A solution was prepared by dissolving 0.2500 g of Na₃A in 20 mL of distilled water. The following curve was obtained by titrating the solution with 0.1000 M HCl. The acid dissociation constants for H₃A are $K_{a1} = 5.0 \times 10^{-3}$, $K_{a2} = 1.0 \times 10^{-7}$, and $K_{a3} = 3.0 \times 10^{-12}$.

(a) Write the three equilibrium reactions that correspond to the three acid dissociation constants for H₃A.

\[
\begin{align*}
H_3A + H_2O & \rightleftharpoons H_2A^- + H_3O^+ \\
H_2A^- + H_2O & \rightleftharpoons HA^{2-} + H_3O^+ \\
HA^{2-} + H_2O & \rightleftharpoons A^{3-} + H_3O^+
\end{align*}
\]

(b) What is the predominant form(s) of H₃A in the analyte solution before the titration begins (point A)?

$A^{3-}$

(c) On the titration curve, locate the equivalence points. Indicate (on titration curve) the predominant form(s) of H₃A at each equivalence point.
(d) Identify the titrant.  \( \text{HCl} \)

(e) Identify the analyte.  \( A^{3-} \) or \( \text{Na}_3\text{A} \)

(f) Write the neutralization reaction for the titration to the first equivalence point.

\[
\text{HCl} + \text{Na}_3\text{A} \rightarrow \text{Na}_2\text{HA} + \text{NaCl}
\]

\text{or}\n
\[
\text{H}_3\text{O}^+ + A^{3-} \rightarrow \text{HA}^{2-} + \text{H}_2\text{O}
\]

(g) Based upon the titration to the first equivalence point, how many moles of \( \text{Na}_3\text{A} \) are you starting with?

\[
n_{\text{Na}_3\text{A}} = \left( \frac{0.1000 \text{ mmol HCl}}{\text{ml}} \right) \left( 20 \text{ mL} \right) \left( \frac{1 \text{ mol Na}_3\text{A}}{1 \text{ mol HCl}} \right)
\]

\[
n_{\text{Na}_3\text{A}} = 2.0 \text{ mmol Na}_3\text{A}
\]

(h) What is the pH at point \( B \)?

\[
7.00 \quad (=pK_{a2})
\]

(i) Write the neutralization reaction for the titration from point \( A \) to point \( C \).

\[
2\text{HCl} + \text{Na}_3\text{A} \rightarrow \text{NaH}_2\text{A} + 2\text{NaCl}
\]

\text{or}\n
\[
2\text{H}_3\text{O}^+ + A^{3-} \rightarrow \text{H}_2\text{A}^- + 2\text{H}_2\text{O}
\]

(j) What is the pH at point \( C \)?

use amphiprotic equation for \( \text{H}_2\text{A}^- \) with

\[
[H_3O^+] = \sqrt{\frac{K_{a2}c_{\text{H}_2\text{A}^-} + K_w}{1 + c_{\text{H}_2\text{A}^-}/K_{a1}}}
\]

\[
c_{\text{H}_2\text{A}^-} = \frac{2.0 \text{ mmol}}{(40 + 20)\text{ mL}} = 3.3 \times 10^{-2} \text{ M};
\]

\[
\text{pH} = 4.68;
\]
(i) Of the following, which would be the best choice for an indicator if you were titrating to point C?

- Methyl orange \( \text{pK}_a = 3.5 \)
- **Bromocresol green** \( \text{pK}_a = 4.7 \)
- Bromocresol purple \( \text{pK}_a = 6.1 \)
- Phenol red \( \text{pK}_a = 7.8 \)
- Creosol purple \( \text{pK}_a = 8.4 \)
- Thymolphthalein \( \text{pK}_a = 10.5 \)

(j) Explain your choice of indicator.

The indicator changes color when the pH = \( \text{pK}_a \) (of the indicator). Choose the one that has a \( \text{pK}_a \) nearest the pH of the equivalence point of the titration.

(k) Based upon the titration curve shown and the information given at the beginning of this problem, determine the molecular weight of \( \text{Na}_3A \).

\[
MW = \frac{m_{\text{Na}_3A}}{n_{\text{Na}_3A}} = \frac{0.2500 \text{ g}}{2.0 \times 10^{-3} \text{ mol}} = 125 \frac{\text{g}}{\text{mol}} = 1.3 \times 10^2 \frac{\text{g}}{\text{mol}}
\]