Practice Problems: Applications of Aqueous Equilibria

CHEM 1B

1. Ammonia (NH₃) is a weak base with a \( K_b = 1.8 \times 10^{-5} \).

   a) Write the balanced chemical equation for the reaction of ammonia with water. Using the I.C.E. method, calculate the pH and % ionization of a 1.75 M NH₃ solution in 2.50 M NH₄Cl.

\[
\begin{align*}
\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(l) & \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^- \text{(aq)} \\
\text{I} & \quad 1.75 \quad - \quad 2.50 \quad 0 \quad \checkmark \text{Check (% ionization):} \\
\text{C} & \quad -X \quad - \quad +X \quad +X \quad \text{X} \quad \frac{X}{[\text{NH}_3]_{\text{init}}} (100\%) = \frac{1.26 \times 10^{-5} \text{ M}}{1.75 \text{ M}} (100\%) = 0.00072 \% \text{ ionization} \quad \checkmark \text{assumption okay (<5\%)} \\
\text{E} & \quad 1.75 - X \quad - \quad 2.50 + X \quad X \\
\end{align*}
\]

\[
K_b = \frac{[\text{NH}_4^+] \cdot [\text{OH}^-]}{[\text{NH}_3]} = \frac{(2.50 + X) \cdot X}{(1.75 - X)} \approx \frac{2.50X}{1.75} = 1.8 \times 10^{-5} \\
\text{assuming X is negligible} \\
X = 1.26 \times 10^{-5} \text{ M} \\
[\text{OH}^-]_{\text{eq}} = X = 1.26 \times 10^{-5} \text{ M OH}^- \\
pOH = -\log [\text{OH}^-] \\
pOH = -\log (1.26 \times 10^{-5} \text{ M}) \\
pOH = 4.899629455 \\
pH + pOH = 14 \\
pH = 9.10 \\
\]

b) How would the % ionization and pH have been different without the NH₄Cl? What is this effect called?

The % ionization would be \textcolor{blue}{\textbf{larger}} / \textcolor{red}{\textbf{smaller}} (circle one),

and the pH would be \textcolor{blue}{\textbf{higher}} / \textcolor{red}{\textbf{lower}} (circle one)

without the \textcolor{blue}{\textbf{common ion effect}}

(c) Is this solution a buffer? Explain.

Yes, this solution is a buffer, because it contains a weak acid - weak base conjugate pair.

d) Other than with the ICE method, how else could you have solved this problem?

Method: \textcolor{blue}{\textbf{using the Henderson-Hasselbalch equation}}
2. A buffer is made from acetic acid (HC\(_2\)H\(_3\)O\(_2\)) and sodium acetate (NaC\(_2\)H\(_3\)O\(_2\)). 1.5 moles of acetic acid and 2.5 moles of sodium acetate are added to enough water to make 1.5 liter of solution. The ionization constant (K\(_a\)) for acetic acid is 1.8 x 10\(^{-5}\).

a) Write the equation for the ionization of acetic acid in water, and using a stress-shift-equilibrium arrow diagram, show how the buffer would minimize the effect of adding a base to the solution.

Stress:  
\[
\text{HC}_2\text{H}_3\text{O}_2^{\text{(aq)}} \rightleftharpoons \text{H}^+^{\text{(aq)}} + \text{C}_2\text{H}_3\text{O}_2^-^{\text{(aq)}}
\]

Shift:  
\[
\downarrow \quad \rightarrow \quad \uparrow \quad \uparrow
\]

Equilibrium:  
\[
\downarrow \quad \downarrow \quad \uparrow \quad \uparrow
\]

b) Using the Henderson-Hasselbalch equation, find the pH of this buffer solution.

\[
\text{pH} = \text{pK}_a + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right)
\]

\[
\text{pH} = \text{pK}_a + \log \left( \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \right)
\]

\[
\text{pH} = -\log (1.8 \times 10^{-5}) + \log \left( \frac{(2.5 \text{ mol} / 1.5 \text{ L})}{(1.5 \text{ mol} / 1.5 \text{ L})} \right)
\]

\[
\text{pH} = 4.744727495 + 0.2218487496 = 4.966576245
\]

\[
\text{pH} = 4.97
\]

Note: Assume no ionization (a good assumption due to the common ion effect).

Also note: The volume of the solution cancels out. Dilution does not affect the pH of a buffer!

c) Calculate the percent ionization of the acetic acid in this solution.

\[
\text{pH} = -\log [\text{H}^+]
\]

\[
[\text{H}^+] = 10^{-\text{pH}}
\]

\[
[\text{H}^+] = 10^{-4.966576245} = 1.08 \times 10^{-5} \text{ M H}^+
\]

\[
\% \text{ ionization} = \frac{[\text{H}^+]_{eq}}{[\text{HC}_2\text{H}_3\text{O}_2]_{init}} (100\%) = \frac{1.08 \times 10^{-5} \text{ M H}^+}{1.0 \text{ M HC}_2\text{H}_3\text{O}_2} (100\%) = 0.00108 \% \text{ ionization}
\]

\[
\% \text{ ionization} = 0.0011 \%
\]

d) At what pH would this solution have the largest buffering capacity in both directions?

\[
\text{pH}_{\text{soln}} = \text{pK}_a + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right)
\]

\[
\text{pH}_{\text{soln}} = -\log (1.8 \times 10^{-5}) + 0
\]

\[
\text{pH} = 4.74
\]
3. Based on the titration curve to the right and the tables of $K_a$ values below, determine the following:

a) The most appropriate indicator for the titration.

$$\text{pH (at eq. pt.)} = \text{p}K_{a \text{ ind}} = 9.3$$

$$K_{a \text{ ind}} = 10^{-\text{p}K_a} = 10^{-9.3} = 5 \times 10^{-10}$$

**Phenolphthalein**

b) Whether the unknown acid is a **strong** acid or a **weak** acid (circle one). How do you know?

$$\text{pH (at eq. pt.)} > 7$$

c) The most likely identity of the unknown acid.

$$\text{pH (at }\frac{1}{2}\text{ eq. pt.)} = \text{p}K_{a \text{ unk}} = 4.8$$

$$K_{a \text{ unk}} = 10^{-\text{p}K_a} = 10^{-4.8} = 2 \times 10^{-5}$$

**acetic acid**

d) The original concentration of the 100.0 mL sample of unknown monoprotic acid.

$$a\;M_a\;V_a = b\;M_b\;V_b$$

$$(1)\;M_a\; (100.0 \;\text{mL}) = (1)\; (0.50 \;\text{M})\; (120. \;\text{mL})$$

$$M_a = \;0.60 \;\text{M acetic acid}$$
4. Based on the titration curve for a diprotic acid above, answer the following:

a) Identify in the table to the right which species exist in solution at each point on the curve (using H₂A to represent a generic diprotic acid).

<table>
<thead>
<tr>
<th>Point</th>
<th>Species from the unknown</th>
<th>Species from the titrant</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>H₂A</td>
<td>–</td>
</tr>
<tr>
<td>B</td>
<td>H₂A, HA⁻</td>
<td>Na⁺</td>
</tr>
<tr>
<td>C</td>
<td>HA⁻</td>
<td>Na⁺</td>
</tr>
<tr>
<td>D</td>
<td>HA⁻, A²⁻</td>
<td>Na⁺</td>
</tr>
<tr>
<td>E</td>
<td>A²⁻</td>
<td>Na⁺</td>
</tr>
<tr>
<td>F</td>
<td>A²⁻</td>
<td>Na⁺, OH⁻</td>
</tr>
</tbody>
</table>

b) Given the table of ionization constants, identify the unknown acid.

\[
\text{pH (at 1st ½ eq. pt.)} = \text{pK}_{\text{a1 unk}} = 1.8
\]
\[
\text{K}_{\text{a1 unk}} = 10^{-\text{pK}_{\text{a1 unk}}} = 10^{-1.8} = 2 \times 10^{-2}
\]
\[
\text{pH (at 2nd ½ eq. pt.)} = \text{pK}_{\text{a2 unk}} = 7.0
\]
\[
\text{K}_{\text{a2 unk}} = 10^{-\text{pK}_{\text{a2 unk}}} = 10^{-7.0} = 1 \times 10^{-7}
\]

sulfurous acid

Note: The 2nd eq. pt. is a better choice since it is sharper (making estimating more precise), and has a larger volume (making estimating errors proportionally smaller).

c) Calculate the concentration of the original diprotic acid solution.

**From the first equivalence point**

\[\text{a M}_a \text{ V}_a = \text{b M}_b \text{ V}_b\]
\[(1) \text{ M}_a (250.0 \text{ mL}) = (1) (0.10 \text{ M}) (70. \text{ mL})\]
\[\text{M}_a = \boxed{0.028 \text{ M sulfurous acid}}\]
1 H⁺ neutralized

**From the second equivalence point**

\[\text{a M}_a \text{ V}_a = \text{b M}_b \text{ V}_b\]
\[(2) \text{ M}_a (250.0 \text{ mL}) = (1) (0.10 \text{ M}) (140. \text{ mL})\]
\[\text{M}_a = \boxed{0.028 \text{ M sulfurous acid}}\]
both H⁺ neutralized
5. Based on the titration curve to the right and the tables of $K_b$ values below, determine the following:

a) The most appropriate indicator for the titration.

\[
pH_{(at\ eq\ pt.)} = pK_{a\ ind} = 5.2
\]

\[
K_{a\ ind} = 10^{-pK_a} = 10^{-5.2} = 6 \times 10^{-6}
\]

**Methyl Red**

b) Whether the unknown base is a **strong** base or a **weak** base (circle one). How do you know?

\[
pH_{(at\ eq\ pt.)} < 7
\]

c) The most likely identity of the unknown base.

\[
14 = pK_a + pK_b
\]

\[
pK_{b\ unk} = 4.2
\]

\[
K_{b\ unk} = 10^{-pK_b} = 10^{-4.2} = 6 \times 10^{-5}
\]

**trimethylamine**

d) The original concentration of the 150.0 mL sample of unknown base.

\[
a M_a V_a = b M_b V_b
\]

\[
(1) (0.25 \text{ M}) (140. \text{ mL}) = (1) M_b (150.0 \text{ mL})
\]

\[
M_b = 0.23 \text{ M trimethylamine}
\]
6. The $K_{sp}$ of silver chromate ($\text{Ag}_2\text{CrO}_4$) is $1.9 \times 10^{-12}$.
   a) Write the balanced complete ionic equation for the dissociation of $\text{Ag}_2\text{CrO}_4$.
   b) Using the I.C.E. method and the equilibrium expression, find the molar solubility of $\text{Ag}_2\text{CrO}_4$. (Hint: you are solving for $X$)

\[
\begin{align*}
\text{Ag}_2\text{CrO}_4(s) & \rightleftharpoons 2 \text{Ag}^+_{(aq)} + \text{CrO}_4^{2-}_{(aq)} \quad & \text{Initial Conc.} & \quad & \text{Change in Conc.} & \quad & \text{Equilib. Conc.} \\
\text{ } & \quad & 0 & \quad & -X & \quad & 2X \\
\text{ } & \quad & 0 & \quad & +2X & \quad & +X \\
\text{ } & \quad & 0 & \quad & -2X & \quad & X \\
\end{align*}
\]

\[
K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = (2X)^2 (X) \\
K_{sp} = 4X^3 \\
1.9 \times 10^{-12} = 4X^3 \\
X = \left( \frac{1.9 \times 10^{-12}}{4} \right)^{1/3} = 7.8 \times 10^{-5} \text{ M} \\
\] 

\[
7.8 \times 10^{-5} \text{ M} \text{Ag}_2\text{CrO}_4
\]

7. The molar solubility of chromium (III) hydroxide in water at 25°C is $1.26 \times 10^{-8}$ M Cr(OH)$_3$.
   a) Write the balanced complete ionic equation for the dissociation of Cr(OH)$_3$.
   b) Using the I.C.E. method and the equilibrium expression, find the $K_{sp}$ of Cr(OH)$_3$.

\[
\begin{align*}
\text{Cr(OH)}_3(s) & \rightleftharpoons \text{Cr}^{3+}_{(aq)} + 3 \text{OH}^-_{(aq)} \quad & \text{Initial Conc.} & \quad & \text{Change in Conc.} & \quad & \text{Equilib. Conc.} \\
\text{ } & \quad & 0 & \quad & -X & \quad & X \\
\text{ } & \quad & 0 & \quad & +X & \quad & 3X \\
\text{ } & \quad & 0 & \quad & -3X & \quad & 3X \\
\end{align*}
\]

\[
K_{sp} = [\text{Cr}^{3+}] [\text{OH}^-]^3 = (X) (3X)^3 \\
K_{sp} = 27X^4 \\
K_{sp} = 27(1.26 \times 10^{-8} \text{ M})^4 \\
K_{sp} = \underline{6.80527915 \times 10^{-31}} \underline{= 6.81 \times 10^{-31}} \\
\]

8. The molar solubilities of two ionic compounds can be directly compared, but not always the $K_{sp}$ values. Circle the two compounds for which the $K_{sp}$ values could be compared and indicate which one of the two is more soluble in water.

<table>
<thead>
<tr>
<th># ions:</th>
<th>PbCrO$_4$</th>
<th>Mg(OH)$_2$</th>
<th>Cu$_3$(PO$_4$)$_2$</th>
<th>Ag$_2$SO$_4$</th>
<th>Al(OH)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 &amp; 1</td>
<td>$K_{sp} = 2.8 \times 10^{-13}$</td>
<td>$K_{sp} = 5.6 \times 10^{-12}$</td>
<td>$K_{sp} = 1.4 \times 10^{-37}$</td>
<td>$K_{sp} = 1.2 \times 10^{-5}$</td>
<td>$K_{sp} = 1.9 \times 10^{-33}$</td>
</tr>
<tr>
<td>1 &amp; 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 &amp; 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 &amp; 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 &amp; 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

more soluble