate the K for the following reaction using Table 17.1 and appendix D.
AgCl(s) + 2NH₃(aq) ⇌ Ag(NH₃)⁺(aq) + Cl⁻(aq)

In water the [Ag⁺] is 1.3x10⁻⁵ M (insoluble) but in 2.00 M NH₃ the [Ag(NH₃)⁺] is .11 M (soluble)

-Predict if a ppt forms
Qₚₛₚ>Kₛₚ ppt forms
Qₚₛₚ<Kₛₚ ppt(if present) dissolves
Qₛₚₚ=Kₛₚ system @ equil.

Will a ppt form if 1.00ml of
.002M solution of AgNO₃ solution is mixed with 1.00 ml of .002M NaCl? 

K_{sp}(AgCl) = 1.8 \times 10^{-10}. Repeat the calculation if the initial solutions are 2.0 \times 10^{-6} M.

A solution is .0100M in both Cl⁻ and CrO₄²⁻. Solid AgNO₃ is added to the solution. Which silver compound ppts. first

AgCl K_{sp} = 1.8 \times 10^{-10} 
Ag₂CrO₄ K_{sp} = 1.9 \times 10^{-12}

What is the [Cl⁻] when Ag₂CrO₄ begins to ppt.
CHEM 104 Chapter 17 problem

For the titration of 25.0ml of 0.239M hypochlorous acid (WA) with 0.125M NaOH (SB).

\[ \text{HOCl} + \text{NaOH} \rightarrow \text{NaOCl} + \text{H}_2\text{O} \]

Calculate a) the volume of NaOH required to reach the equivalence point b) the initial pH of the HOCl, \( K_a = 3.5 \times 10^{-8} \) c) the pH after the addition of 5.0 ml of base d) the pH at half neutralization e) the pH at the equivalence point and f) the pH at 50.0 ml of NaOH.

a) Calculate the volume of NaOH to reach the equivalence point in the titration

\[ \text{(MV)}_{\text{acid}} = \text{(MV)}_{\text{base}} \]

\[ V_{\text{base}} = \frac{(\text{MV})_{\text{acid}}}{\text{M}_{\text{base}}} = \frac{0.239\text{M}(25.0 \text{ ml})}{0.125\text{M}} = 47.8 \text{ ml} \]

b) Calculate the initial pH of the weak acid

i: .239M 0.0 0.0
f: .239-x x x

\[ K_a = \frac{\text{[OCl}^-]\text{[H}^+]\text{[HOCl]}}{\text{[HOCl]}\text{[H}^+]\text{[OCl}^-]} = x^2/(.239-x) \sim x^2/.239 \]

\[ x = [H^+] = \left[K_a(239)\right]^{1/2} = 9.1 \times 10^{-5} \]

pH = 4.04

c) Calculate the pH after the addition of 5.0 ml of base (Buffer region) \( V_{\text{base}} = 5.0 \text{ ml} \)

\[ \text{pH} = \text{pK}_a + \log\left(\frac{\text{[OCl}^-]\text{[HOCl]}}{\text{[HOCl]}\text{[H}^+]\text{[OCl}^-]}\right) = \text{pK}_a + \log\left(\frac{(\text{MV})_{\text{base}}}{(\text{MV})_{\text{acid}} - (\text{MV})_{\text{base}}}\right) \]

\[ = 7.46 + \log\left(\frac{5.0x1.25}{(25.0x0.239) - (5.0x1.25)}\right) = 7.46 + \log\left(\frac{5.98}{5.35}\right) = 7.46 + \log(.117) = 6.53 \]

d) Calculate pH at half neutralization. (Buffer region) \( V_{\text{base}} = 23.9 \text{ ml} \) (this is \( \frac{1}{2} \) of 47.8 ml to get to the equivalence point)

\[ \text{pH} = \text{pK}_a + \log\left(\frac{\text{[OCl}^-]\text{[HOCl]}}{\text{[HOCl]}\text{[H}^+]\text{[OCl}^-]}\right) = \text{pK}_a + \log(1) = 7.46 + 0 = 7.46 \]

e) Calculate pH at equivalence point. \( V_{\text{base}} = 47.8 \text{ ml} \), Total volume is 72.8 ml This is just the pH of a OCl\(^-\) solution as all of the acid is now reacted.

\[ [\text{OCl}^-] = 25.0 \text{ ml}(0.239\text{M})/(25.0 + 47.8 \text{ ml}) = .0821 \text{ M} \]

The solution is basic due to hydrolysis.

\[ \text{OCl}^- + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{OH}^- \quad \text{K}_b = K_w/K_a = 2.9 \times 10^{-7} \]

i: .0821 0.0 0.0
f: .0821-x x x

\[ K_b = [\text{HOCl}][\text{OH}^-]/[\text{OCl}^-] = x^2/(.0821-x) \sim x^2/.0821 \]

\[ x = [\text{OH}^-] = (.0821K_b)^{1/2} = 1.5 \times 10^{-4} \text{ M} \quad \text{pOH} = 3.81 \quad \text{pH} = 10.19 \text{ (BASIC)} \]

f) Calculate the pH at 50.0 ml base. Total volume = 75.0 ml (pH after the equivalence point, pH of diluted base)

\[ [\text{OH}^-] = [(\text{MV})_{\text{base}} - (\text{MV})_{\text{acid}}]/V_{\text{Total}} = [(50.0x1.25) - (25.0x.239)]/75.0 = (6.25 -5.98)/75.0 = 3.7 \times 10^{-3} \text{ M} \]

\[ \text{pOH} = 2.44 \quad \text{pH} = 11.56 \]
Consider the titration of 25.0ml of .239M hypochlorous acid (WA) with .125M NaOH (SB)

a) Calculate the volume of NaOH to reach the equivalence point in the titration

\[
\text{HOCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaOCl}(aq) + \text{H}_2\text{O}
\]

\[
(V_{\text{acid}}) = (V_{\text{base}})
\]

\[
V_{\text{base}} = \frac{(V_{\text{acid}})}{M_{\text{base}}} = \frac{.239\text{M}(25.0\text{ ml})}{.125\text{M}} = 47.8\text{ ml}
\]

b) Calculate the initial pH of the weak acid. \(V_{\text{base}} = 0.0\text{ ml}\)

\[
\text{HOCl}(aq) \_ \text{OCl}^-(aq) + \text{H}^+(aq) \quad K_a=3.5\times10^{-8} \quad \text{pK}_a = 7.46
\]

\[
i: \quad .239\text{M} \quad 0.0 \quad 0.0
\]

\[
f: \quad .239-x \quad x \quad x
\]

\[
K_a = \frac{[\text{OCl}^-][\text{H}^+]}{[\text{HOCl}]} = \frac{x^2}{(.239-x)} \sim \frac{x^2}{.239}
\]

\[
x = [\text{H}^+] = (K_a(.239))^{\frac{1}{2}} = 9.1\times10^{-5} \quad \text{pH} = 4.04
\]

Buffer region

c) Calculate pH after the addition of 5.0 ml of base. \(V_{\text{base}} = 5.0\text{ ml}\)
pH = pK_a + log{[[OCl^-]/[HOCl]]} = pK_a + log{\((MV)_{\text{base}}/((MV)_{\text{acid}}-(MV)_{\text{base}}))\}

= 7.46 + log\{(5.0x.125)/[(25.0x.239)-(5.0x.125)]\} = 7.46 + log\{.625/[5.98-.625]\} = 7.46 + log{.625/5.35}

= 7.46 + log (.117) = 6.53

d) Calculate pH at half neutralization. \(V_{\text{base}} = 23.9\) ml

pH = pK_a + log{[[OCl^-]/[HOCl]]} = pK_a + log(1) = 7.46 + 0 = 7.46

e) Calculate pH at equivalence point. \(V_{\text{base}} = 47.8\) ml, Total volume is 72.8 ml

This is just the pH of a OCl^- solution as all of the acid is now reacted.

\[\text{[OCl}^-\text{]} = 25.0\text{ ml(.239M)}/(25.0 + 47.8\text{ ml}) = .0821\text{ M}\]

The solution is basic due to hydrolysis.

\[\text{OCl}^- + \text{H}_2\text{O} \_\text{ HOCl} + \text{OH}^- \quad K_b = K_w/K_a = 2.9x10^{-7}\]

i: .0821 0.0 0.0
f: .0821-x x x
\[ K_b = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-]} = \frac{x^2}{0.0821-x} \sim \frac{x^2}{0.0821} \]

\[ x = [\text{OH}^-] = (0.0821K_b)^{0.5} = 1.5 \times 10^{-4} \text{ M} \quad \text{pOH} = 3.81 \quad \text{pH} = 10.19 \text{ (BASIC)} \]

**pH after the equivalence point**

f) Calculate the pH at 50.0 ml base. Total volume = 75.0 ml

**pH of diluted base**

\[ [\text{OH}^-] = \frac{[(\text{MV})_{\text{base}} - (\text{MV})_{\text{acid}}]}{V_{\text{Total}}} = \frac{(50.0 \times 0.125) - (25.0 \times 0.239)}{75.0} = \frac{6.25 - 5.98}{75.0} = 3.67 \times 10^{-3} \text{ M} \]

\[ \text{pOH} = 2.44 \quad \text{pH} = 11.56 \]