REVIEW QUESTIONS
Chapter 17

1. A buffer is prepared by adding 20.0 g of acetic acid (HC\textsubscript{2}H\textsubscript{3}O\textsubscript{2}) and 20.0 g of sodium acetate (NaC\textsubscript{2}H\textsubscript{3}O\textsubscript{2}) in enough water to prepare 2.00 L of solution. Calculate the pH of this buffer? (K\textsubscript{a} = 1.8\times10^{-5})

\[ \text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_2\text{H}_3\text{O}_2^- \]

\[
\begin{align*}
20.0 \text{ g HAc} \times \frac{1 \text{ mol}}{60.0 \text{ g}} \times \frac{1}{2.00 \text{ L}} &= 0.167 \text{ M} \\
20.0 \text{ g NaAc} \times \frac{1 \text{ mol}}{82.0 \text{ g}} \times \frac{1}{2.00 \text{ L}} &= 0.122 \text{ M}
\end{align*}
\]

\[
\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = 4.74 + \log \frac{0.122 \text{ M}}{0.167 \text{ M}}
\]

\[
\text{pH} = 4.74 - 0.136 = 4.60
\]

2. What is the ratio of HCO\textsubscript{3}\textsuperscript{-} to H\textsubscript{2}CO\textsubscript{3} in blood of pH 7.4? (K\textsubscript{a} for H\textsubscript{2}CO\textsubscript{3} = 4.3\times10^{-7})

\[ \text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCO}_3^- \]

\[
\text{pH} = \text{pK}_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 7.4 = 6.37 + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}
\]

\[
\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \text{antilog} (7.4 - 6.37) = 10^{1.03} = 11
\]

3. How many grams of NaBrO should be added to 1.00 L of 0.200 M HBrO to form a buffer with a pH of 8.80? (K\textsubscript{a} for HBrO = 2.5\times10^{-9})

\[ \text{HBrO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{BrO}^- \]

\[
\text{pH} = \text{pK}_a + \log \frac{[\text{BrO}^-]}{[\text{HBrO}]} = 8.80 = 8.60 + \log \frac{[\text{BrO}^-]}{[\text{HBrO}]}
\]

\[
\frac{[\text{BrO}^-]}{[\text{HBrO}]} = \text{antilog} (8.80 - 8.60) = 10^{0.20} = 1.6
\]

\[
[\text{BrO}^-] = 1.6 \times (0.200 \text{ M}) = 0.32 \text{ M} \]

\[
1.00 \text{ L} \times \frac{0.32 \text{ mol}}{1 \text{ L}} \times \frac{118.9 \text{ g}}{1 \text{ mol}} = 38 \text{ g}
\]
4. Acetylsalicylic acid (aspirin, \( \text{HC}_9\text{H}_7\text{O}_4 \)) is a weak acid with \( K_a = 2.75 \times 10^{-5} \) at 25°C. 3.00 g of sodium acetylsalicylate (\( \text{NaC}_9\text{H}_7\text{O}_4 \)) is added to 200.0 mL of 0.100 M solution of this acid. Calculate the pH of the resulting solution at 25°C.

\[
\text{H}_3\text{O}^+ + \text{C}_9\text{H}_7\text{O}_4^- \rightleftharpoons \text{HC}_9\text{H}_7\text{O}_4 + \text{H}_2\text{O}
\]

\[
[\text{NaC}_9\text{H}_7\text{O}_4] = 3.00 \text{ g} \times \frac{1 \text{ mol}}{202 \text{ g}} \times \frac{1}{0.200 \text{ L}} = 0.0743 \text{ M}
\]

\[
\text{pH} = \text{pK}_a + \log \left( \frac{[\text{H}_3\text{O}^+]}{[\text{HA}]} \right) = 4.56 + \log \frac{0.0743 \text{ M}}{0.100 \text{ M}} = \text{pH} = 4.56 \pm 0.129 = 4.43
\]

5. The equations and dissociation constants for three different acids are given below:

- \( \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \quad K_a = 4.2 \times 10^{-7} \quad \text{pK}_a = 6.4 \)
- \( \text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-} \quad K_a = 6.2 \times 10^{-8} \quad \text{pK}_a = 7.2 \)
- \( \text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-} \quad K_a = 1.3 \times 10^{-2} \quad \text{pK}_a = 1.9 \)

Identify the conjugate pair that is best for preparing a buffer with a pH of 7.2. Clearly explain your choice.

The best conjugate pair would be \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \)

The pH = pKa = 7.2 for this buffer when \( [\text{H}_2\text{PO}_4^-] = [\text{HPO}_4^{2-}] \)

\[
\text{pH} = \text{pK}_a + \log \left( \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \right)
\]

6. A sample of 25.0 mL of 0.100 M solution of \( \text{HBr} \) is titrated with 0.200 M \( \text{NaOH} \). Calculate the pH of solution after 10.0 mL of the base is added.

<table>
<thead>
<tr>
<th></th>
<th>HBr</th>
<th>NaOH</th>
<th>NaBr</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>2.50 mmol</td>
<td>2.00 mmol</td>
<td>0</td>
<td>----</td>
</tr>
<tr>
<td>Δ</td>
<td>-2.00 mmol</td>
<td>-2.00 mmol</td>
<td>+2.00 mmol</td>
<td>----</td>
</tr>
<tr>
<td>Final</td>
<td>0.50 mmol</td>
<td>0</td>
<td>2.00 mmol</td>
<td>----</td>
</tr>
</tbody>
</table>

\[
[H^+] = [\text{HBr}] = \frac{0.50 \text{ mmol}}{35.0 \text{ mL}} = 0.0143 \text{ M} \quad \text{pH} = -\log (0.0143) = 1.85
\]
A buffer solution is prepared by adding 0.10 L of 2.0 M acetic acid solution to 0.10 L of 1.0 M NaOH solution.

a) Calculate the pH of this buffer solution.

\[
\begin{align*}
0.10 \text{ L} &\times \frac{2.0 \text{ mol}}{1 \text{ L}} = 0.20 \text{ mol HC}_2\text{H}_3\text{O}_2 \\
0.10 \text{ L} &\times \frac{1.0 \text{ mol}}{1 \text{ L}} = 0.10 \text{ mol NaOH}
\end{align*}
\]

\[
\text{HC}_2\text{H}_3\text{O}_2^- + \text{NaOH} \rightarrow \text{NaC}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O}
\]

<table>
<thead>
<tr>
<th></th>
<th>HC(_2)H(_3)O(_2)</th>
<th>+</th>
<th>NaOH</th>
<th>\rightarrow</th>
<th>NaC(_2)H(_3)O(_2)</th>
<th>+</th>
<th>H(_2)O</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
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<td></td>
<td>0.10</td>
<td></td>
<td>0</td>
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<td>----</td>
<td></td>
</tr>
<tr>
<td>(\Delta)</td>
<td>−0.10</td>
<td></td>
<td>−0.10</td>
<td>+0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final</td>
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<td></td>
<td>0</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\text{[C}_2\text{H}_3\text{O}_2^-] = \frac{0.10 \text{ mol}}{0.20 \text{ L}} = 0.50 \text{ M} \quad \text{[HC}_2\text{H}_3\text{O}_2] = \frac{0.10 \text{ mol}}{0.2 \text{ L}} = 0.50 \text{ M}
\]

\[
\text{pH} = pK_a + \log \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}
\]

From textbook \(K_a = 1.7 \times 10^{-5}\) \(pK_a = 4.77\)

\[
pH = 4.77 + \log \frac{0.50}{0.50} = 4.77
\]

b) 0.10 L of 0.20 M HCl is added to 0.40 L of the buffer solution above. What is the pH of the resulting solution?

The \(H_3O^+\) ions provided by HCl react with the acetate ions in the buffer.

\[
\text{[H}_3\text{O}^+] = (0.10 \text{L})(0.20 \text{ M}) = 0.020 \text{ mol}
\]

\[
\text{[C}_2\text{H}_3\text{O}_2^-] = \text{[HC}_2\text{H}_3\text{O}_2] = (0.40 \text{ L})(0.50 \text{ M}) = 0.20 \text{ mol}
\]

<table>
<thead>
<tr>
<th></th>
<th>C(_2)H(_3)O(_2)</th>
<th>+</th>
<th>H(_3)O(^+)</th>
<th>\rightarrow</th>
<th>HC(_2)H(_3)O(_2)</th>
<th>+</th>
<th>H(_2)O</th>
<th></th>
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<td>Initial</td>
<td>0.20</td>
<td></td>
<td>0.020</td>
<td></td>
<td>0.20</td>
<td></td>
<td>----</td>
<td></td>
</tr>
<tr>
<td>(\Delta)</td>
<td>−0.020</td>
<td></td>
<td>−0.020</td>
<td>+0.020</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final</td>
<td>0.18</td>
<td></td>
<td>0</td>
<td>0.22</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\text{[C}_2\text{H}_3\text{O}_2^-] = \frac{0.18 \text{ mol}}{0.50 \text{ L}} = 0.36 \text{ M} \quad \text{[HC}_2\text{H}_3\text{O}_2] = \frac{0.22 \text{ mol}}{0.50 \text{ L}} = 0.44 \text{ M}
\]

\[
\text{pH} = pK_a + \log \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}
\]

From textbook \(K_a = 1.7 \times 10^{-5}\)

\[
pK_a = 4.77 \quad \text{pH} = 4.77 + \log \frac{0.36}{0.44} = 4.68
\]
8. A 10.0 mL solution of 0.100 M NH₃ (Kₐ = 1.8 x 10⁻⁵) is titrated with a 0.100 M HCl solution. Calculate the pH of this solution at equivalence point.

At equivalence point all NH₃ (1.00 mmol) reacts with all HCl (1.00 mmol) to produce 1.00 mmol of NH₄Cl. Since only salt is present at this point, the pH of solution is based on hydrolysis of this salt.

\[
[\text{NH}_4^+] = \frac{1.00 \text{ mmol}}{20.0 \text{ mL}} = 0.0500 \text{ M}
\]

<table>
<thead>
<tr>
<th></th>
<th>NH₄⁺</th>
<th>+</th>
<th>H₂O</th>
<th>\rightleftharpoons</th>
<th>NH₃</th>
<th>+</th>
<th>H₃O⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.0500</td>
<td></td>
<td>----</td>
<td></td>
<td>0</td>
<td></td>
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</tr>
<tr>
<td>Δ</td>
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<td></td>
<td>----</td>
<td>+x</td>
<td>+x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equil.</td>
<td>0.0500−x</td>
<td></td>
<td>----</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \\
K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{(x)(x)}{0.050 - x} = 5.6 \times 10^{-10}
\]

\[
[\text{H}_3\text{O}^+] = x = \sqrt{(0.050)(5.6 \times 10^{-10})} = 5.3 \times 10^{-6} \\
pH = -\log(5.3 \times 10^{-6}) = 5.28
\]

9. A 10.0-mL solution of 0.300 M NH₃ is titrated with a 0.100 M HCl solution. Calculate the pH after the following additions of the HCl solution: (a) 0.0 mL, (b) 10.0 mL, (c) 30.0 mL

a) Since no acid has been added, the pH of solution is based on the ionization of NH₃.

\[
\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \\
\text{From textbook, } K_b = 1.8 \times 10^{-5}
\]

\[
K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(x)(x)}{0.300 - x} = 1.8 \times 10^{-5} \\
x = [\text{OH}^-] = \sqrt{(0.300)(1.8 \times 10^{-5})} = 2.32 \times 10^{-3}
\]

\[
pOH = -\log(2.32 \times 10^{-3}) = 2.63 \\
pH = 14.00 - 2.63 = 11.37
\]

b) Addition of 10.0 mL of acid neutralizes some of the ammonia, as shown below:

<table>
<thead>
<tr>
<th></th>
<th>NH₃</th>
<th>+</th>
<th>HCl</th>
<th>→</th>
<th>NH₄⁺</th>
<th>+</th>
<th>Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>3.00 mmol</td>
<td></td>
<td>1.00 mmol</td>
<td></td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δ</td>
<td>−1.00 mmol</td>
<td></td>
<td>−1.00 mmol</td>
<td>+1.00 mmol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final</td>
<td>2.00 mmol</td>
<td></td>
<td>0</td>
<td></td>
<td>1.00 mmol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\[
[NH_3] = \frac{2.00 \text{ mmol}}{20.0 \text{ mL}} = 0.100 \text{ M} \quad \quad [NH_4^+] = \frac{1.00 \text{ mmol}}{20.0 \text{ mL}} = 0.0500 \text{ M}
\]

\[
K_a = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} \quad \quad pK_a = \log K_a = 9.25
\]

\[
\text{pH} = pK_a + \log \frac{[\text{base}]}{[\text{acid}]} = 9.25 + \log \frac{0.100}{0.0500} = 9.55
\]

c) After addition of 30.0 mL of HCl equivalence point is reached. At this point all NH\textsubscript{3} (3.00 mmol) reacts with all HCl (3.00 mmol) to produce 3.00 mmol of NH\textsubscript{4}Cl. Since only salt is present at this point, the pH of solution is based on hydrolysis of this salt.

\[
[NH_4^+] = \frac{3.00 \text{ mmol}}{40.0 \text{ mL}} = 0.0750 \text{ M}
\]

|          | NH\textsubscript{4}\textsuperscript{+} + H\textsubscript{2}O & \rightleftharpoons & NH\textsubscript{3} + H\textsubscript{3}O\textsuperscript{+} |
|----------|--------------------------------------------------|------------------|--------------------------------------------------|
| Initial  | 0.0750                                           | 0                | 0                                                 |
| \(\Delta\) | \(-x\)                                            | +++               | +x                                                 |
| Equil.   | 0.0750--x                                         | x                 | x                                                 |

\[
K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{(x)(x)}{(0.0750 - x)} = 5.56 \times 10^{-10}
\]

\[
x = [H_3O^+] = \sqrt{(0.0750)(5.56 \times 10^{-10})} = 6.46 \times 10^{-6} \quad \quad \text{pH} = -\log(6.46 \times 10^{-6}) = 5.19
\]
10. A 45.0-mL sample of 0.200 M acetic acid is titrated with 0.180 M NaOH. Calculate the pH of the solution (a) before addition of NaOH, (b) after addition of 20.0 mL of NaOH and (c) at the equivalence point.

a) Since no base has been added, the pH of solution is based on the ionization of acid.

\[
\text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_3\text{O}_2^- + \text{H}_3\text{O}^+ \]

From textbook, \( K_a = 1.7 \times 10^{-5} \)

\[
K_a = \frac{[\text{CHO}^-][\text{H}_3\text{O}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(x)(x)}{0.200 - x} = 1.7 \times 10^{-5}
\]

\[
x = [\text{H}_3\text{O}^+] = \sqrt{(0.200)(1.7 \times 10^{-5})} = 1.84 \times 10^{-3}
\]

\[
\text{pH} = \log(1.84 \times 10^{-3}) = 2.73
\]

b) Addition of 20.0 mL of NaOH neutralizes some of the acetic acid, as shown below:

\[
\begin{array}{l}
\text{Initial} & 9.00 \text{ mmol} & 3.60 \text{ mmol} & 0 & \text{----} \\
\Delta & -3.60 \text{ mmol} & -3.60 \text{ mmol} & +3.60 \text{ mmol} & \text{----} \\
\text{Final} & 5.40 \text{ mmol} & 0 & 3.60 \text{ mmol} & \text{----} \\
\end{array}
\]

\[
[\text{HC}_2\text{H}_3\text{O}_2] = \frac{5.40 \text{ mmol}}{65.0 \text{ mL}} = 0.0831 \text{ M} \quad [\text{C}_2\text{H}_3\text{O}_2^-] = \frac{3.60 \text{ mmol}}{65.0 \text{ mL}} = 0.0554 \text{ M}
\]

\[
K_a = 1.7 \times 10^{-5} \quad \text{pK}_a = \log K_a = 4.77 \quad \text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]} = 4.77 + \log \frac{0.0554}{0.0831} = 4.59
\]

c) At equivalence point:

\[
45.0 \text{ mL acid} \times \frac{0.200 \text{ mol}}{1 \text{ L}} \times \frac{1 \text{ mol base}}{1 \text{ mol acid}} \times \frac{1 \text{ L}}{0.180 \text{ mol}} = 50.0 \text{ mL of base}
\]

At this point all the acid (9.00 mmol) is neutralized by the base (9.00 mmol) to produce 9.00 mmol of salt. Since only salt is present, the pH of the solution is based on hydrolysis of this salt.

\[
[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{9.00 \text{ mmol}}{95.0 \text{ mL}} = 0.09474 \text{ M}
\]

\[
\begin{array}{l}
\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^- \\
\text{Initial} & 0.09474 & \text{----} & 0 & 0 \\
\Delta & -x & \text{----} & +x & +x \\
\text{Equil.} & 0.09474-x & \text{----} & x & x \\
\end{array}
\]

\[
K_b = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.88 \times 10^{-10} \quad \text{pOH} = -\log(7.47 \times 10^{-6}) = 5.13
\]

\[
\text{pH} = 14.00 - 5.13 = 8.87
\]
11. Calculate the molar solubility of AgBr (Ksp= 5.0x10^{-13}) in 0.50 M NaBr solution.

\[
\text{AgBr (s)} \rightarrow \text{Ag}^+ (aq) + \text{Br}^- (aq)
\]

<table>
<thead>
<tr>
<th>Initial</th>
<th>AgBr (s)</th>
<th>$\rightarrow$</th>
<th>$\text{Ag}^+$ (aq)</th>
<th>$\text{Br}^-$ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>----</td>
<td>0</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>$\Delta$</td>
<td>$-x$</td>
<td>$+x$</td>
<td>$+x$</td>
<td></td>
</tr>
<tr>
<td>Final</td>
<td>-----</td>
<td>$x$</td>
<td>0.50 + x</td>
<td></td>
</tr>
</tbody>
</table>

$K_{sp} = [\text{Ag}^+][\text{Br}^-] = (x)(0.50 + x) = 5.0 \times 10^{-13}$

Solubility = $x = \frac{5.0 \times 10^{-13}}{0.50} = 1.0 \times 10^{-12}$ M

12. A solution is made by mixing 10.0 mL of 0.10 M Pb(NO$_3$)$_2$ and 10.0 mL of 0.0010 M Na$_2$SO$_4$. Will a precipitate form? (Ksp for PbSO$_4$ = 1.06x10$^{-8}$)

\[\text{PbSO}_4 (s) \rightarrow \text{Pb}^{2+} (aq) + \text{SO}_4^{2-} (aq)\]

\[
\left[\text{Pb}^{2+}\right] = \frac{(0.10 \text{ M})(10.0 \text{ mL})}{(20.0 \text{ mL})} = 0.0500 \text{ M} \\
\left[\text{SO}_4^{2-}\right] = \frac{(0.0010 \text{ M})(10.0 \text{ mL})}{(20.0 \text{ mL})} = 5.00 \times 10^{-4} \text{ M}
\]

\[Q_{sp} = \left[\text{Pb}^{2+}\right]\left[\text{SO}_4^{2-}\right] = (0.0500)(5.00 \times 10^{-4}) = 2.50 \times 10^{-5}
\]

Since $Q_{sp} > K_{sp}$, precipitation will occur

13. The solubility of iron (II) hydroxide, Fe(OH)$_2$, is 1.43x10$^{-3}$ g/L.
   a) Calculate the Ksp for iron (II) hydroxide.

\[\text{Fe(OH)}_2 (s) \rightarrow \text{Fe}^{2+} (aq) + 2 \text{OH}^- (aq)\]

\[
\left[\text{Fe}^{2+}\right] = \left[\text{Fe(OH)}_2\right] = \frac{1.43 \times 10^{-3} \text{ g}}{1 \text{ L}} \times \frac{1 \text{ mol}}{89.85 \text{ g}} = 1.59 \times 10^{-5} \text{ M}
\]

\[
\left[\text{OH}^-\right] = 2(1.59 \times 10^{-5}) = 3.18 \times 10^{-5} \text{ M}
\]

\[
K_{sp} = \left[\text{Fe}^{2+}\right]\left[\text{OH}^-\right]^2 = (1.59 \times 10^{-5})(3.18 \times 10^{-5})^2 = 1.61 \times 10^{-14}
\]

b) Calculate pH of a saturated solution of iron (II) hydroxide.

From part (a) $[\text{OH}^-] = 3.18 \times 10^{-5}$ M

\[
\left[\text{H}^+\right] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{3.18 \times 10^{-5}} = 3.14 \times 10^{-10} \text{ M}
\]

\[
\text{pH} = -\log \left[\text{H}^+\right] = 9.50
\]
c) A 50.0 mL sample of 3.00x10^{-3} M FeSO\(_4\) solution is added to 50.0 mL of 4.00x10^{-6} M NaOH solution. Does a precipitate form?

\[
\begin{align*}
\text{[Fe}^{2+}\text{]} & = \frac{(3.00\times10^{-3}\text{ M})(50.0 \text{ mL})}{(100.0 \text{ mL})} = 1.50\times10^{-3}\text{ M} \\
\text{[OH}^-\text{]} & = \frac{(4.00\times10^{-6}\text{ M})(50.0 \text{ mL})}{(100.0 \text{ mL})} = 2.00\times10^{-6}\text{ M} \\
Q_{sp} & = [\text{Fe}^{2+}][\text{OH}^-]^2 = (1.50\times10^{-3})(2.00\times10^{-6})^2 = 6.00\times10^{-15}
\end{align*}
\]
Since \(Q_{sp} < K_{sp}\), precipitation will not occur.

14. Lead iodate, Pb(\text{IO}_3\text{)}_2, is a slightly soluble salt with a Ksp of 2.6x10^{-13} at 25°C. To 35.0 mL of 0.150 Pb(NO\text{)}_3\text{)}_2 solution is added 15.0 mL of 0.800 M KIO\text{)}_3. A precipitate of Pb(\text{IO}_3\text{)}_2 results. What are the [Pb\text{\textsuperscript{2+}}] and [IO\text{\textsuperscript{3-}}] in the final solution?

\[
\begin{align*}
\text{[Pb}^{2+}\text{]} & = \frac{(0.150\text{ M})(35.0 \text{ mL})}{(50.0 \text{ mL})} = 0.105\text{ M} \\
\text{[IO}_3^-\text{]} & = \frac{(0.800\text{ M})(15.0 \text{ mL})}{(50.0 \text{ mL})} = 0.240\text{ M}
\end{align*}
\]

Using bounce-back method, first assume all Pb\text{\textsuperscript{2+}} reacts with all IO\text{\textsuperscript{3-}} ion to produce Pb(\text{IO}_3\text{)}_2, and then some of the precipitate dissolves back to the ions.

<table>
<thead>
<tr>
<th></th>
<th>Pb(\text{IO}_3\text{)}_2 (s) \rightarrow Pb^{2+} (aq) + 2 IO\text{\textsuperscript{3-}} (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>----</td>
</tr>
<tr>
<td>(\Delta_1)</td>
<td>+0.105</td>
</tr>
<tr>
<td>Precipitate</td>
<td>----</td>
</tr>
<tr>
<td>(\Delta_2)</td>
<td>-x</td>
</tr>
<tr>
<td>Finish</td>
<td>----</td>
</tr>
</tbody>
</table>

\[
K_{sp} = [\text{Pb}^{2+}][\text{IO}_3^-]^2 = (x)(0.030 + x)^2 = 2.6x10^{-13}
\]

\[
\text{[Pb}^{2+}\text{]} = x = \frac{2.6x10^{-13}}{(0.030)^2} = 2.9x10^{-10}\text{ M}
\]

\[
[\text{IO}_3^-] = 0.030 + 2x = 0.030\text{ M}
\]
15. Consider a solution that is 0.010 M in Ba\\textsuperscript{2+} and 0.020 M in Ca\\textsuperscript{2+}. If sodium sulfate is added to this solution to selectively precipitate one of the cations, which will precipitate first? What is the minimum concentration of Na\\textsubscript{2}SO\\textsubscript{4} that would trigger the precipitation of this cation?

From textbook,

\[ K_{sp} \text{ for BaSO}_4 = 1.07 \times 10^{-10} \]
\[ K_{sp} \text{ for CaSO}_4 = 7.10 \times 10^{-5} \]

Since the solution stoichiometry for both these compounds are similar, it would be appropriate to relate \( K_{sp} \) and molar solubility. Since the lower \( K_{sp} \) value would require the lower sulfate ion concentration in order to precipitate, it would then follow that Ba\\textsuperscript{2+} would precipitate first.

\[ \text{BaSO}_4 (s) \rightarrow \text{Ba}^{2+} (aq) + \text{SO}_4^{2-} (aq) \]

\[ K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.07 \times 10^{-10} \]

\[ [\text{SO}_4^{2-}] = \frac{K_{sp}}{[\text{Ba}^{2+}]} = \frac{1.07 \times 10^{-10}}{0.010 \text{ M}} = 1.07 \times 10^{-8} \text{ M} \]

16. What is the Cr\\textsuperscript{3+} concentration when 0.010 mol of Cr(NO\\textsubscript{3})\\textsubscript{3} is dissolved in a liter of solution buffered at pH of 10.0. Cr\\textsuperscript{3+} forms a complex ion with hydroxide shown below:

\[ \text{Cr}^{3+} (aq) + 4 \text{OH}^- (a) \rightleftharpoons \text{Cr(OH)}_4^- \quad K_f = 8 \times 10^{29} \]

\[ \text{pOH} = 14.0 - 10.0 = 4.0 \quad [\text{OH}^-] = \text{antilog pOH} = 1.0 \times 10^{-4} \]

Due to the large \( K_f \) all of Cr\\textsuperscript{3+} is converted to the complex ion, and some subsequently dissociates back to Cr\\textsuperscript{3+}. Then at equilibrium,

\[ \text{Cr}^{3+} (aq) + 4 \text{OH}^- (a) \rightleftharpoons \text{Cr(OH)}_4^- \]

\[ x \quad 1.0 \times 10^{-4} \quad 0.010 - x \]

\[ K_f = \frac{[\text{Cr(OH)}_4^-]}{[\text{Cr}^{3+}][\text{OH}^-]^4} = \frac{(0.010 - x)}{x (1.0 \times 10^{-4})^4} = 8 \times 10^{29} \]

\[ [\text{Cr}^{3+}] = x = 1.2 \times 10^{-16} \text{ M} \]

\textbf{Note:} Since the solution is buffered, [OH\\textsuperscript{-}] will remain constant during the reaction.
17. A 0.10-mol sample of AgNO₃ is dissolved in 1.00 L of 1.00 M NH₃. If 0.010 mol of NaCl is added to this solution, will AgCl ($K_{sp} = 1.8 \times 10^{-10}$) precipitate? (Ag⁺ and NH₃ form the complex ion $[Ag(NH_3)_2]^+$ with $K_f = 1.6 \times 10^7$)

To determine if a precipitate forms, we need to determine the concentration of Ag⁺ in the solution, and then calculate $Q_{sp}$ to determine if a precipitate forms.

To determine the concentration of Ag⁺, due to the large $K_f$ value, assume all of the Ag⁺ reacts to form the complex and then some dissociates back.

<table>
<thead>
<tr>
<th></th>
<th>Ag⁺ (aq)</th>
<th>2 NH₃ (aq)</th>
<th>Ag(NH₃)₂⁺ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.10</td>
<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>$\Delta_1$</td>
<td>−0.10</td>
<td>−0.20</td>
<td>+0.10</td>
</tr>
<tr>
<td>Complex</td>
<td>0</td>
<td>0.80</td>
<td>0.10</td>
</tr>
<tr>
<td>$\Delta_2$</td>
<td>+x</td>
<td>+2x</td>
<td>−x</td>
</tr>
<tr>
<td>Finish</td>
<td>x</td>
<td>0.80+2x</td>
<td>0.10−x</td>
</tr>
</tbody>
</table>

Kₐ = $\frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = \frac{(0.10 - x)}{x(0.80+2x)^2} = 1.6 \times 10^7$

$[Ag^+] = x = \frac{0.20}{(0.80)^2(1.6 \times 10^7)} = 9.8 \times 10^{-9}$ M

$Q_{sp} = [Ag^+][Cl^{-}] = (9.8 \times 10^{-9})(0.010) = 9.8 \times 10^{-11} < 1.8 \times 10^{-10}$

AgCl will NOT precipitate
18. AgNO₃ is added to a solution that is 0.10 M in NaCl and 0.010 M K₂CrO₄. Assume no
dilution caused by the addition of AgNO₃. Given the Ksp values below:

\[ \text{Ksp for AgCl} = 1.6 \times 10^{-10} \]
\[ \text{Ksp for Ag₂CrO₄} = 9.0 \times 10^{-12} \]

a) Which precipitates first, AgCl or Ag₂CrO₄? Calculate the [Ag⁺] when precipitation
first begins.

Since the solution stoichiometry for both these compounds are not the same, it
would not be appropriate to relate Ksp and molar solubility.

To determine which ion precipitates first, we must calculate the cation
concentration required for each precipitation. The lower value required for
precipitation would indicate the ion that would precipitate first.

\[ [\text{Ag}^+] \text{ required for AgCl precipitation:} \]
\[
\text{AgCl (s)} \rightarrow \text{Ag}^+ (aq) + \text{Cl}^- (aq)
\]
\[
K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10}
\]
\[
[\text{Ag}^+] = \frac{K_{sp}}{[\text{Cl}^-]} = \frac{1.6 \times 10^{-10}}{0.10 \text{ M}} = 1.6 \times 10^{-9} \text{ M}
\]

\[ [\text{Ag}^+] \text{ required for Ag₂CrO₄ precipitation:} \]
\[
\text{Ag₂CrO₄ (s)} \rightarrow 2 \text{Ag}^+ (aq) + \text{CrO₄}^{2-} (aq)
\]
\[
K_{sp} = [\text{Ag}^+]^2[\text{CrO₄}^{2-}] = 9.0 \times 10^{-12}
\]
\[
[\text{Ag}^+] = \sqrt{\frac{K_{sp}}{[\text{CrO₄}^{2-}]}} = \sqrt{\frac{9.0 \times 10^{-12}}{0.010 \text{ M}}} = 3.0 \times 10^{-5} \text{ M}
\]

The precipitation occurs for the salt which requires the smallest [Ag⁺] at equilibrium.
Therefore AgCl precipitates first at a [Ag⁺] of 1.6 \times 10^{-9} \text{ M}

b) What is the [Cl⁻] when Ag₂CrO₄ first begins to precipitate?

Calculations above show that in order of Ag₂CrO₄ to precipitate, the [Ag⁺]
must equal 3.0 \times 10^{-5} \text{ M}. Therefore,

\[ K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (3.0 \times 10^{-5})[\text{Cl}^-] = 1.6 \times 10^{-10} \]
\[
[\text{Cl}^-] = \frac{1.6 \times 10^{-10}}{3.0 \times 10^{-5}} = 5.3 \times 10^{-6} \text{ M}
\]
19. Blood is buffered by \( \text{H}_2\text{CO}_3/\text{HCO}_3^- \) system. Normal blood plasma is 0.024 M \( \text{HCO}_3^- \) and 0.0012 M \( \text{H}_2\text{CO}_3 \). \( pK_a \) for \( \text{H}_2\text{CO}_3 \) at body temperature is 6.1.

a) What is pH of blood plasma?

\[
\text{pH} = pK_a + \log \frac{[\text{base}]}{[\text{acid}]} = 6.1 + \log \frac{0.024}{0.0012} = 7.4
\]

b) If the volume of blood in a normal adult is 5.0 L, what mass of HCl can be neutralized by the buffering system in blood before the pH falls below 7.0 (which would result in death)?

For pH to drop by 0.4 to below 7.0, the ratio of base to acid in the buffer must change to 8 (from the current 20). The amount of the components of the buffer in 5.0 L of blood are:

- \( \text{mol \ HCO}_3^- = (5.0 \text{ L} \times 0.024 \text{ M}) = 0.12 \text{ mol} \)
- \( \text{mol \ H}_2\text{CO}_3 = (5.0 \text{ L} \times 0.0012 \text{ M}) = 0.0060 \text{ mol} \)

The HCl neutralized by the buffer reacts with \( \text{HCO}_3^- \) to form \( \text{H}_2\text{CO}_3 \). Therefore, after \( x \)-mol HCl is neutralized, the amounts of buffer components will be:

- \( \text{mol \ HCO}_3^- = 0.12 \text{ mol} - x \)
- \( \text{mol \ H}_2\text{CO}_3 = 0.0060 \text{ mol} + x \)

\[
\frac{[\text{base}]}{[\text{acid}]} = \frac{0.12 - x}{0.0060 + x} = 8
\]

Solving for \( x \) (mol HCl neutralized):

\[
x = 0.008 \text{ mol HCl} \times 36.5 \text{ g/mol} = 0.3 \text{ g HCl}
\]

c) For the same adult in (b), what mass of NaOH can be neutralized before the pH rises above 7.8?

For pH to rise by 0.4 to above 7.8, the ratio of base to acid in the buffer must change to 50 (from the current 20). The NaOH neutralized by the buffer reacts with \( \text{H}_2\text{CO}_3 \) to form \( \text{HCO}_3^- \). Therefore, after \( x \)-mol NaOH is neutralized, the amounts of buffer components will be:

- \( \text{mol \ HCO}_3^- = 0.12 \text{ mol} + x \)
- \( \text{mol \ H}_2\text{CO}_3 = 0.0060 \text{ mol} - x \)

\[
\frac{[\text{base}]}{[\text{acid}]} = \frac{0.12 + x}{0.0060 - x} = 50
\]

Solving for \( x \) (mol NaOH neutralized):

\[
x = 0.0035 \text{ mol NaOH} \times 40.0 \text{ g/mol} = 0.14 \text{ g NaOH}
\]
20. An important buffer used in biochemical analysis is made by dissolving TRIS \([(\text{HOCH}_2)_3\text{CNH}_2]\) in dilute HCl. A biochemist prepares a buffer by dissolving an unknown amount of TRIS in 1L of 0.095 M HCl solution. The pH of the resulting buffer solution was measured to be 8.53. How many grams of TRIS was used in this buffer? Assume volume of solution did not change after addition of TRIS.

(Molar mass of TRIS = 121.14 g/mol; pK$_b$ of TRIS = 5.91)

$$\text{TRIS} + \text{HCl} \rightarrow \text{TRISH}^+ + \text{Cl}^-$$

$$pK_a = 14.00 - 5.91 = 8.09$$

$$\text{pH} = pK_a + \log \frac{[\text{TRIS}]}{[\text{TRISH}^+]}$$

$$\frac{[\text{TRIS}]}{[\text{TRISH}^+]} = 10^{\text{pH} - pK_a} = 10^{8.53 - 5.91} = 2.75$$

In order to prepare the buffer, all the HCl in solution must react with added TRIS to form the conjugate acid and leave excess TRIS as the weak base. Therefore,

$$\text{TRIS} + \text{HCl} \rightarrow \text{TRISH}^+ + \text{Cl}^-$$

<table>
<thead>
<tr>
<th>In</th>
<th>x</th>
<th>0.095</th>
<th>0.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta$</td>
<td>-0.095</td>
<td>-0.095</td>
<td>+0.095</td>
</tr>
<tr>
<td>End</td>
<td>x-0.095</td>
<td>0.00</td>
<td>0.095</td>
</tr>
</tbody>
</table>

$$\frac{[\text{TRIS}]}{[\text{TRISH}^+]} = \frac{x - 0.095}{0.095} = 2.75$$

Solve for x (mol TRIS added)

$$x = 0.356 \text{ mol TRIS} \times 121.14 \text{ g/mol} = 43.1 \text{ g TRIS}$$