PART III: Problems

23. Calculate the molar solubility of bismuth sulfide \([\text{Bi}_2\text{S}_3]\) in:
\[K_{sp}(\text{Bi}_2\text{S}_3) = 1.6 \times 10^{-72}\]

a) pure water

\[\text{Bi}_2\text{S}_3(s) \rightarrow 2\text{Bi}^{3+}(aq) + 3\text{S}^{2-}(aq)\]

Initial \((M)\): ? 0 0

Change \((M)\): 

<table>
<thead>
<tr>
<th></th>
<th>-x</th>
<th>+2x</th>
<th>+3x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final ((M)):</td>
<td>? -x</td>
<td>2x</td>
<td>3x</td>
</tr>
</tbody>
</table>

\[K_{sp} = [\text{Bi}^{3+}]^2[\text{S}^{2-}]^3\]
\[1.6 \times 10^{-72} = (2x)^2(3x)^3\]
\[1.6 \times 10^{-72} = 108x^5\]
\[x = 1.7 \times 10^{-15} M\]

b) in 0.10 \(M\) \(\text{K}_2\text{S}\)

\[\text{Bi}_2\text{S}_3(s) \rightarrow 2\text{Bi}^{3+}(aq) + 3\text{S}^{2-}(aq)\]

Initial \((M)\): ? 0 0.10

Change \((M)\): 

<table>
<thead>
<tr>
<th></th>
<th>-x</th>
<th>+2x</th>
<th>+3x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final ((M)):</td>
<td>? -x</td>
<td>2x</td>
<td>0.10 + 3x</td>
</tr>
</tbody>
</table>

\[K_{sp} = [\text{Bi}^{3+}]^2[\text{S}^{2-}]^3\]
\[1.6 \times 10^{-72} = (2x)^2(0.10 + 3x)^3\]
\[1.6 \times 10^{-72} \approx (2x)^2(0.10)^3\]
\[x = 2.0 \times 10^{-35} M\]

24. A buffer solution is 0.80 \(M\) \(\text{HCN}/0.80 M\) \(\text{NaCN}\). \([K_a(\text{HCN}) = 4.9 \times 10^{-10} M]\]

a) What is the \(pH\) of this buffer solution? [2 pts]

\[\text{pH} = \text{p}K_a\]
\[\text{pH} = 9.31\]

b) 0.12 mol of HCl is added to 1.0 L of this buffer. What is the \(pH\) after addition of HCl? (Assume no change in volume upon addition of HCl) [5 pts]

\[\text{CN}^- + \text{HCl} \rightarrow \text{HCN} + \text{Cl}^-\]

<table>
<thead>
<tr>
<th>Initial (mol):</th>
<th>0.80</th>
<th>0.12</th>
<th>0.80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change (mol):</td>
<td>-0.12</td>
<td>-0.12</td>
<td>+0.12</td>
</tr>
<tr>
<td>Final (mol):</td>
<td>0.68</td>
<td>0</td>
<td>0.92</td>
</tr>
</tbody>
</table>

\[\text{HCN} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{CN}^-\]

<table>
<thead>
<tr>
<th>Initial (M):</th>
<th>0.92</th>
<th>0</th>
<th>0.68</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change (M):</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Final (M):</td>
<td>0.92 - x</td>
<td>x</td>
<td>0.68 + x</td>
</tr>
</tbody>
</table>


\[ K_a = \frac{[H_3O^+][CN^-]}{[HCN]} \]

\[ 4.9 \times 10^{-10} = \frac{(x)(0.68 + x)}{(0.92 - x)} \approx \frac{(x)(0.68)}{0.92} \]

\[ x = [H_3O^+] = 6.63 \times 10^{-10} \, M \]

\[ \text{pH} = 9.18 \]

OR, use Henderson-Hasselbalch equation, plugging in \([\text{CN}^-] = 0.68 \, M\) and \([\text{HCN}] = 0.92 \, M\).

25. Consider the titration of 40.0 mL of 0.30 \( M \) LiOH with 0.70 \( M \) HI.

a) How many \textbf{mL} of HI must be added to reach the equivalence point of this titration? [2 pts]

0.30 mol/L \times 0.0400 L = 0.0120 mol LiOH

The mole ratio between LiOH and HI is 1:1, so moles of HI at the equivalence point are also 0.0120 mol.

\[
M = \frac{\text{mol}}{L}
\]

\[
0.70 \, M = \frac{0.0120 \, \text{mol}}{? \, L}
\]

? L = 0.0171 L = \textbf{17.1 mL}

b) What is the \textbf{initial pH} of the solution? (Before any HI is added.) [2 pts]

\([\text{OH}^-] = 0.30 \, M \]

\[
\text{pOH} = 0.52
\]

\[
\text{pH} = 13.48
\]

c) What is the \textbf{pH} at the equivalence point? [2 pts]

\[
\text{pH} = 7
\]

d) What is the \textbf{pH} after the addition of 25.0 mL of HI? [4 pts]

\[
\text{LiOH} + \text{HI} \rightarrow \text{LiCl} + \text{H}_2\text{O}
\]

Initial (mol): 
0.0120 
0.0175

Change (mol): 
−0.0120 
−0.0120

Final (mol): 
0 
0.0055

\[
[H_3O^+] = \frac{0.0055 \, \text{mol}}{0.0650 \, \text{L}} = 0.0846 \, M
\]

\[
\text{pH} = 1.07
\]

e) The indicator, bromthymol blue, has a \( K_a \) value of approximately \( 5.0 \times 10^{-8} \). Would bromthymol blue be a \textit{good} choice as an indicator for the above titration? You \textbf{must} show a calculation to receive credit. [2 pts]

\[
\text{p}K_a = 7.30 \quad \text{(This is the pH at which the indicator changes color). Since the pH = 7 at the equivalence point, this indicator would be a good choice.}
\]