1. Using the table in Appendix 1 (it is attached to the back of the exam), estimate

   a. (5 points) All ionization fraction values (α) associated with a hydrocyanic acid solution at a pH of 8.3 and 9.3.

   \[
   \begin{align*}
   &\text{At pH} = 8.3 \\
   &\text{pH} = 9.3 - 1 \\
   &\alpha_0 = 0.9091 \\
   &\alpha_1 = 0.0909 \\
   \\
   &\text{At pH} = 9.3 \\
   &\text{pH} = 9.3 + 0 \\
   &\alpha_0 = 0.5 \\
   &\alpha_1 = 0.5 \\
   \end{align*}
   \]

   b. (5 points) All ionization fraction values (α) associated with a hydrogen sulfide solution at a pH of 7.0

   \[
   \frac{pK_a_1 + pK_a_2}{2} = \frac{7.1 + 14}{2} = 10.55 > \text{pH} \\
   \alpha_0 = 0.5573 \\
   \alpha_1 = 0.4427 \\
   \alpha_2 = 0 \\
   \]

   c. (6 points) Calculate the buffer intensity for hydrocyanic acid at a pH of 8.3 and 9.3. At which pH is the system best buffered? You must explain for credit.

   \[
   \beta = 2.3 \left( [H^+] + [\text{OH}^-] + \alpha_0 \alpha_1 C_{\text{T, A}} \right) \\
   \begin{align*}
   &\frac{[H^+]}{10^{-8.3}} \\
   &\frac{[\text{OH}^-]}{10^{-5.7}} \\
   &\frac{\beta}{1.95 \times 10^{-4}} \\
   &10^{-9.3} \\
   &10^{-4.7} \\
   &10^{-4.7} \\
   \end{align*}
   \]

   \[
   \text{Best Buffered at pH} = 9.3 \\
   \beta_{9.3} > \beta_{8.3} \\
   \text{pH} \sim pK_a
   \]
2. (5 points) If 30 ml of 1 M H₂SO₄ is added to 1 Liter of 0.1 M NaOH, what is the equivalence fraction?

\[
f = \frac{\text{equiv acid added}}{\text{mol base}} = \frac{30 \text{ ml}}{L} \times \frac{1 \text{ mol}}{1 \text{ L}} \times \frac{\text{H}_2\text{SO}_4}{2 \text{ equiv}} \times \frac{1 \text{ L}}{1000 \text{ ml}} = 0.6
\]

3. Consider the titration curve shown below to answer the following questions. Assume that NaOH will be added incrementally to the buffered solution.

![Titration Curve Graph](image)

a. (3 points) Label the 3 inflection points on the graph.

b. (3 points) What is the pKₐ of the solution? \( pK_a = 3.2 \)

c. (3 points) What acid-conjugate base pair could have been used to buffer the solution? Hydrofluoric acid / Fluoride ion

\[
\text{HF} / \text{F}^-
\]

d. (3 points) At what equivalence fraction does the salt of the acid concentration equal \( C_f \)? Write the molecular formula for this salt? \( f = 1.0 \) NaF

e. (3 points) In what region is the system well buffered?

\[
\text{around } f = 0.5
\]
4. (14 points) Complete the following table to show how $C_T$ and alkalinity change when NaOH, HCl, CO$_2$, etc. is added to an aqueous solution in a closed system.

$\uparrow$ indicates the term increase

--- indicates the term remains the same

$\downarrow$ indicates the term decreases

<table>
<thead>
<tr>
<th>Compound Added</th>
<th>$C_T$</th>
<th>Alkalinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td></td>
<td>$\uparrow$</td>
</tr>
<tr>
<td>HCl</td>
<td>$\uparrow$</td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td></td>
<td>$\downarrow$</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>$\uparrow$</td>
<td></td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>$\uparrow$</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td></td>
<td>$\uparrow$</td>
</tr>
</tbody>
</table>

Recall: $NH_4^+ \Leftrightarrow NH_3 + H^+ \ pK_a = 9.3$

5. (15 points) Explain the wet chemistry process used to determine both the carbonate and total alkalinity of a water sample. (Give me plenty of info here so that I'm confident that you understand the process/reactions taking place).

Titrate with standard solution of strong acid.

\[
\text{acid} \quad \rightarrow\quad \text{acid} \quad \rightarrow\quad \text{acid} \quad \rightarrow\quad \text{acid} \quad \rightarrow
\]

- H$_2$CO$_3$
- $HCO_3^-$
- $CO_3^{2-}$
- $OH^-$

$H^+$ is added to complete above reaction

- PH$_{HCO_3^-}$ $\leq$ 10.5
called caustic alkalinity

- PH$_{HCO_3^-} = 8.3$
called carbonate alkalinity

Phenolphthalein will change from red $\Rightarrow$ colorless

$H^+ + OH^- \rightarrow H_2O$

Complete $H^+ + CO_3^{2-} \rightarrow HCO_3^-$

$H^+$ is added to the reaction below:

- total alkalinity or methyl orange alkalinity

\[
\begin{align*}
\text{HCO}_3^- + H^+ & \rightarrow \text{CO}_3^{2-} \\
pH & \approx 4.5 - 4.8
\end{align*}
\]

Titrate to methyl orange indicator endpoint.
6. Wastewater having $C_T = 2.0 \times 10^{-4} \text{ M}$ and alkalinity $= 1.0 \times 10^{-3} \text{ eqv/L}$ is discharged to lake water having $C_T = 2.2 \times 10^{-3} \text{ M}$ and alkalinity $= 2.5 \times 10^{-3} \text{ eqv/L}$. **Assume the system is closed.**

a. (5 points) What are the $C_T$ and Alkalinity of this mixture assuming a 1:10 dilution (1 part wastewater, 9 parts lake water)?

b. (5 points) What is the pH of the mixture?

\[
(a) \quad C_{T,\text{mix}} = \frac{(1)(2 \times 10^{-4}) + 9(2.2 \times 10^{-3})}{10} = 2 \times 10^{-3} \text{ M}
\]

\[
Alk_{\text{mix}} = \frac{(1)(1.0 \times 10^{-3}) + 9(2.5 \times 10^{-3})}{10} = 2.35 \times 10^{-3} \text{ eqv/L}
\]

From DoHyeos Diagram

\[
\text{pH} = 9.6
\]
7. (10 points) Budget cuts have left a researcher with a sparsely stocked laboratory. Besides pure water, sodium bicarbonate (NaHCO₃) and sodium carbonate (Na₂CO₃) are the only chemicals available. Describe how a solution having pH 9.0 can be prepared if no interaction is allowed to take place with the atmosphere.

\[
pH = pK_a + \log \left( \frac{\text{salt}}{\text{acid}} \right)
\]

\[9 = 10.3 + \log \frac{Na_2CO_3}{NaHCO_3}\]

\[\frac{[Na_2CO_3]}{[NaHCO_3]} = 10^{-1.3} = 5.01 \times 10^{-2}\]

The number of moles will depend on the desired molarity of the final solution.

If \( x \) molar

\[x = [Na_2CO_3] + [NaHCO_3]\]
8. (15 points) Draw the pC-pH diagram for an open system containing SO₂. The partial pressure of SO₂ is \( P_{SO_2} = 2 \times 10^{-8} \text{ atm} \). Show your work.

The following are relevant system equations with their corresponding equilibrium constant values.

\[
\begin{align*}
SO_{2(g)} & \rightleftharpoons SO_{2(aq)} \approx H_2SO_3 \\
H_2SO_3 & \rightleftharpoons HSO_3^- + H^+ \\
HSO_3^- & \rightleftharpoons SO_3^{2-} + H^+
\end{align*}
\]

\[
\begin{align*}
K_H &= 1.25 \text{ mol/L atm} \\
pK_{a,1} &= 1.9 \\
pK_{a,2} &= 7.2
\end{align*}
\]

(b) Based on the diagram, what is the pH of a pure SO₂ – water system?

\[
[H^+] = [OH^-] + [HSO_3^-] + 2[SO_3^{2-}] \\
pH \approx 4.8
\]

\[
[H_2SO_3] = P_{SO_2} K_{HSO_2} = \left(2 \times 10^{-8} \text{ atm}\right) \left(1.25 \text{ mol/L atm}\right) = 2.5 \times 10^{-8} \text{ M}
\]

\[
P[H_2SO_3] = 7.6
\]

\[
K_{a,1} = \frac{[H^+][HSO_3^-]}{[H_2SO_3]}
\]

\[
[HSO_3^-] = K_{a,1} \frac{[H_2SO_3]}{[H^+]}
\]

\[
\frac{P[HSO_3^-]}{[H^+]} = \frac{9.5 - pH}{[H^+]}
\]
\[ K_{a_2} = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]} \]

\[ [SO_3^{2-}] = \frac{K_{a_2} [HSO_3^-]}{[H^+]} = \frac{K_{a_2} 10^{-9.5}}{[H^+]^2} = \frac{10^{-7.2}}{10^{-9.5}} \]

\[ [SD_3^{2-}] = \frac{10^{-16.7}}{[H^+]^2} \]

\[ p \left[ SD_3^{2-} \right] = 16.7 - 2 \text{pH} \]