A. An acid, HA, is titrated with the strong base, NaOH. The titration curve shown below is obtained.

a) Write the net ionic equation for the neutralization reaction that takes place.
   
   Molecular eq:  \text{HA (aq) + NaOH (aq)} \rightarrow \text{NaA (aq) + H}_2\text{O (l)}
   
   Net ionic eq:  \text{HA (aq) + OH}^-\text{(aq) \rightarrow A}^-\text{(aq) + H}_2\text{O (l)}

b) Is HA a strong acid or a weak acid?  weak acid

c) Place a dot (•) on the curve at the equivalence point and label it “equivalence pt”

d) What is the pH at the equivalence point?  \approx 8.5

e) Explain why the pH at the equivalence point is acidic, neutral, basic by describing the predominant species in the solution at the equivalence pt.
   
   At the equivalence point the weak acid, HA, has fully reacted to form its conjugate base, A^-.
   A^- is a weak base so the solution is slightly basic.

f) What volume of base was needed to reach the equivalence point?  25 mL

g) Place a box (■) on the curve at the “half-equivalence pt.” This is the point halfway to the equivalence point (Half the volume of base has been added compared to at equiv. pt.)

h) At the half-equivalence point, why does the pH of the solution equal the pK_a of the acid?
   
   Hint: What is in the solution?
   
   At the half- equivalence point, half of the HA has reacted to form A^-.
   Thus, [HA] = [A^-]. If one plugs these concentrations into HH, one gets...
   
   \[ \text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]} \]  ; so with [HA] = [A^-],  \text{pH} = \text{pK}_a

i) What is the pK_a of HA?  \approx 4.5  What is the K_a of HA? 3.2 \times 10^{-5}

16.24 A 5.00 g quantity of a diprotic acid (H_2A) was dissolved in enough water to make 250.0 mL of solution. Calculate the molar mass of the acid (H_2A) if 25.0 mL of the solution required exactly 11.1 mL of 1.00 M KOH for neutralization. (Assume both protons of the acid were ionized.)

First: Write the neutralization reaction:  2KOH(aq) + H_2A(aq) \rightarrow K_2A(aq) + 2H_2O(l)

Second: Get moles of H_2A reacted
   
   \[
   \text{11.1 mL KOH} \times \frac{1.00 \text{ mol KOH}}{1000 \text{ mL}} \times \frac{1 \text{ mol H}_2\text{A}}{2 \text{ mol KOH}} = 5.55 \times 10^{-3} \text{ mol H}_2\text{A}
   \]

Third: Find molar mass of H_2A. (Be careful, not all of the 5.00 g of H_2A was actually used in titration.)

We know that 0.500 g of the diprotic acid were reacted (Because only 25 ml of the original 250 mL solution was titrated. Thus, only 1/10 of the original 5.00 g was tested.)

\[
\mathcal{M} (\text{H}_2\text{A}) = \frac{0.500 \text{ g H}_2\text{A}}{5.55 \times 10^{-3} \text{ mol H}_2\text{A}} = 90.1 \text{ g/mol}
\]
16.29 Calculate the pH at the equivalence point for the following titration: 100.0 mL of 0.20 M methylamine (CH₃NH₂) is titrated with 0.20 M HCl.

Steps: First, how many mL of HCl will be required to reach equivalence point? (Hint-Molarities are same.)
Second, use an ICF chart (with mole values) to determine moles of the conjugate acid produced.
Third, use ICE chart (with molarities!) to do hydrolysis of the conjugate acid to get pH.

\[
\text{HCl}(aq) + \text{CH}_3\text{NH}_2(aq) \rightleftharpoons \text{CH}_3\text{NH}_3^+(aq) + \text{Cl}^-(aq)
\]

Initial (mol): 0.020 mol 0.020 mol 0
Change (mol): −0.020 −0.020 +0.020
Final (mol): 0 0 0.020 mol

But now total volume is 100 mL + 100 mL = 200 mL. Thus, \([\text{CH}_3\text{NH}_3^+] = 0.020 \text{ mol}/0.200 \text{ L} = 0.10 \text{ M}\)

The conjugate acid undergoes hydrolysis.

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

Initial (M): 0.10 M 0 0
Change (M): −x +x +x
Equilibrium (M): 0.10 − x x x

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3^+]} = 2.3 \times 10^{-11} = \frac{x^2}{0.10 - x} = \frac{x^2}{0.10}
\]

\[
x = [\text{H}_3\text{O}^+] = 1.5 \times 10^{-6} \text{ M}
\]

\[
\text{pH} = 5.82
\]

16.35 Referring to Table 16.1, specify which indicator or indicators you would use for the following titrations: Justify each.

(a) HCOOH vs. NaOH:
- Weak acid vs. strong base → basic salt solution
- Need indicator to have intermediate color in basic solution.
- Suitable indicators are cresol red and phenolphthalein.

(b) HCl vs KOH:
- Strong acid vs. strong bases produces neutral salt.
- Need intermediate color close to pH of 7, but large pH range near equivalence point so can use any indicator except a few on the extremes.
- Suitable indicators are all those listed with the exceptions of thymol blue, bromphenol blue, and methyl orange.

(c) HNO₃ vs. CH₃NH₂:
- Strong acid vs. weak base → acidic salt solution
- Suitable indicators are bromphenol blue, methyl orange, methyl red, and chlorphenol blue.
37  The $K_a$ of a particular indicator, HIn, is $1.0 \times 10^{-6}$. The indicator’s nonionized form (HIn) is red, and its ionized form (In-) is yellow. What is the color of this indicator in a solution whose pH is 4.00?

The weak acid equilibrium is

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

$$\text{Step 1:}$$

From the pH, we can calculate the $H^+$ concentration. $[H^+] = 10^{-pH} = 10^{-4} = 1.0 \times 10^{-4} M$

$$\frac{[HIn]}{[In^-]} = \frac{1.0 \times 10^{-4}}{1.0 \times 10^{-6}} = 100 \text{ or use HH to find the ratio.}$$

Since the concentration of HIn is 100 times greater than the concentration of In-, the color of the solution will be that of HIn, the nonionized form. The color of the solution will be **red**.

38  The $K_a$ of a particular indicator is $2.0 \times 10^{-6}$. The color of HIn is green and that of In- is red. A few drops of the indicator are added to a HCl solution which is titrated against an NaOH solution. At what pH will the indicator change color from green (HIn) to red (In-)?

The indicator color changes at the point when $[HIn] \approx [In^-]$; we can write:

$$\text{pH} = pK_a + \log\left(\frac{[In^-]}{[HIn]}\right); \text{ since } \frac{[In^-]}{[HIn]} = 1, \text{ pH} = pK_a = -\log(2.0 \times 10^{-6}) = 5.70$$

**B. How many mL of 0.0850 M NaOH are required to titrate 25.0 mL of 0.128 M CH$_2$CICOOH (chloroacetic acid, $K_a = 1.38 \times 10^{-3}$) to the equivalence point?**  What is the pH of the solution at the equivalence point? **Hint:** First, do stoichiometry to determine mL of NaOH required to reach equivalence point.

Second, use an ICF chart (with mole values) to determine moles of the conjugate base produced.

Third, use ICE chart (with molarities!) to do hydrolysis of the conjugate base to get pH.

$$\text{Step 1:}$$

$$\text{mol NaOH} = \text{mol CH}_2\text{CICOOH} = \frac{0.128 \text{ mol CH}_2\text{CICOOH}}{1000 \text{ mL}} \times 25.0 \text{ mL} = 0.00320 \text{ mol NaOH}$$

$$V_{NaOH} = \frac{\text{mol NaOH}}{M \text{ NaOH}} = \frac{0.00320 \text{ mol NaOH} \times 1000 \text{ mL}}{0.0850 \text{ mol NaOH}} = 37.6 \text{ mL NaOH}$$

**Step 2:** To determine pH, first determine the concentration of CH$_2$CICOO$^-$ at the equivalence point.

$$\begin{array}{c|c|c|c|c}
\text{I (mol)} & 0.00320 & 0.00320 & 0 & 0 \\
\text{C (mol)} & -0.00320 & 0.00320 & +0.0320 \\
\text{F (mol)} & 0 & 0 & 0.0320 \\
\end{array}$$

$$[\text{CH}_2\text{CICOO}^-] = \frac{0.00320 \text{ mol}}{(25.0 + 37.6) \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.0516 \text{ M}$$

**Step 3:** Now, use ICE to re-equilibrate the system:

$$\begin{array}{c|c|c|c|c}
\text{CH}_2\text{CICOO}^- & + & \text{H}_2\text{O} (l) & \iff & \text{CH}_2\text{CICOOH} & + & \text{OH}^- (aq) \\
\text{I (M)} & 0.0516 & 0 & 0 \\
\text{C (M)} & -x & +x & +x \\
\text{E (M)} & 0.0516 - x & x & x \\
\end{array}$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.38 \times 10^{-3}} = 7.24 \times 10^{-12}$$

$$K_b = \frac{[\text{CH}_2\text{CICOOH}]\text{[OH}^-]}{[\text{CH}_2\text{CICOO}^-]} = \frac{x^2}{0.0516 - x} = \frac{x^2}{0.0516} = 7.24 \times 10^{-12};$$

$$x = [\text{OH}^-] = \sqrt{(7.24 \times 10^{-12}) (0.0516)} = 6.11 \times 10^{-7} \text{ M}$$

$$\text{pOH} = 6.14; \text{ pH} = 14.00 - 6.14 = 7.86$$