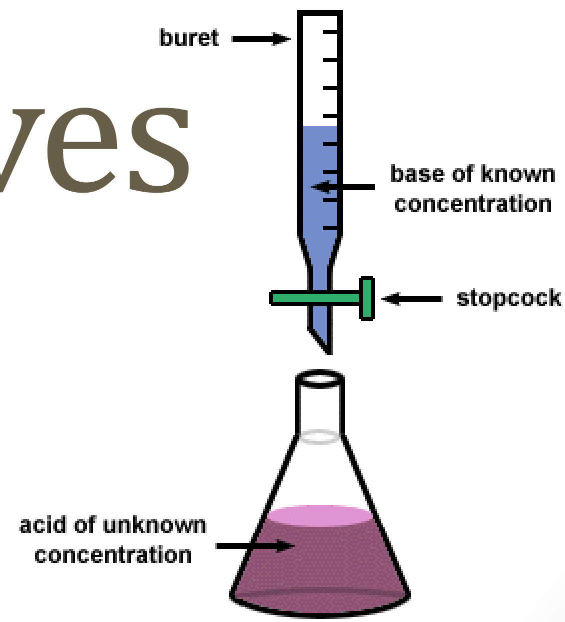
Titration curves

Titration of a weak acid



Titration of a strong acid

- When a strong acid is titrated with a strong base the pH at any point is determined solely by the concentration of un-titrated acid or excess base.
- The conjugated base that is formed has no effect on pH.

Titration of a weak acid

- When a weak acid is titrated with a strong base, the weak acid dissociates to yield a small amount of H^+.
- Weak acids or bases do not dissociate completely, therefore an equilibrium expression with K_a must be used.

Titration of a weak acid

- Weak acid dissociates in aqueous solution partially to give a small amount of H^+ ions.

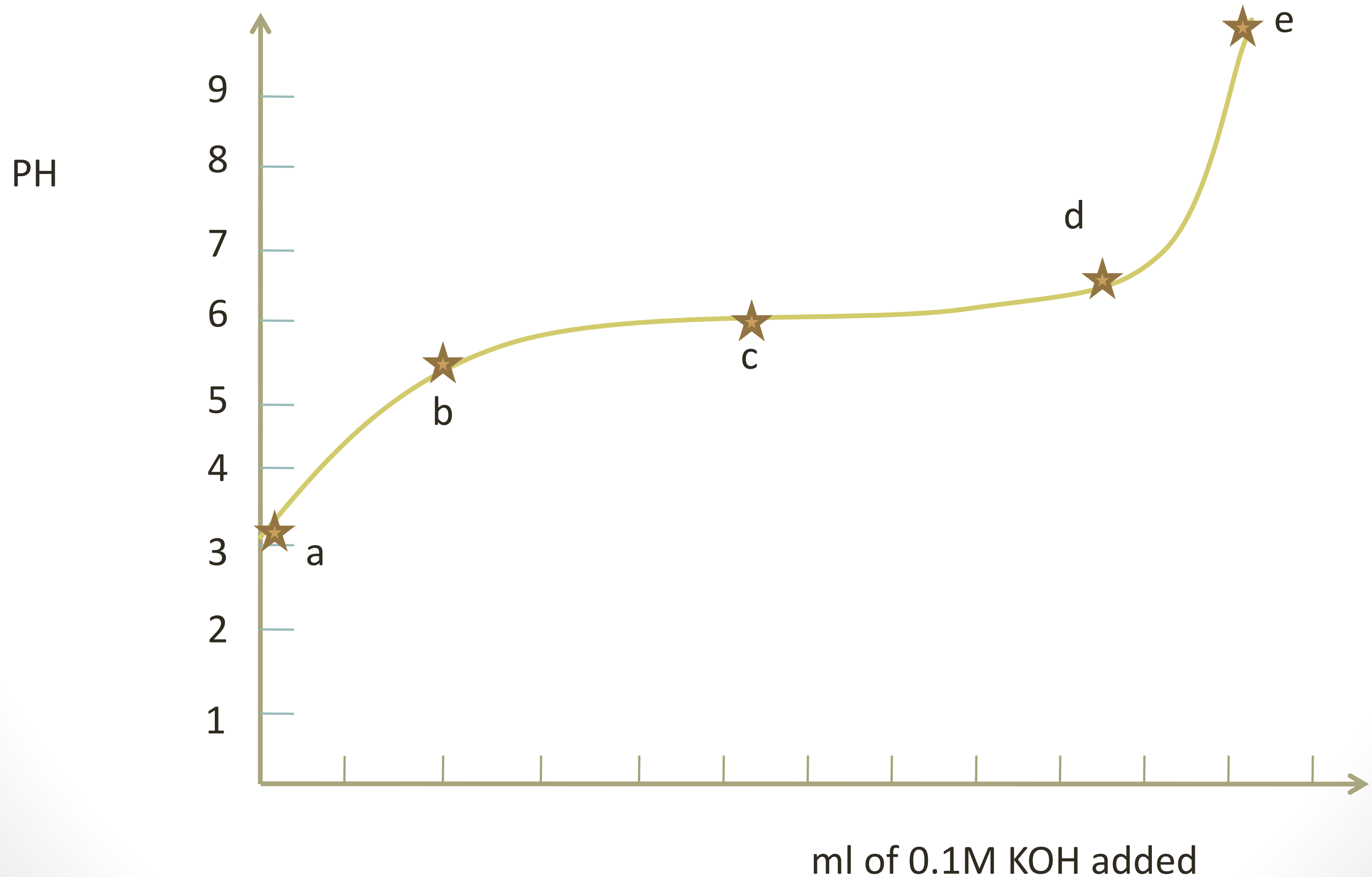
$$HA \Longleftrightarrow H^+ + A^-$$

- When OH^- ions are added during titration it is neutralized by H^+ ions to produce H_2O.
- The removal of the H^+ ions disturbs the equilibrium thus more HA molecules will ionize to produce H^+ ions to re-establish the equilibrium.

Titration of a weak acid cont'ed

- This process will continue until all the HA molecules are ionized.
- Thus the no. of moles of HA will be equal to the no. of moles of proton.

Titration curve of a monoprotic weak acid



Example

- Calculate the appropriate values and draw the curve for the titration of 500 ml of 0.1 M weak acid HA; with 0.1 M KOH; $pK_a = 5$; $pK_b = 9$

Point a: the pH before the addition of any base

$pH = ½ (pK_a + p [HA])$

$pH = ½ [(5 + (-\log 0.1)]$

$pH = 3$

NOTE: at any point during the titration the pH should be calculated using Henderson-Hasselbalch equation.

Point b: the pH after the addition of 100 ml of KOH

$$pH = pK_a + Log \frac{[A^-]}{[HA]}$$

The no. of moles OH^- ***added*** = M × V = 0.1 × 0.1 = 0.01 mole

Thus 0.01 moles of KOH will ***react*** with 0.01 mole of HA to produce 0.01 mole A^-

The no. of moles of HA ***originally*** present = 0.1 × 0.5 = 0.05 mole

- The no. of HA ***remaining*** = 0.05 – 0.01 = 0.04 mole

  Total volume = 500 + 100 = 600 ml

- Here we will use the no. of moles because when we calculate the volume it will give the same ratio at the end $\frac{[A^-]}{[HA]}$

pH = pK_a + Log

pH = 5 + Log (0.01/0.04)

pH = 4.4

Point c: the pH after the addition of 250 ml of KOH (half)

$$pH = pK_a + Log \frac{[A^-]}{[HA]}$$

The no. of moles OH^- ***added*** = M × V = 0.1 × 0.25 = 0.025 mole

Thus 0.025 moles of KOH will ***react*** with 0.025 mole of HA to produce 0.25 mole A^-

The no. of moles of HA ***remaining*** = 0.05 – 0.025 = 0.025 mole

$$pH = pK_a + Log \frac{[A^-]}{[HA]}$$

pH = 5 + Log (0.025/0.025)

pH = 5

OR

At this point half the weak acid HA is titrated, since the reaction between HA and KOH is one to one reaction and they both have the same concentration

$$HA + KOH \Longleftrightarrow H_2O + KA$$

$$[HA] = [A^-]$$

Monoprotic acid (one proton) that reacts with a base containing one hydroxyl group (one OH^-)

$$\text{Ratio} = [A^-]/[HA] = 1$$

$$pH = pK_a + \text{Log } [A^-]/[HA]$$

$$pH = 5 + \text{Log } 1$$

$$pH = 5 + 0 = 5$$

Point d: the pH after the addition of 375 ml of KOH

$$pH = pK_a + \text{Log} \frac{[A^-]}{[HA]}$$

The no. of moles OH^- ***added*** = M × V = 0.1 × 0.375 = 0.0375 mole

Thus 0.0375 moles of KOH will ***react*** with 0.0375 mole of HA to produce 0.0375 mole A^-

The no. of moles of HA ***remaining*** = 0.05 – 0.0375 = 0.0125 mole

$$pH = pK_a + \text{Log} \frac{[A^-]}{[HA]}$$

pH = 5 + Log (0.0375/0.0125)

pH = 5.48

NOTICE:

- When the acid is *less* than half titrated the pH is less than pK_a
- When the acid is *half* titrated the $pH = pK_a$
- When the acid is *more* than half titrated the pH is greater than pK_a

Point e: When 500 ml of KOH is added

$pOH = ½ (pK_b + p [A^-])$

The no. of moles OH^- ***added*** = M × V = 0.1 × 0.5 = 0.05 mole

Thus 0.05 moles of KOH will ***react*** with 0.05 mole of HA to produce 0.05 mole A^-

Molarity of A^- = no. of moles / vol. in L

The total volume of whole solution = 1000 ml = 1 L

Molarity of A^- = no. of moles / vol. in L

Molarity of A^- = 0.05 / 1 = 0.05 M

$p[A^-] = -\log[A^-]$

$p[A^-] = -\log 0.05$

$p[A^-] = 1.3$

$K_w = K_a \times K_b$

$K_b = K_w / K_a = 10^{-14}/10^{-5} = 10^{-9}$

$$pOH = \frac{1}{2} (pK_b + p [A^-])$$

$$pOH = \frac{1}{2} (9 + 1.3)$$

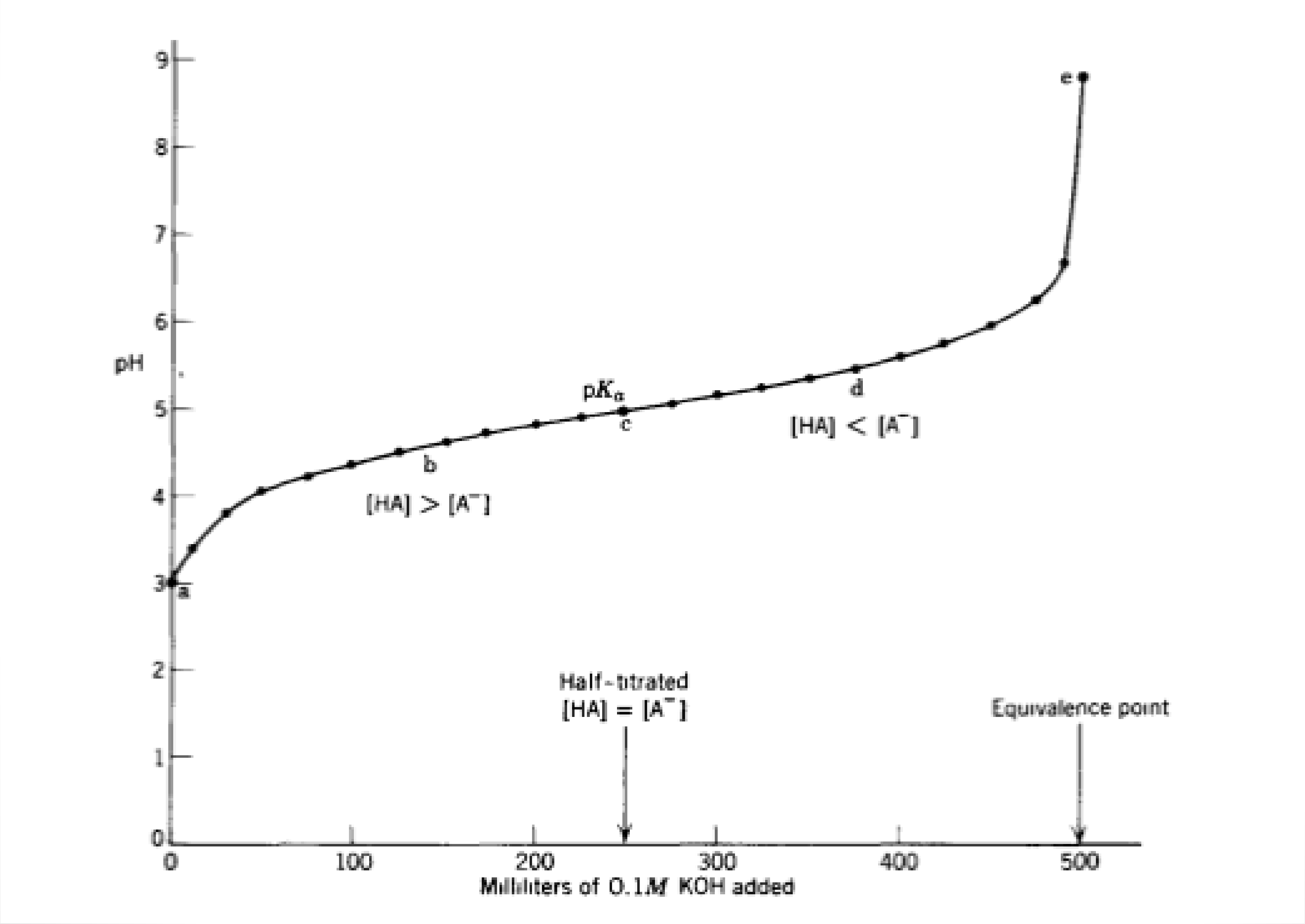
$$pOH = 5.15$$

$$pK_w = pH + pOH$$

$$pH = pK_w - pOH$$

$$pH = 14 - 5.15 = 8.85$$

Titration of a Weak Acid Cont'ed



Titration of a Weak Acid Cont'ed

- From the previous example:

a) All HA is in the form of CH_3COOH

b) $[CH_3COOH] > [CH_3COO^-]$

c) $[CH_3COOH] = [CH_3COO^-]$

d) $[CH_3COOH] < [CH_3COO^-]$

e) All as CH_3COO^-

How to calculated the pH!

- The pH is calculated through different ways:
- ➢ At starting point pH= (pKa+p[HA])/2

- ➢ At any point within the curve (after, in or after middle titration) pH = pKa+ log[A^-]/[HA]

- ➢ At end point pOH = (pKb+p[A^-])/2

  pH = pK_w – pOH