YOU MUST SHOW YOUR COMPLETE WORKING ON EACH OF PROBLEMS 5-7 TO RECEIVE FULL CREDIT.
STATE AND JUSTIFY ANY APPROXIMATIONS YOU MAKE.

Relevant Data:

Definitions:

\[ \text{pH} = - \log_{10} [H_3O^+] \]

\[ \text{pOH} = - \log_{10} [OH^-] \]

\[ \text{pK}_a = - \log_{10} K_a \]

\[ \text{pK}_b = - \log_{10} K_b \]

Autoionization of water:

\[ K_w = [H_3O^+] [OH^-] = 1.0 \times 10^{-14} \ @ 25 \degree C \]

Therefore \( \text{pK}_a + \text{pK}_b = 14.00 \ @ 25 \degree C \)

The Henderson-Hasselbalch Equation:

\[ pH = pK_a + \log_{10} \left( \frac{[A^-]}{[HA]} \right) \]

Solution of the quadratic equation \( ax^2 + bx + c = 0 \) is given by:

\[ x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]
Multiple Choice and short answer problems (you do not need to show working for problems 1 - 4):

**Question 1** Which of the following compounds has the lowest solubility in mol L\(^{-1}\) in water at 25\(^\circ\)C?

(a) Ag\(_3\)PO\(_4\) \(K_{sp} = 1.8 \times 10^{-18}\)
(b) Sn(OH)\(_2\) \(K_{sp} = 3 \times 10^{-27}\)
(c) CdS \(K_{sp} = 1.0 \times 10^{-28}\)
(d) CaSO\(_4\) \(K_{sp} = 6.1 \times 10^{-5}\)
(e) Al(OH)\(_3\) \(K_{sp} = 2 \times 10^{-32}\)

(5 points)

**Question 2** If the following salts are dissolved in water, will the solution be acidic, basic or neutral? Check the appropriate box for each salt.

<table>
<thead>
<tr>
<th></th>
<th>Acidic</th>
<th>Basic</th>
<th>Neutral</th>
</tr>
</thead>
<tbody>
<tr>
<td>KF</td>
<td></td>
<td>✗</td>
<td></td>
</tr>
<tr>
<td>Na(_2)CO(_3)</td>
<td></td>
<td></td>
<td>✗</td>
</tr>
<tr>
<td>CsNO(_3)</td>
<td></td>
<td></td>
<td>✗</td>
</tr>
<tr>
<td>FeCl(_3)</td>
<td>✗</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH(_4)Br</td>
<td>✗</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(5 points)
**Question 3)** Silver chloride, AgCl \((s)\), is more soluble in:

(a) Pure water
(b) Aqueous NH\(_3\) solution
(c) Sea water
(d) Has the same solubility in each of the above solutions

(5 points)

**Question 4)** Considering the molecular structure of the following acids and bases, assign the relative acid and base strengths:

(a) 1 is a stronger base than 2, and 3 is a stronger acid than 4
(b) 1 is a stronger base than 2, and 4 is a stronger acid than 3
(c) 2 is a stronger base than 1, and 4 is a stronger acid than 3
(d) 2 is a stronger base than 1, and 3 is a stronger acid than 4

(5 points)
**Long Answers.** You must show all your working.

**Question 5)** Codeine is a derivative of morphine that is used as an analgesic. Codeine is a weak base as follows:

\[
C_{18}H_{21}O_3N(aq) + H_2O(l) \leftrightarrow C_{18}H_{21}O_3NH^+(aq) + OH^-(aq)
\]

pK_b for codeine is 6.05. Calculate the pH of a 10.0 mL solution of codeine containing 5.0 mg codeine. (Use molecular weights in periodic table; pK_b = -\log_{10} K_b)

\[
\frac{5.0 \times 10^{-3} \text{ g}}{(12 \times 18 + 21 \times 1.008 + 3 \times 16 + 14.01) \text{ g/mol}} = \text{# mol codeine} = \frac{5.0 \times 10^{-3} \text{ g}}{293 \text{ g/mol}} = 1.7 \times 10^{-5} \text{ mol}
\]

Initial concentration of codeine = \(\frac{1.7 \times 10^{-5}}{10 \times 10^{-3}} = 1.7 \times 10^{-3} \text{ mol/L}\)

<table>
<thead>
<tr>
<th></th>
<th>Codeine + H_2O \rightleftharpoons Codeine-H^+ + OH^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1.7 \times 10^{-3}</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
</tr>
</tbody>
</table>
| Equilibrium    | (1.7 \times 10^{-3} - x) 

K_b = 10^{-6.05} = \frac{8.9 \times 10^{-7}}{1.7 - x} = \frac{x^2}{(1.7 - x)}

\[x^2 = (8.9 \times 10^{-7})(1.7 \times 10^{-3}) = 1.5 \times 10^{-3}\]

Assuming \(x \ll 1.7 \times 10^{-3}\)

\[x = 3.9 \times 10^{-5}\]

\[\text{[OH}^-\text{]} = 3.9 \times 10^{-5}\]

pOH = -\log_{10} (3.9 \times 10^{-5}) = 4.41

\[\text{pH} = 14.00 - 4.41 = 9.59\]

(20 points)
Question 6) (30 points)

You own an Olympic size swimming pool (volume $3.7 \times 10^6$ liters) at your Bel-Air mansion. To be safe for swimmers, not only does pool water need to be chlorinated but the pH of the water needs to be closely regulated; the pH needs to remain at 7.45. One chemical that is used to "chlorinate" swimming pools is a buffer of sodium hypochlorite (NaOCl) and hypochlorous acid (HOCl). $K_a$ of HOCl is $3.5 \times 10^{-8}$

(a) What does the ratio of $[\text{OCI}^-]$ to $[\text{HOCl}]$ need to be to maintain the desired pH? Why?

\[
\text{pK}_a \text{ of HOCl} = -\log_{10} (3.5 \times 10^{-8}) = 7.46
\]

Using the Henderson-Hasselbalch equation for a buffer:

\[
\text{pH} = \text{pK}_a + \log_{10} \left( \frac{[\text{OH}^-]}{[\text{HOCl}]} \right)
\]

If pH desired = 7.45 = pK$_a$\n
\[
\text{pH} = \text{pK}_a + \log_{10} \left( \frac{[\text{OH}^-]}{[\text{HOCl}]} \right) = 7.45 \Rightarrow \frac{[\text{OH}^-]}{[\text{HOCl}]} = 1
\]

(b) After filling the pool from fresh tap water at the beginning of the summer, you start adding the chemicals necessary to make up the buffer. First, you add a total of 55 kg of NaOCl (molecular weight 74.5 g/mol) solid to the pool. Calculate the initial $[\text{OCI}^-]$ in the pool.

\[
\text{# mol of NaOCl} = \frac{55 \times 10^3 \text{ g}}{74.5 \text{ g/mol}} = 738 \text{ mol}
\]

\[
\text{volume} = 3.7 \times 10^6 \text{ L}
\]

\[
\Rightarrow [\text{OCI}^-] = \frac{738 \text{ mol}}{3.7 \times 10^6 \text{ L}} = 2.0 \times 10^{-4} \text{ mol L}^{-1}
\]
(c) OCl\(^-\) is of course a base. What is the pH of the pool water at this stage?

<table>
<thead>
<tr>
<th></th>
<th>OC(_1^-) + H(_2)O</th>
<th>⇌</th>
<th>HOC(_1) + OH(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2 \times 10^{-4}</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>-x</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>(\bar{E})</td>
<td>(2 \times 10^{-4} - x)</td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>

\[
\frac{x^2}{2 \times 10^{-4} - x} = K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{3.5 \times 10^{-8}} = 2.9 \times 10^{-7}
\]

Assume \(x \ll 2 \times 10^{-4}\)

\[
x^2 = (2.0 \times 10^{-4})(2.9 \times 10^{-7}) = 5.8 \times 10^{-11}
\]

\[
x = 7.6 \times 10^{-6}
\]

\[
\Rightarrow [OH^-] = 7.6 \times 10^{-6} \text{ mol L}^{-1}
\]

\[
\Rightarrow pOH = 5.12
\]

\[
\Rightarrow pH = 14.00 - 5.12 = 8.88
\]
(d) In your pool supply store you find another product called "Negative pH balancer". The label on the plastic container say "Contents: Muriatic Acid (HCl) 1 molar solution". What volume of the muriatic acid pool additive do you need to add to achieve the desired buffer at pH 7.45?

Have 7.38 mol of OCl⁻ in pool and need to achieve [OCl⁻] = [HOCl] to get to correct pH. Thus I need to add 369 mol of H⁺ to achieve following reaction:

$$\text{OCl}^- + \text{H}^+ \rightarrow \text{HOCl}$$

<table>
<thead>
<tr>
<th>Initial</th>
<th>7.38</th>
<th>369</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final</td>
<td>369</td>
<td>0</td>
</tr>
</tbody>
</table>

So to add 369 mol of H⁺ to pool I need 369 liters of 1.0 M H⁺ solution (added volume is negligible compare to pool volume)

[This is almost 100 gallons of H⁺!]
**Question 7** (30 points)

A 40.0 mL sample of 0.15 M \( \text{Ba(OH)}_2 \) (a strong base) is titrated with 0.400 M \( \text{HNO}_3 \). Calculate the pH after addition of the following volumes of acid:

(a) 0.0 mL acid added

\[
0.15 \text{ M } \text{Ba(OH)}_2 \text{ has } 0.30 \text{ M } \text{OH}^- \\
\text{Ba(OH)}_2(\text{s}) \rightarrow \text{Ba}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})
\]

\[
\text{pOH} = -\log(0.3) = 0.52 \\
\text{pH} = 13.48
\]

(b) 20.0 mL added

\[
\text{HNO}_3 \text{ strong acid } \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^-
\]

\[
20.0 \text{ mL } \times 0.400 \text{ mol/L} = 8 \text{ mmol } \text{H}_3\text{O}^+ \text{ added}
\]

\[
\text{mol of } \text{OH}^- \text{ originally } = 40.0 \text{ mL } \times 0.30 \text{ mol/L} \\
= 12 \text{ mmol}
\]

\[
\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}
\]

Insert 8

Find 4

Now have \[ 4 \text{ mmol of OH}^- \text{ in } 60 \text{ mL of solution } \]

\[
\text{So } [\text{OH}^-] = \frac{4 \text{ mmol}}{60 \text{ mL}} = 0.067 \text{ M}
\]

\[
\text{pOH} = 1.18 \\
\text{pH} = 12.82
\]
(c) 30.0 mL added  

\[ \text{As per (b)} \quad 30 \times 0.4 = 12 \text{ mmol } H_3O^+ \text{ added} \]

\[ H_3O^+ + OH^- \rightarrow 2H_2O \]

<table>
<thead>
<tr>
<th>Initial</th>
<th>12</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>After</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Exactly removed all OH\(^-\). Major species Ba\(^{2+}\), NO\(_3^-\)

\[ pH = 7.00 \]

\( \text{EQUVALENCE POINT} \)

(d) 40.0 mL added

\[ \text{Total of} \quad 40 \times 0.4 = 16 \text{ mmol } H_3O^+ \text{ added} \]

\[ H_3O^+ + OH^- \rightarrow 2H_2O \]

<table>
<thead>
<tr>
<th>Initial</th>
<th>16</th>
<th>12</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\[ [H_3O^+] = \frac{4 \text{ mmol}}{80 \text{ mL}} = 0.05 \text{ mol L}^{-1} \]

\[ pH = 1.30 \]
(e) Plot a graph of pH versus mL of HNO₃ added using the points you have calculated. Sketch a line going through these points based on your knowledge of the shapes of titration curves. Mark on your graph the equivalence point.