Part I (48 points). Show your work. Evaluation based on correctness, completeness and clarity. Use appropriate number of significant figures in your final result.

1. (16) The following questions deal with the titration of 50.0 mL of 0.100 M sodium cyanide (NaCN) with 0.200 M perchloric acid (HClO₄). For HCN, $K_a = 6.2 \times 10^{-10}$.

   a) Write the net reaction for this titration.

   $$\text{Na}_2\text{CN} + \text{HClO}_4 \rightarrow \text{HCN} + \text{NaClO}_4$$

   b) Calculate the pH of the solution at the equivalence point.

   $$V_e = \frac{V_B \cdot C_B}{C_A} = \frac{(50.0 \text{ mL})(0.100 \text{ mmol/mL})}{0.200 \text{ mmol/mL}} = 25.0 \text{ mL}$$

   Solution is HCN + NaClO₄ ; $n_{HCN} = (50.0 \text{ mL})(0.100 \text{ mmol/mL}) = 5.00$

   $$C_{HCN} = \frac{5.00 \text{ mmol}}{50.0 + 25.0 \text{ mL}} = 0.0667 \text{ M}.$$

   $$\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-$$

   $$K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} \approx \frac{[\text{H}^+]^2}{C_{HCN}}$$

   $$[\text{H}^+] = \sqrt{K_a \cdot C_{HCN}}$$

   $$= \sqrt{(6.2 \times 10^{-10})(0.0667)} = 6.43 \times 10^{-6}$$

   $$\text{pH} = 5.19$$
2. (16) 10.0 mL of 0.200 M HCl is added to 100.0 mL of a buffer solution containing 0.200 M acetic acid and 0.400 M sodium acetate. Write the balanced net reaction that occurs, and calculate the pH of the resulting solution. For acetic acid, $K_a = 1.8 \times 10^{-5}$.

\[
\begin{align*}
\eta_{\text{HCl}} &= (10.0 \text{ mL})(0.200 \text{ M}) = 2.0 \text{ mmol} \\
\eta_{\text{HOAc}} &= (100 \text{ mL})(0.200 \text{ M}) = 20.0 \text{ mmol} \\
\eta_{\text{NaOAc}} &= (100 \text{ mL})(0.400 \text{ M}) = 40.0 \text{ mmol}
\end{align*}
\]

**Reaction:**

\[
\text{NaOAc} + \text{HCl} \rightarrow \text{HOAc} + \text{NaCl}
\]

\[
\begin{array}{ccc}
\text{mmol: Start} & 40.0 & 2.0 & 20.0 \\
\text{Reacted} & -2.0 & -2.0 & +2.0 \\
\text{Final} & 38.0 & - & 22.0
\end{array}
\]

**Buffer**

\[
\text{HOAc} \rightleftharpoons \text{H}^+ + \text{OAc}^-
\]

\[
K_a = \frac{[\text{H}^+][\text{OAc}^-]}{[\text{HOAc}]}
\]

\[
[\text{H}^+] = K_a \frac{[\text{HOAc}]}{[\text{OAc}^-]} \approx K_a \frac{\eta_{\text{HOAc}}}{\eta_{\text{OAc}^-}}
\]

\[
= 1.8 \times 10^{-5} \left(\frac{22.0}{38.0}\right)
\]

\[
= 1.04 \times 10^{-5}
\]

\[
\text{pH} = 4.5 + \log 1.04 \times 10^{-5} \approx 4.98
\]
3. (16) A 0.4200-g sample of impure sodium carbonate was titrated with 0.1000 M HCl, yielding the following titration curve. The exact volume required to reach the second equivalence point was 39.84 mL. The molar mass of Na₂CO₃ is 106.0 g/mol.

![Titration Curve]

For the pH curve:

\[ V_{\text{HCl}} = 39.84 \]

a) Write the overall balanced reaction corresponding to titration of the sodium carbonate to the second equivalence point.

\[ \text{Na}_2\text{CO}_3 + 2 \text{HCl} \rightarrow 2 \text{NaCl} + \text{H}_2\text{CO}_3 \]

b) Annotate the titration curve showing the points where pH is equal to pKₐ₁ and pKₐ₂ for carbonic acid. Also write your estimates of these values here (volume of titrate, pKa).

\[ \text{pH} = \text{pK}_a = 6.3 \text{ at } V_{\text{HCl}} = 30 \text{ mL} \]

\[ \text{pH} = \text{pK}_a = 10.3 \text{ at } V_{\text{HCl}} = 10 \text{ mL} \]

c) Calculate the percent sodium carbonate in the sample.

\[ \% \text{Na}_2\text{CO}_3 = \left( \frac{\text{Volume}_{\text{HCl}} \cdot \frac{\text{Molarity}_{\text{HCl}} \cdot \text{Formula Mass}_{\text{Na}_2\text{CO}_3}}{2 \cdot \text{Molarity}_{\text{HCl}}}}{\text{Sample Mass}} \right) \times 100 \]

\[ = \left( \frac{39.84 \cdot (0.1000) \cdot (\frac{1}{2}) \cdot (0.1060)}{0.4200} \right) \times 100 \]

\[ = 50.27 \% \]