Lecture 8 – Acid/Base Equilibria and Titrations

Monoprotic Systems

$$HA \xleftrightarrow{K_a} H^+ + A^-$$

$$K_a = \frac{[H^+][A-]}{[HA]}$$

Mass Balance = F = [HA] + [A-]

Fraction in form HA: $\alpha_{HA} = \frac{[HA]}{F} = \frac{[H^+]}{[H^+] + K_a}$

Fraction in the form A^-: $\alpha_A = \frac{[A-]}{F} = \frac{[K_a]}{[H^+] + K_a}$

Diprotic Systems

$$H_2A \xleftrightarrow{K_1} H^+ + HA^-$$

$$HA \xleftrightarrow{K_2} H^+ + A^{2-}$$

Mass Balance:

$F = [H_2A] + [HA-] + [A^{2-}]$

$$F = [H_2A] + \frac{K_1}{[H^+]}H_2A + \frac{K_1K_2}{[H^+]^2}[H_2A]$$

$$F = [H_2A] + (1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2})$$

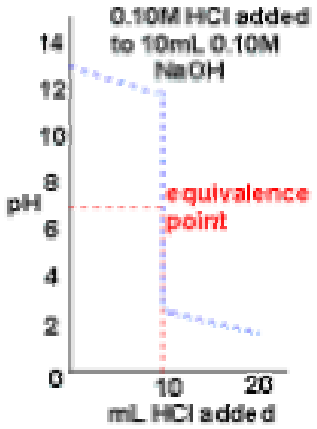
Fraction in form H_2A: $\alpha_{H2A} = \frac{H_2A}{F} = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_1 + K_1K_2}$

Fraction in form HA-: $\alpha_{HA-} = \frac{[HA-]}{F} = \frac{K_1[H^+]}{[H^+]^2 + [H^+]K_1 + K_1K_2}$

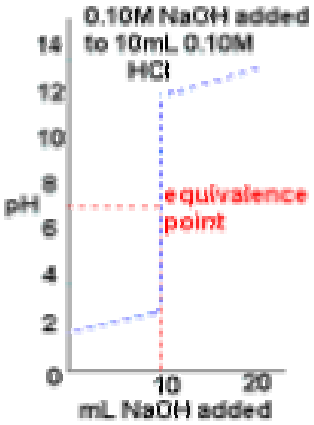
Fraction in form A^{2-}: $\alpha_{A^{2-}} = \frac{[A^{2-}]}{F} = \frac{K_1K_2}{[H^+]^2 + [H^+]K_1 + K_1K_2}$

See Figure 11-3 in book, pg. 217

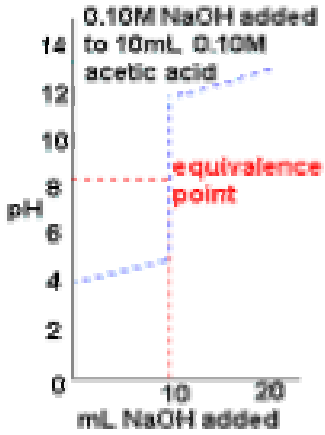
Common Titration curves



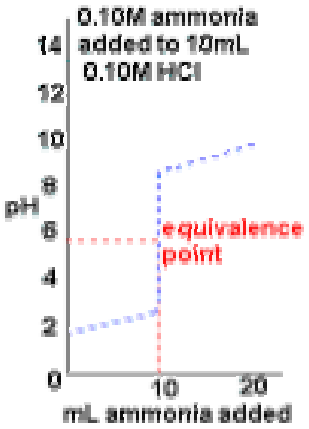
Strong acid, strong base



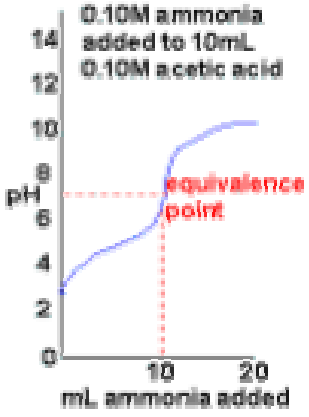
Strong base, strong acid



Weak acid, strong base

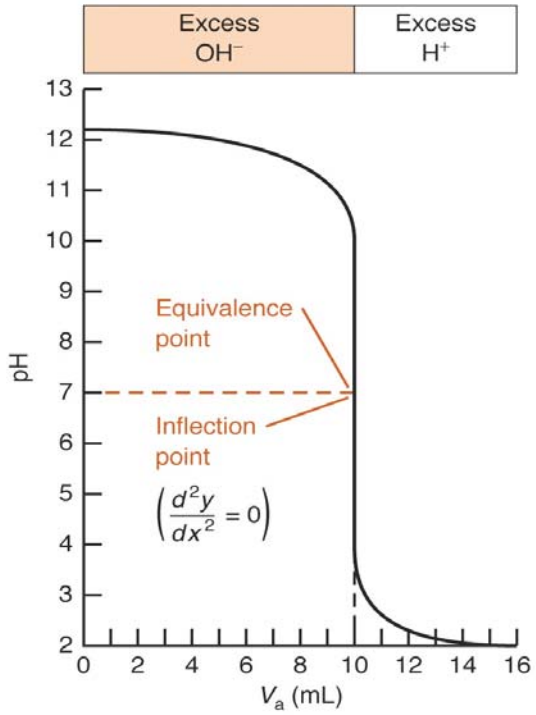


Strong acid, weak base



Weak acid, weak base

Strong acid with strong base



1. Before the equivalence point: excess OH^-

2. At the equivalence point: pH = 7.00

3. After the equivalence point: excess H

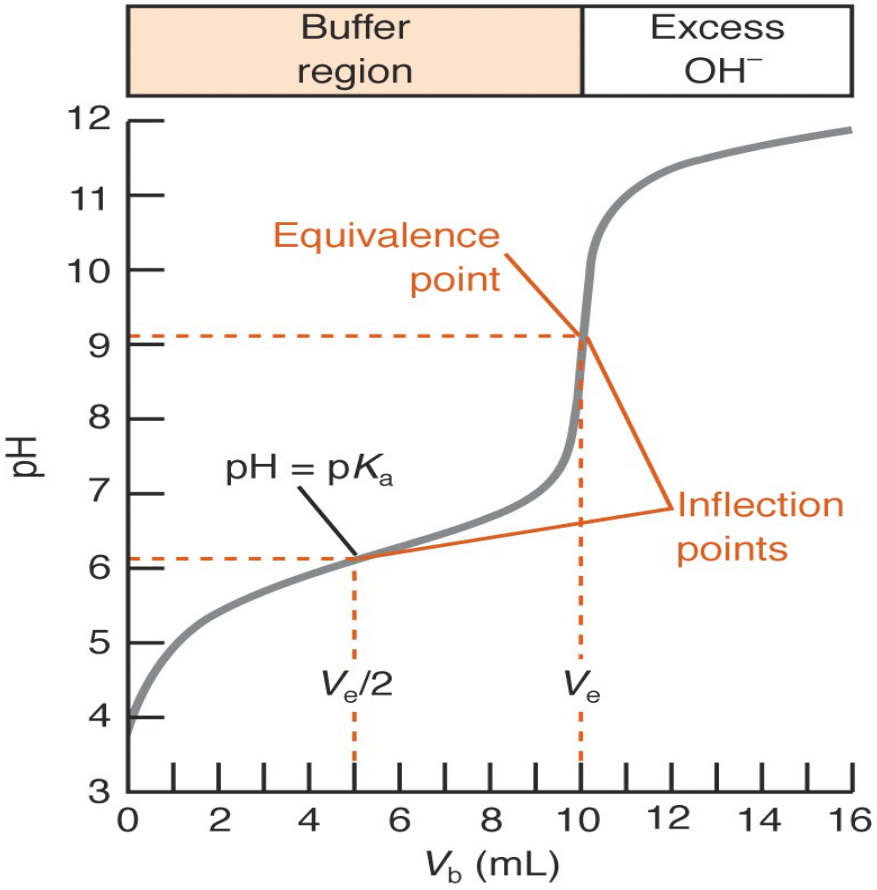
Titration of 50.0 mL of 0.0200M KOH with 0.100M HBr.

1. Before EP (e.g. v=3.00 mL)

2. At EP (i.e. v=10.00mL)

3. After EP (i.e. v=10.50 mL)

Titration of Weak Acid with Strong Base



1. Before any base is added: weak acid
2. Before the equivalence point: buffer
3. At the equivalence point: All HA converted to HA^-
4. After the equivalence point: excess of OH^-

Titration of 50.00 mL MES with 0.1000 M NaOH. MES is 2-(*N*-morpholino) ethanesulfonic acid, weak acid with $pK_a = 6.15$

1. Before base is added (i.e. v=0) Weak acid calculation

2. Before EP (e.g. v=3.00 mL) Buffer

3. At EP (i.e. v=10.00mL) Solution of weak base A

4. After EP (e.g. v+10.10 mL) Excess of OH^-

Titration of weak base with strong acid ($B + H^+ \rightarrow BH^+$)

Reverse of the titration of a weak acid with a strong base:

1. Before acid is added (i.e. v= 0)- Calculation of weak base

$$B + H_2O \xleftrightarrow{K_b} BH^+ + OH$$

*when V_a (vol of added acid) = 0

2. Before EP – Buffer containing B & BH^+

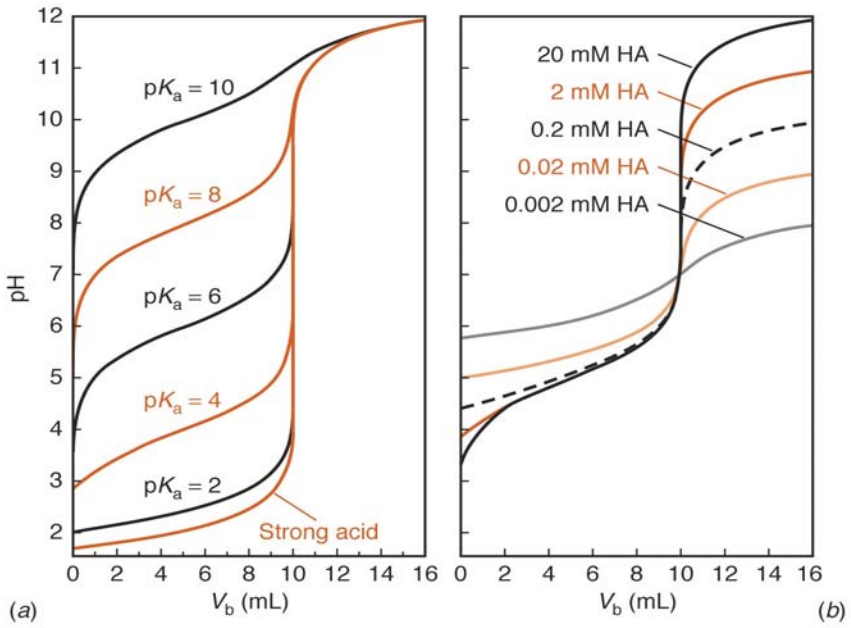
pH = pK_a (for BH^+) + $\log\left(\frac{[B]}{[BH^+]}\right)$

3. At EP – Solution of weak acid BH^+ (when $V_a=V_e$)

$BH^+ \leftrightarrow B^+ + H^+$

4. After EP – excess of H, neglect contribution of weak acid

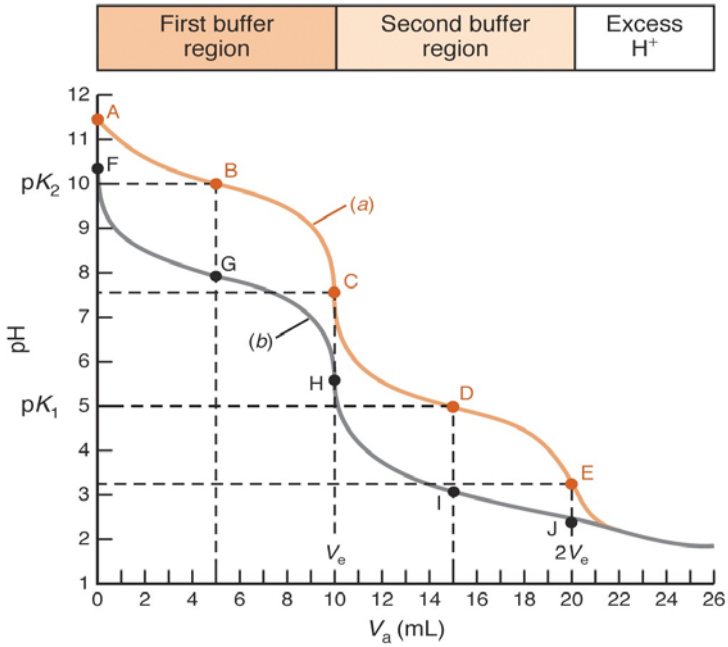
Note that the pH at EP is below 7.00 because the solution contains the weak acid BH^+



*Titration curve depends on the acid dissociation constant of HA and on the concentrations of reactants.

-HA becomes a weaker acid or the concentration of analyte and titrant decrease…..inflection deceases.

Titrations in diprotic systems



Titration of 10.0 mL of 0.100 M base (pK_{b1} = 4.00, pK_{b2} = 9.00) with 0.100 M HCl.

6 different regions, with two equivalence points (C&E)

Points B and D are the half-neutralization points, whose pH values equal pK_{a2} and pK_{a1}

Point A – (i.e. v = 0) Solution of weak base B

$$B + H_2O \xleftrightarrow{K_{b1}} BH^+ + OH^-$$

Point B – before 1st EP (e.g. v=1.5 mL) Buffer sol'n with B and BH^+

Point C – at 1st EP (e.g. V_{e1} = 10.0 mL) Sol'n with all B converted to the intermediate form BH^+

Point D – between EP1 and EP2 (e.g. v=17.2 mL) Buffer containing BH^+ and BH_2^+

Point E – at EP2 (i.e. V_{e2} = 20.0 mL) Sol'n with all BH^+ converted to the weak acid BH_2^+

Summary: Acid-base Titrations

To determine the points on a curve for:

a. strong acid/strong base (problem 12-2)

b. weak acid/strong base (problem 12-6)

c. weak base/strong acid (problem 12-12)

d. diprotic systems (problem 12-25)

Read sections 12-5 to 12-8