Chapter 10

① The end point of a titration is the point at which the equivalence point is detected. Usually by the observation of a large change in a property of the solution such as a color change, or change in pH.

The equivalence point is the point at which just enough titrant has been added to use up all of the original analyte.

② $V_a = 0\,mL$: $[OH^-] = 0.100\,M$

$[H^+] = 10^{-14}/0.100 = 1\times10^{-13}$ **pH = 13.0**

$V_a = 1.0\,mL$: $100.0\,mL \left| \frac{0.100\,mmol}{1\,mL} \right| = 10\,mmol\ OH$ $-1\,mmol$ $= \frac{9\,mmol}{101\,mL} = 0.089\,M\ OH$

$1.0\,mL \left| \frac{1\,mmol}{1\,mL} \right| = 1\,mmol\ H^+$

$[H^+] = 1.12\times10^{-13}$ **pH = 12.9**

$V_a = 5.0\,mL$: $5.0\,mL \left| \frac{1\,mmol}{1\,mL} \right| = 5\,mmol$

$10 - 5 = \frac{5\,mmol}{105\,mL} = 0.048\,M\ OH^-$, $[H^+] = 2.1\times10^{-13}\,M$

pH = 12.7

$V_a = 9.0\,mL$: $9.0\,mL = 9\,mmol$

$10 - 9 = \frac{1\,mmol}{109\,mL} = 9.17\times10^{-3}\,M\ OH^-$

$[H^+] = 1.09\times10^{-12}\,M$ **pH = 11.96**

$V_a = 9.9\,mL$: $9.9\,mmol$

$10 - 9.9 = \frac{0.1\,mmol}{109.9} = 9.10\times10^{-4}\,M\ OH^-$

$[H^+] = 1.10\times10^{-11}\,M$ **pH = 10.96**

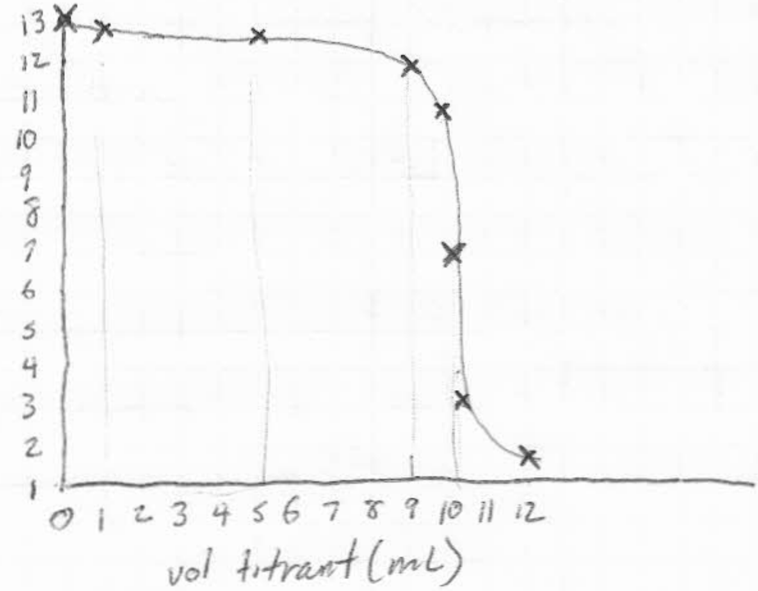
$V_a = 10\,mL$: $10\,mmol$

$10 - 10 = 0$ **pH = 7.00**

$V_a = 10.1\,mL$ $10.1\,mmol \rightarrow \frac{0.1\,mmol\ H^+}{110.1\,mL} = 9.08\times10^{-4}\,M\ H^+$ **pH = 3.04**

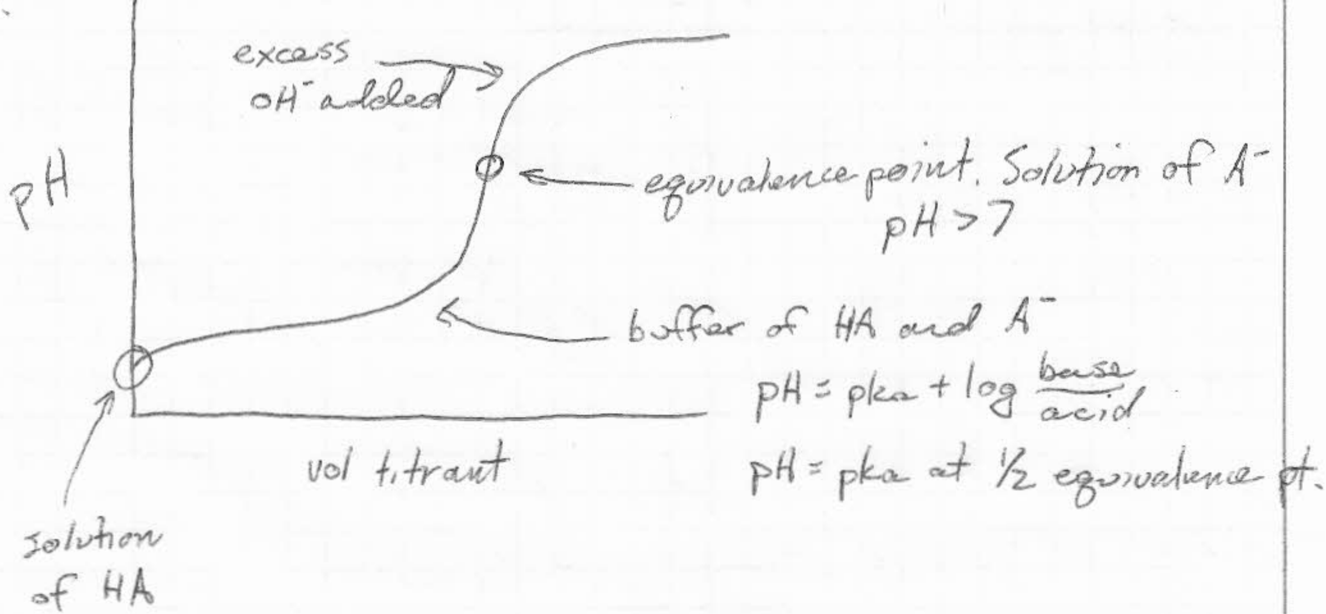
$V_a = 12\,mL$ $12\,mmol \rightarrow \frac{2\,mmol\ H^+}{112\,mL} = 0.0176\,M\ H^+$ **pH = 1.75**

② cont



③ The pH scale is logarithmic. Before the equivalence point, added titrant is being used up. Near the equivalence point the amount of H^+, or OH^- jumps orders of magnitude, causing the pH to either rise or drop with only a small addition of titrant.

④.



⑥ $V_b = 0\,mL$: $\dfrac{x^2}{0.100 - x} = 10^{-5}$ $x = 1\times10^{-3} = [H^+]$ **pH = 3**

$HA + OH^- \rightarrow H_2O + A^-$

$V_b = 1\,mL$: $100\,mL \left| \dfrac{0.100\,mmol}{1\,mL} \right| = 10\,mmol - 1 = 9\,mmol\ HA$

$1\,mL \left| \dfrac{1\,mmol}{1\,mL} \right| = 1\,mmol\ A^-$ $pH = 5.00 + \log\dfrac{1}{9} =$ **4.05**

$V_b = 5\,mL$ $5\,mL \left| \dfrac{1\,mmol}{1\,mL} \right| = 5\,mmol$

$10 - 5 = 5\,mmol\ HA$ $pH = 5.00 + \log\dfrac{5}{5} =$ **5.00**

$5\,mmol\ A^-$

$V_b = 9\,mL$ $9\,mmol\ A^-$ $pH = 5.00 + \log\dfrac{9}{1} =$ **5.95**

$10 - 9 = 1\,mmol\ HA$

$V_b = 9.9\,mL$ $9.9\,mmol\ A^-$

$10 - 9.9 = 0.1\,mmol\ HA$ $pH = 5.00 + \log\dfrac{9.9}{0.1} =$ **7.00**

$V_b = 10\,mL$ - solution of A^- $\dfrac{10\,mmol}{110\,mL} = 0.0909\,M$ $K_b = 10^{-9}$

$\dfrac{x^2}{0.0909 - x} = 10^{-9}$

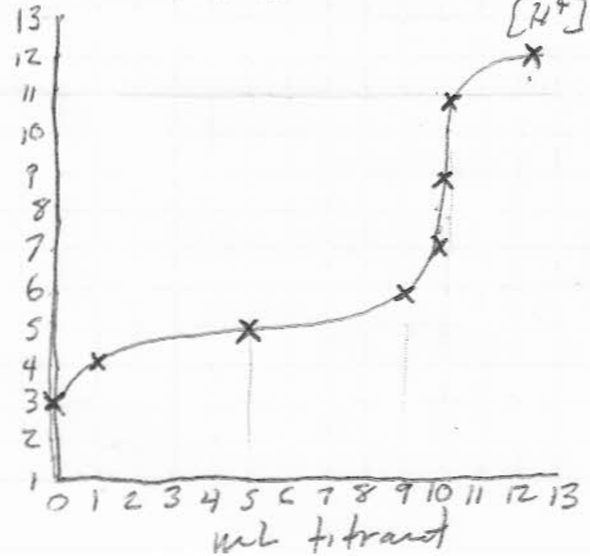
$x = 9.53\times10^{-6}\,M\ [OH^-]$ $[H^+] = 1.05\times10^{-9}$ **pH = 8.98**

$V_b = 10.1\,mL \rightarrow \dfrac{0.1\,mmol\ excess\ OH^-}{110.1\,mL} = 9.08\times10^{-4}\,M\ OH^-$

$[H^+] = 1.101\times10^{-11}$ **pH = 10.96**

$V_b = 12\,mL$ $\dfrac{2\,mmol\ excess\ OH^-}{112\,mL} = 0.0179\,M\ OH^-$

$[H^+] = 5.6\times10^{-13}$ **pH = 12.25**



(8) since the concentration of titrant is ½ concentration of analyte, the volume of titrant needed to reach the equivalence point must be double the original volume of solution. At the equivalence point there is a solution of A^- (hydroxy acetate) with the concentration $= \frac{0.100M}{3} = 0.0333M$ $pka = 3.832$

1 part original solution → 3
2 parts titrant

$K_b = 6.79\times10^{-11}$

$$\frac{x^2}{0.0333-x} = 6.79\times10^{-11}$$

$x = 1.50\times10^{-6} = [OH^-]$ $[H^+] = 6.65\times10^{-9}$ **pH = 8.18**

(10) $pka = 9.39$ $9.24 = 9.39 + \log\frac{base}{acid}$ $\frac{base}{acid} = 0.708$

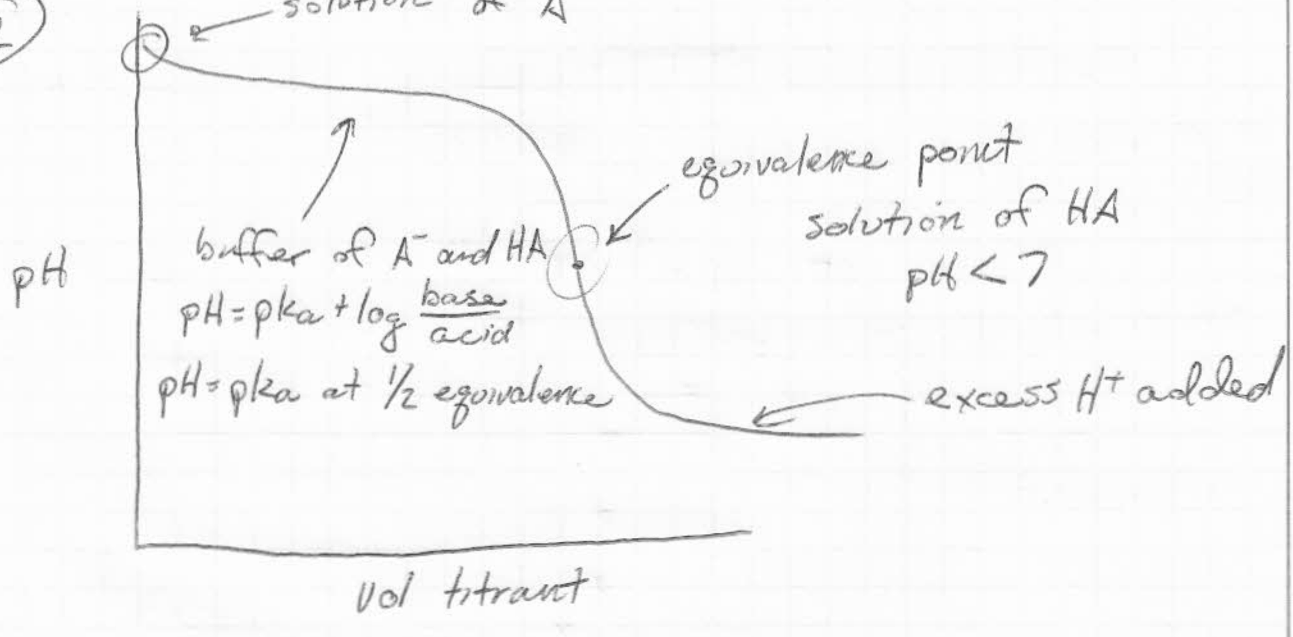
base + acid $= 5.86\times10^{-3}$ acid $= 5.86\times10^{-3}$ − base

$1.214\,g\,HA \left| \frac{1\,mol}{207.29\,g} \right| = 5.86\times10^{-3}\,mol\,HA$

$$\frac{base}{5.86\times10^{-3} - base} = 0.708$$

$\frac{2.43\times10^{-3}\,mol\,OH}{0.02263\,mL} =$ **0.107M**   base $= 2.43\times10^{-3}$ mol OH^-

(12)



(13) At the equivalence point there is a solution of weak acid. The pH must be acidic (< 7).

(14) $V_a = 0\,mL$: $\frac{x^2}{0.100 - x} = 10^{-5}$

$x = 1\times10^{-3} = [OH^-]$ $[H^+] = 10^{-11}$ **pH = 11**

$V_a = 1.0\,mL$: $100\,mL \left| \frac{0.100\,mmol}{1\,mL} \right| = 10\,mmol\,A^-$ $- \frac{1}{9}\,mmol\,A^-$ $A^- + H \rightarrow HA$

$1.0\,mL \left| \frac{1.00\,mmol\,H^+}{1\,mL} \right| = 1\,mmol = 1\,mmol\,HA$ $pH = 9.00 + \log\frac{9}{1} =$ **9.95**

$V_a = 5.0\,mL$: $10 - 5\,mmol = 5\,mmol\,A^-$, $5\,mmol\,HA$ $pH = 9.00 + \log\frac{5}{5} =$ **9.00**

$V_a = 9\,mL$: $10 - 9\,mmol = 1\,mmol\,A^-$, $9\,mmol\,HA$ $pH = 9.00 + \log\frac{1}{9} =$ **8.05**

$V_a = 9.9\,mL$: $10 - 9.9 = 0.1\,mmol\,A^-$, $9.9\,mmol\,HA$ $pH = 9.00 + \log\frac{0.1}{9.9} =$ **7.00**

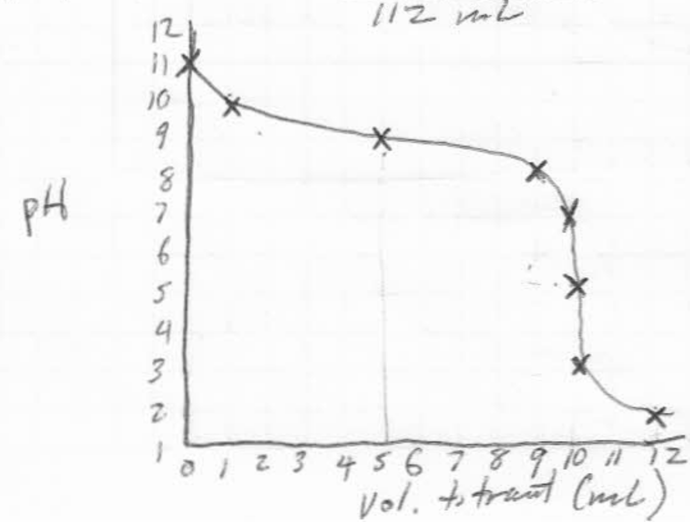
$V_a = 10\,mL$: $10 - 10 = 0 \Rightarrow$ solution of HA $K_a = 10^{-9}$

$\frac{10\,mmol}{110\,mL} = 0.909\,M$

$\frac{x^2}{0.909 - x} = 10^{-9}$ $x = 9.53\times10^{-6}\,M = [H^+]$ **pH = 5.02**

$V_a = 10.1\,mL$: $\frac{0.1\,mmol\ \text{excess}\ H^+}{110.1\,mL} = 9.08\times10^{-4}\,M\,H^+$ **pH = 3.04**

$V_a = 12\,mL$: $\frac{2\,mmol\ \text{excess}\ H^+}{112\,mL} = 0.0179\,M\,H^+$ **pH = 1.75**



(15) When HA = A^- or half way to the equivalence point

(18) $pK_a = 9.21$ $\quad 50.0\,mL \left| \frac{0.100\,mmol}{1\,mL} \right| = 5.00\,mmol\ A^-$

$A^- + H^+ \rightarrow HA$

a. $4.20\,mL \left| \frac{0.438\,mmol}{1\,mL} \right| = 1.84\,mmol\ H^+$

$5.00 - 1.84 = 3.16\,mmol\ A^-$

$1.84\,mmol\ HA$

$pH = 9.21 + \log \frac{3.16}{1.84} = \boxed{9.44}$

b. $11.82\,mL \left| \frac{0.438\,mmol}{mL} \right| = 5.18\,mmol\ H^+$

$\frac{0.18\,mmol\ excess\ H^+}{61.82\,mL} = 2.91 \times 10^{-3}\,M\ H^+$ $\boxed{pH = 2.54}$

c. equiv. pt $5.00\,mmol\ A^- \left| \frac{1\,mmol\ H^+}{1\,mmol\ A^-} \right| \frac{1\,mL\ H^+}{0.438\,mmol\ H^+} \right| = 11.42\,mL\ H^+$ added

$\frac{5.00\,mmol\ HA}{61.42\,mL} = 0.0814\,M\ HA$ $\quad K_a = 6.17 \times 10^{-10}$

$\frac{x^2}{0.0814 - x} = 6.17 \times 10^{-10}$ $\quad x = 7.08 \times 10^{-6} = [H^+]$

$\boxed{pH = 5.15}$