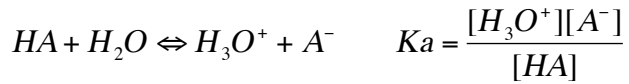


APPLICATIONS OF TITRATIONS

I. Monoprotic Systems



MBE:

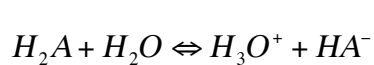
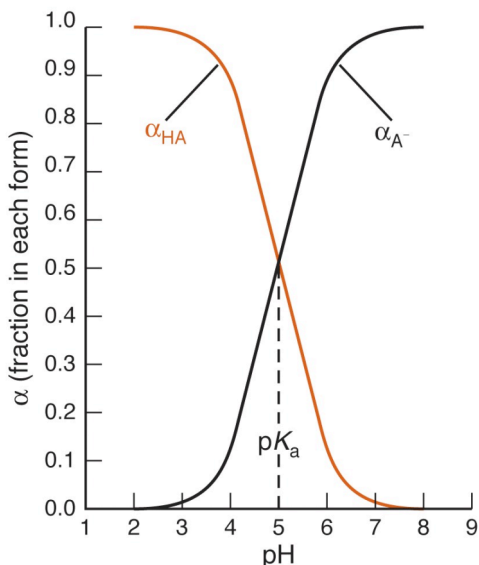
$$F = [HA] + [A^-] = [HA] + \frac{K_a [HA]}{[H_3O^+]} = [HA] \left(1 + \frac{K_a}{[H_3O^+]} \right)$$

$$\alpha_{HA} = \frac{[HA]}{F} = \frac{[HA]}{[HA] \left(1 + \frac{K_a}{[H_3O^+]} \right)} = \frac{1}{1 + \frac{K_a}{[H_3O^+]}} = \frac{[H_3O^+]}{[H_3O^+] + K_a}$$

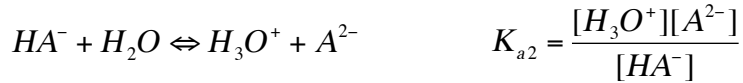
$$\alpha_{A^-} = \frac{[A^-]}{F} = \frac{[A^-]}{\frac{[H_3O^+][A^-]}{K_a} + [A^-]} = \frac{[A^-]}{[A^-] \left(1 + \frac{[H_3O^+]}{K_a} \right)} = \frac{1}{1 + \frac{[H_3O^+]}{K_a}} = \frac{K_a}{K_a + [H_3O^+]}$$

If $\alpha_{HA} = \alpha_{A^-}$:

$$\frac{[H_3O^+]}{[H_3O^+] + K_a} = \frac{K_a}{K_a + [H_3O^+]} \Rightarrow [H_3O^+] = K_a \quad \text{or} \quad pH = pK_a$$



$$K_{a1} = \frac{[H_3O^+][HA^-]}{[H_2A]}$$

**MBE:**

$$F = [H_2A] + [HA^-] + [A^{2-}] = [H_2A] + \frac{K_{a1}[H_2A]}{[H_3O^+]} + \frac{K_{a2}}{[H_3O^+]} \frac{K_{a1}[H_2A]}{[H_3O^+]} \Rightarrow$$

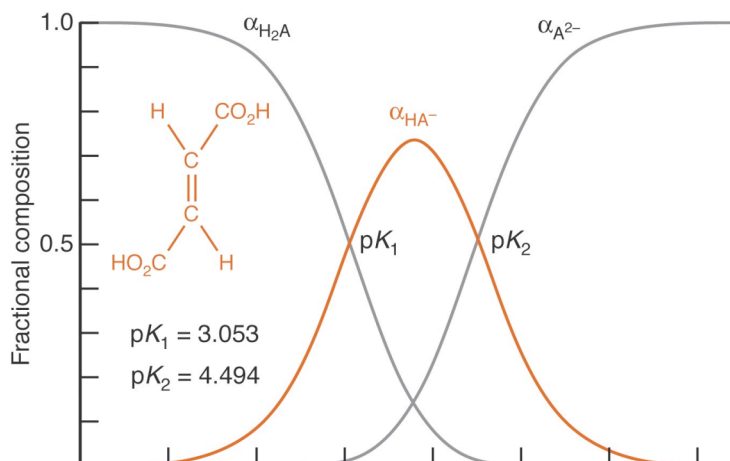
$$F = [H_2A] \left(1 + \frac{K_{a1}}{[H_3O^+]} + \frac{K_{a1}K_{a2}}{[H_3O^+]^2} \right)$$

$$\alpha_{H_2A} = \frac{[H_2A]}{F} = \frac{[H_2A]}{[H_2A] \left(1 + \frac{K_{a1}}{[H_3O^+]} + \frac{K_{a1}K_{a2}}{[H_3O^+]^2} \right)} = \frac{[H_3O^+]^2}{[H_3O^+]^2 + K_{a1}[H_3O^+] + K_{a1}K_{a2}}$$

$$\alpha_{HA^-} = \frac{[HA^-]}{F} = \frac{K_{a1}[H_2A]/[H_3O^+]}{[H_2A] \left(1 + \frac{K_{a1}}{[H_3O^+]} + \frac{K_{a1}K_{a2}}{[H_3O^+]^2} \right)} = \frac{K_{a1}[H_3O^+]}{[H_3O^+]^2 + K_{a1}[H_3O^+] + K_{a1}K_{a2}}$$

$$\alpha_{A^{2-}} = \frac{[A^{2-}]}{F} = \frac{K_{a1}K_{a2}[H_2A]/[H_3O^+]^2}{[H_2A] \left(1 + \frac{K_{a1}}{[H_3O^+]} + \frac{K_{a1}K_{a2}}{[H_3O^+]^2} \right)} = \frac{K_{a1}K_{a2}}{[H_3O^+]^2 + K_{a1}[H_3O^+] + K_{a1}K_{a2}}$$

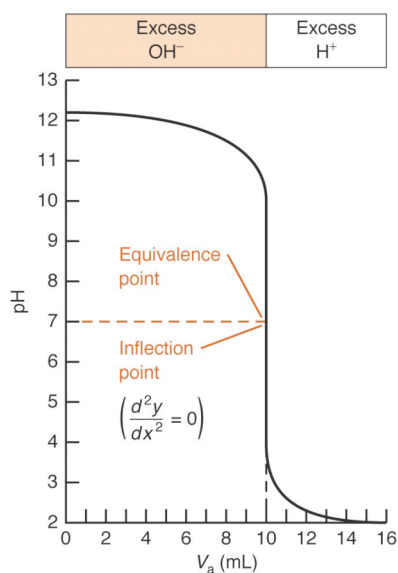
See picture below.



III. Common titration systems

1. Strong acid (SA) + Strong base (SB)
2. SB + SA
3. Weak acid (WA) + SB
4. SA + Weak base (WB)
5. WA + WB

Sample: 50 mL of 0.02 M KOH is titrated with 0.1M HBr.



There are three regions:

1. Before equivalence point
2. Equivalence point
3. Excess of H_3O^+

Equivalence point is 10 mL (of acid added):

$$V_a M_a = V_b M_b$$

1. pH before the equivalence point. After 3 mL of the HBr are added.

$$[OH^-] = \frac{10 - 3}{10} \underbrace{(0.02)}_{\text{Initial concentration of the KOH}} \frac{50}{50 + 3} = 0.0132M$$

Fraction titrated
DF

$$[H_3O^+] = \frac{K_w}{[OH^-]} = 7.58 \cdot 10^{-13} M \quad \Rightarrow \quad pH = 12.12$$

2. Equivalence point

$$[H_3O^+] = [OH^-]$$

$$\text{If } [H_3O^+] = x, \text{ then } x^2 = 1 \cdot 10^{-14} \quad \Rightarrow \quad x = 10^{-7} \quad \Rightarrow \quad pH = 7$$

3. Excess of the acid: assume 10.5 mL of the HBr is added.

Excess volume is $(10.5 - 10.0) \text{ mL} = 0.5 \text{ mL}$.

$$[H_3O^+] = 0.1 \left(\frac{0.5}{50.0 + 10.5} \right) = 8.26 \cdot 10^{-4} \text{ M}$$

Initial concentration of the HBr $\underbrace{\hspace{1.5cm}}$ **DF**

$$\text{pH} = 3.08$$

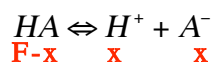
When weak acid (MES: 50 mL, 0.02M, pK_a 6.15) is titrated with the strong base (0.1M NaOH).

The equivalence point is at:

$$V_{\text{equiv}} = \frac{50 \cdot 0.02}{0.1} = 10.0 \text{ mL}$$

The following four regions have to be considered:

1. Before base is added



$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{F-x} = 10^{-6.15}$$

$$x = 1.19 \cdot 10^{-4} \Rightarrow \text{pH} = 3.93$$

2. Before EP ($V_b = 3 \text{ mL}$). Buffer region:

$$\text{pH} = \text{pK}_a + \log \frac{[A^-]}{[HA]} = 6.15 + \log \frac{3/10}{7/10} = 5.78$$

3. At equivalence point:

All HA is converted into A^- , so the following equilibria has to be considered:



$$F' = 0.02 \left(\frac{50}{50 + 10} \right) = 0.0167 \text{ M}$$

Initial concentration $\underbrace{\hspace{1.5cm}}$ **DF**

of the HBr

$$K_b = \frac{x^2}{F - x} = \frac{K_w}{K_a} = 1.43 \cdot 10^{-8} \Rightarrow x = 1.54 \cdot 10^{-5} \Rightarrow pH = 9.18$$

4. After equivalence point: 0.1 mL of extra NaOH is added.

$$[OH^-] = 0.1 \left(\frac{0.1}{50 + 10.10} \right) = 1.66 \cdot 10^{-4} M$$

Initial
concentration
of NaOH **DF**

$$pH = -\log \frac{K_w}{[OH^-]} = 10.22$$