Titration curve

of polyprotic acids

Dissociation of polyprotic acids

- A polyprotic acid has more than one proton per molecule, thus it ionizes in successive steps.
- Example: H_2A a "polyprotic acid", diprotic acid

$$H_2A \overset{K_{a1}}{\Longleftrightarrow} H^+ + HA^- \overset{K_{a2}}{\Longleftrightarrow} H^+ + A^{-2}$$

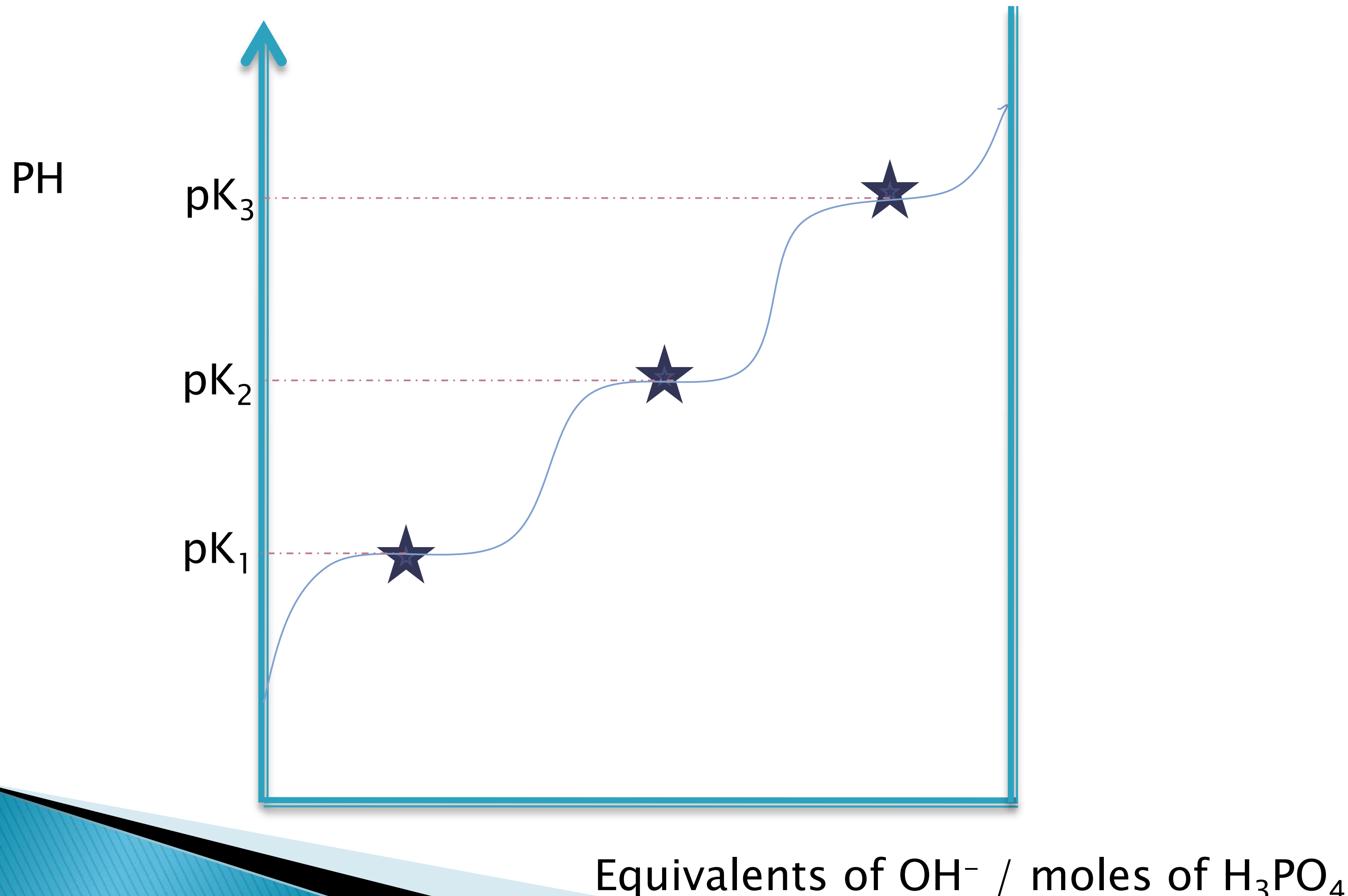
$$K_{a1} = \frac{[H^+][HA^-]}{[H_2A]}$$

$$K_{a2} = \frac{[H^+][A^{-2}]}{[HA^-]}$$

Dissociation of polyprotic acids cont'ed

- K_{a1} is larger than the K_{a2}
- The pH of H_2A solution is mainly dependant on the first ionization step.

Titration curve of H_3PO_4 a poly protic acid



Titration curve of H_3PO_4 a poly protic acid cont'ed

$$H_3PO_4 \overset{K_1}{\Longleftrightarrow} H^+ + H_2PO_4^-$$

$$H_2PO_4^- \overset{K_2}{\Longleftrightarrow} H^+ + HPO_4^{-2}$$

$$HPO_4^{-2} \overset{K_3}{\Longleftrightarrow} H^+ + PO_4^{-3}$$

$$K_{a1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$$

$$K_{a2} = \frac{[H^+][HPO_4^{-2}]}{[H_2PO_4^-]}$$

$$K_{a3} = \frac{[H^+]PO_4^{-3}]}{[HPO_4^{-2}]}$$

Titration curve of H_3PO_4 a poly protic acid cont'ed

$$K_{a1} > K_{a2} > K_{a3}$$

- **Example**

  How many ml of 0.1 M NaOH are required to titrate 100 ml of 0.1 M H_3PO_4?

  No. of moles of $H_3PO_4 = V \times M = 0.1 \times 0.1 = 0.01$ mole

  - No. of moles of $H^+ = V \times M = 0.01 \times 3 = 0.03$ mole

Titration curve of H_3PO_4 a polyprotic acid cont'ed

Thus: we need 0.03 moles of NaOH to titrate the acid

M = no. of moles / V

V = no. of moles / M

V = 0.03 / 0.1

V = 0.3 L = 300 ml

Example 1

- 1.025 g of anhydrous sodium acetate is dissolved in 100 ml of 0.25 M acetic acid CH_3COOH. Calculate:
  - A) The pH of the final solution.
  - B) The molarity of the final solution (resulting buffer)

  Mwt of anhydrous sodium acetate = 82; $pK_a = 4.7$

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

no. of moles of A^- in buffer = wt / Mwt
= 1.025 / 82
= 0.0125 moles

Molarity = no. of moles / v in L
= 0.0125 / 0.1
= 0.125 M

no. of moles of HA in buffer = M × V
= 0.25 × 0.1
= 0.025 moles

Molarity = no. of moles / v in L
= 0.025 / 0.1
= 0.25 M

pH = 4.7 + log (0.125 / 0.25)
pH = 4.39

- B) The molarity of the buffer = the molarity of HA + the molarity of A^-
  Buffer molarity = 0.25 + 0.125 = 0.375 M

<u>OR</u>

No. of moles of buffer = no. of moles of HA + the no. of moles of A^-
No. of moles of buffer = 0.025 + 0.0125 = 0.0375 moles
Molarity of buffer = no. of moles / V in L
Molarity of buffer = 0.0375 / 0.1 = 0.375 M

Example 2

- 5 L of 0.1 M phosphate buffer with a pH = 12.32 was prepared from Na_3PO_4 and Na_2HPO_4.
  Calculate the weight in grams of each component which was used to prepare the buffer, $pK_a = 12$.

- SELF SOLVE!

Titration Curve

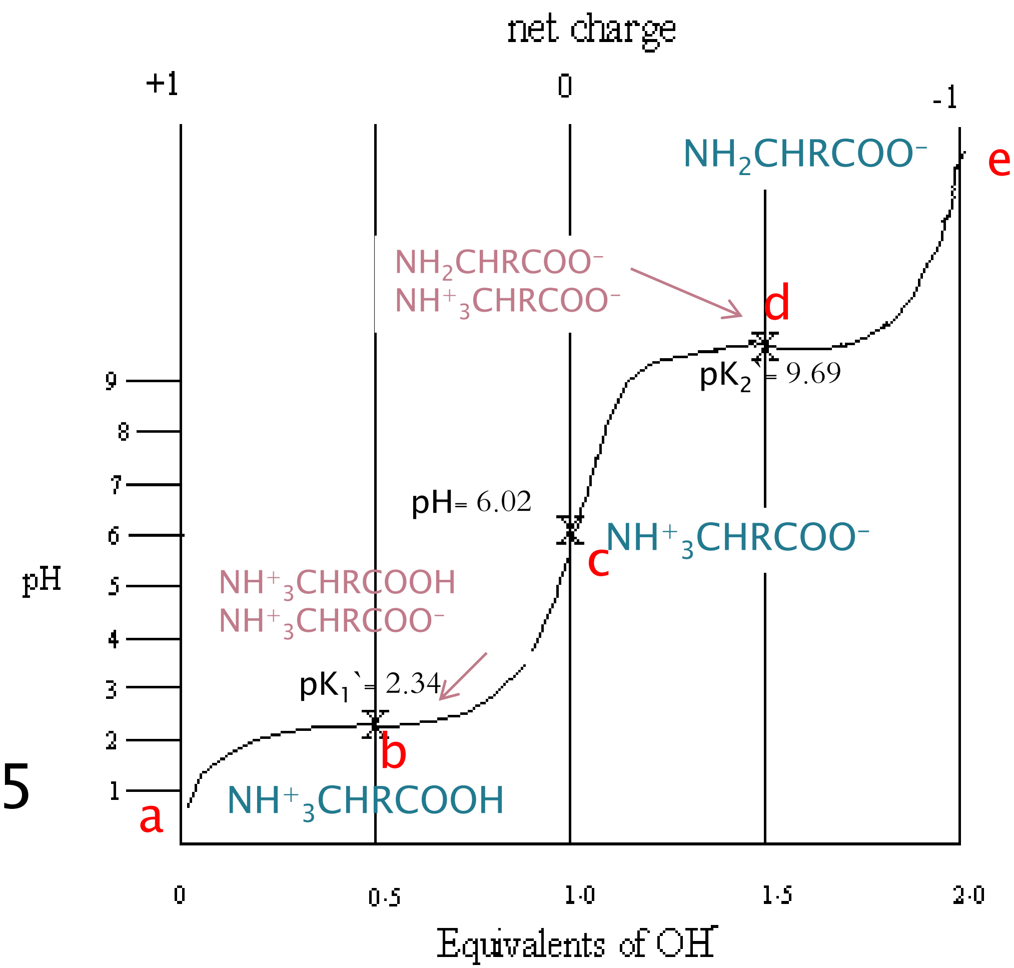
of amino acids

Titration curves

- It is a curve that monitors the pH of a solution as amounts of alkali or acid is added.
- Amino acids are *simple* weak polyprotic acids.
- Neutral amino acids (as alanine, glycine) are treated as diprotic acids.
- Acidic amino acids (as aspartic or glutamic acid) and Basic amino acids (as lysine or histidine) are treated as triprotic acids.

Titration curve of alanine

- **At point a:**
  - Before titration
  - $NH^+{}_3CHRCOOH$
  - The net charge = +1
- **At point b:**
  - Pk_1` = pH
  - Here it has buffering capacity
  - $NH^+{}_3CHRCOOH$ = $NH^+{}_3CHRCOO^-$
  - The net charge = +0.5



Titration curve of alanine cont'ed

- **At point c:**
  - Isoelectric point
  - pI = pH; to calculate pI: from the plot or pI = $(pK_1` + pK_2`) \backslash 2$
  - $NH^+{}_3CHRCOO^-$ a zwitter ion
  - The net charge = 0
- **At point d:**
  - $Pk_2`$ = pH
  - Here it has buffering capacity
  - $NH^+{}_3CHRCOO^- = NH_2CHRCOO^-$
  - The net charge = −0.5

Titration curve of alanine cont'ed

- **At point e:**
  - End of titration
  - $NH_2CHRCOO^-$
  - The net charge = −1
- This curve has two flat zones, at point b and d; meaning it has two ionized groups.