1. Answer the following questions that relate to the chemistry of halogen oxoacids.

(a) Use the information in the table below to answer part (a)(i).

<table>
<thead>
<tr>
<th>Acid</th>
<th>$K_a$ at 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>hypochlorous acid, HOCl</td>
<td>$2.9 \times 10^{-8}$</td>
</tr>
<tr>
<td>hypobromous acid, HOBr</td>
<td>$2.4 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

(i) Which of the two acids is stronger, HOCl or HOBr? Justify your answer in terms of $K_a$.

HOCl is stronger because it has a higher $K_a$.

(ii) Draw a complete Lewis electron-dot diagram for the acid that you identified in part (a)(i).

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H --O --Cl
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(iii) Hypoiodous acid has the formula HOI. Predict whether HOI is a stronger acid or a weaker acid than the acid that you identified in part (a)(i). Justify your prediction in terms of chemical bonding.

Hypoiodous acid would be weaker than HOCl because I has a lower electronegativity than Cl, making its H–O bond less polar. Strength of an oxyacid increases as the electronegativity of the atom bonded to the O increases since it pulls more electron density away from the H–O bond, making it more polar and easier to ionize.

(b) Write the equation for the reaction that occurs between hypochlorous acid and water.

$$\text{HOCl (aq) + H}_2\text{O (aq)} \rightleftharpoons \text{OCl}^- (aq) + \text{H}_3\text{O}^+(aq)$$

(c) A 1.2 M NaOCl solution is prepared by dissolving solid NaOCl in distilled water at 298 K. The hydrolysis reaction $\text{OCl}^- (aq) + \text{H}_2\text{O(l)} \rightleftharpoons \text{HOCl}(aq) + \text{OH}^- (aq)$ occurs.

(i) Write the equilibrium-constant expression for the hydrolysis reaction that occurs between OCl$^-$ (aq) and H$_2$O(l).

$$K_b = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-]}$$

(ii) Calculate the value of the equilibrium constant at 298 K for the hydrolysis reaction.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.9 \times 10^{-8}} = 3.4 \times 10^{-7}$$

(iii) Calculate the value of $[\text{OH}^-]$ in the 1.2 M NaOCl solution at 298 K.

$$\text{OCl}^- (aq) + \text{H}_2\text{O(l)} \rightleftharpoons \text{HOCl}(aq) + \text{OH}^- (aq)$$

<table>
<thead>
<tr>
<th>I (M)</th>
<th>1.2</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (M)</td>
<td>$-x$</td>
<td>$+x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>E (M)</td>
<td>$1.2 + x$</td>
<td>$x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

We can set [OCl$^-$] = 1.2 since x will be negligible due to the low value of $K_b$.

$$K_b = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-]} = \frac{(x)(x)}{1.2} = 3.4 \times 10^{-7}; \ x = [\text{OH}^-] = \sqrt{(1.2)(3.4 \times 10^{-7})} = 6.4 \times 10^{-4} \text{ M}$$
2. A pure 14.85 g sample of the weak base ethylamine, C$_2$H$_5$NH$_2$, is dissolved in enough distilled water to make 500. mL of solution.

(a) Calculate the molar concentration of the C$_2$H$_5$NH$_2$ in the solution.

\[
\text{MM (C}_2\text{H}_5\text{NH}_2) = 2\times12.01 \text{ g} + 7\times1.008 \text{ g} + 14.01 \text{ g} = 45.09 \text{ g/mol}
\]

\[
[C_2\text{H}_5\text{NH}_2] = \frac{14.85 \text{ g}}{45.09 \text{ g/mol}} \times \frac{1 \text{ L}}{0.500 \text{ L}} = 0.659 \text{ M}
\]

(b) The aqueous ethylamine reacts with water when dissolved.

(i) Write the equation for the reaction between C$_2$H$_5$NH$_2$(aq) and water.

\[
\text{C}_2\text{H}_5\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_2\text{H}_5\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})
\]

(ii) Write the equilibrium-constant expression for the reaction.

\[
K_a = \frac{[\text{C}_2\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_2\text{H}_5\text{NH}_2]}
\]

(iii) Of C$_2$H$_5$NH$_2$(aq) and C$_2$H$_5$NH$_3^+(aq)$, which is present in the solution at the higher concentration? Justify your answer.

C$_2$H$_5$NH$_2$ is present at higher concentration. Since it is a weak base, it will have a low $K_b$ value and dissociate to a very small extent in water, producing a much smaller concentration of the conjugate acid, C$_2$H$_5$NH$_3^+$.

(c) A different solution is made by dissolving 0.500 mol of C$_2$H$_5$NH$_3$Cl in enough distilled H$_2$O to make 1.000 L of solution. The pH of the solution is found to be 5.528.

(i) Write the dissociation equation for C$_2$H$_5$NH$_3$Cl.

\[
\text{C}_2\text{H}_5\text{NH}_3\text{Cl}(\text{s}) \rightarrow \text{C}_2\text{H}_5\text{NH}_3^+(\text{aq}) + \text{Cl}^-(\text{aq})
\]

(ii) Write the net-ionic equation that represents the reaction that occurs when the C$_2$H$_5$NH$_3$Cl reacts with H$_2$O.

Cl$^-$ is a neutral ion, so it does not hydrolyze. C$_2$H$_5$NH$_3^+$ is a weak acid and hydrolyzes:

\[
\text{C}_2\text{H}_5\text{NH}_3^+(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_2\text{H}_5\text{NH}_2(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})
\]

(iii) Calculate the concentration of H$^+(aq)$ in the solution (you can neglect the H$^+$ from H$_2$O.)

\[
[H^+] = 10^{-5.528} = 2.97 \times 10^{-6} \text{ M}
\]

(iv) Calculate the value of $K_a$ for C$_2$H$_5$NH$_3^+$.

\[
\begin{array}{ccc}
| & \text{I (M)} & \text{C (M)} & \text{E (M)} \\
\hline
\text{C}_2\text{H}_5\text{NH}_3^+(\text{aq}) + \text{H}_2\text{O}(l) & \text{0.500} & - & \text{0} \\
\text{C}_2\text{H}_5\text{NH}_2(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) & - & +2.97 \times 10^{-6} & +2.97 \times 10^{-6} +2.97 \times 10^{-6} \\
\end{array}
\]

\[
K_a = \frac{[\text{C}_2\text{H}_5\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{C}_2\text{H}_5\text{NH}_3^+]} = \frac{(2.97 \times 10^{-6})^2}{0.500} = 1.76 \times 10^{-11}
\]

(v) Calculate the value of $K_b$ for C$_2$H$_5$NH$_2$.

\[
K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.76 \times 10^{-11}} = 5.67 \times 10^{-4}
\]
3. Sodium benzoate, C₆H₅COONa, is the salt of a weak acid, benzoic acid, C₆H₅COOH. A 0.100 molar solution of sodium benzoate has a pH of 8.60 at 25°C.

(a) Write the net ionic equation for the hydrolysis reaction that occurs:

\[ \text{C}_6\text{H}_5\text{COO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_6\text{H}_5\text{COOH}(aq) + \text{OH}^-(aq) \]

(b) Calculate the \([\text{OH}^-]\) in this sodium benzoate solution.

\[ \text{pH} = 8.60, \text{pOH} = 14.00 - 8.60 = 5.40; [\text{OH}^-] = 10^{-\text{pOH}} = 3.98 \times 10^{-6} \text{ M} \]

(c) Calculate the value for the equilibrium constant for the reaction:

Because of stoichiometry, \([\text{C}_6\text{H}_5\text{COOH}] = [\text{OH}^-] = 3.98 \times 10^{-6} \text{ M} \)

\[ K_b = \frac{[\text{C}_6\text{H}_5\text{COOH}][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{COO}^-]} = \frac{(3.98 \times 10^{-6})^2}{(0.100 - 3.98 \times 10^{-6})} = 1.58 \times 10^{-10} \]

(d) Calculate the value of \(K_a\), the acid dissociation constant for benzoic acid.

\[ K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.58 \times 10^{-10}} = 6.33 \times 10^{-5} \]

(e) A saturated solution of benzoic acid is prepared by adding excess solid benzoic acid to pure water at 25°C. Since this saturated solution has a pH of 2.880, calculate the initial concentration of benzoic acid at 25°C.

\[ [\text{H}^+] = 10^{-\text{pH}} = 10^{-2.880} = 1.32 \times 10^{-3} \text{ M}; [\text{C}_6\text{H}_5\text{COO}^-] = [\text{H}^+] = 1.32 \times 10^{-3} \text{ M} \]

\[ K_a = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} \quad \text{so} \quad [\text{C}_6\text{H}_5\text{COOH}] = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{COO}^-]}{K_a} = \frac{(1.32 \times 10^{-3})^2}{6.33 \times 10^{-5}} = 2.75 \times 10^{-2} \text{ M} \]

total dissolved = (2.75 \times 10^{-2}M + 1.32 \times 10^{-3}M as ions) = 2.88 \times 10^{-2}M

4. Methylamine CH₃NH₂ is a weak base that ionizes in solution as shown by the following equation.

\[ \text{CH}_3\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{NH}_3^+(aq) + \text{OH}^-(aq) \]

(a) At 25°C the percentage ionization in a 0.160 molar solution of CH₃NH₂ is 4.7%. Calculate \([\text{OH}^-]\), \([\text{CH}_3\text{NH}_3^+]\), \([\text{CH}_3\text{NH}_2]\), \([\text{H}_3\text{O}^+]\), and the pH of this solution at 25°C

0.160M CH₃NH₂ \times 4.7\% = 7.5 \times 10^{-3} \text{ M ionized}

@ equilibrium: \([\text{CH}_3\text{NH}_2] = (0.160M - 0.0075M) = 0.153M \]

\[ [\text{CH}_3\text{NH}_3^+] = [\text{OH}^-] = 7.5 \times 10^{-3} \text{ M} \]

\[ [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{7.5 \times 10^{-3}} = 1.3 \times 10^{-12} \text{ M} \]

\[ \text{pH} = -\log [\text{H}_3\text{O}^+] = 11.89 \]

(b) Calculate the value for \(K_b\), the ionization constant for CH₃NH₂, at 25°C.

\[ K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{(7.5 \times 10^{-3})^2}{0.152} = 3.7 \times 10^{-4} \]