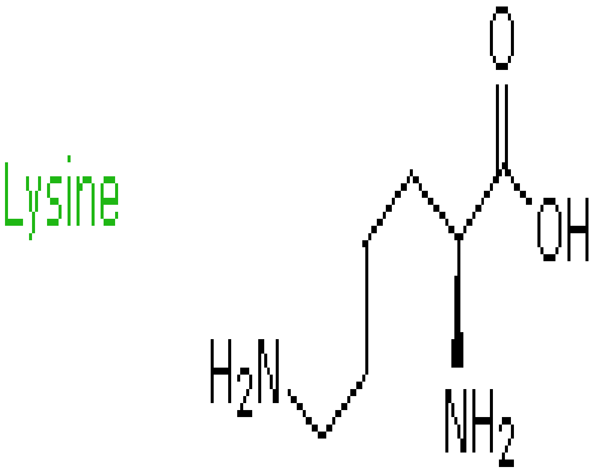
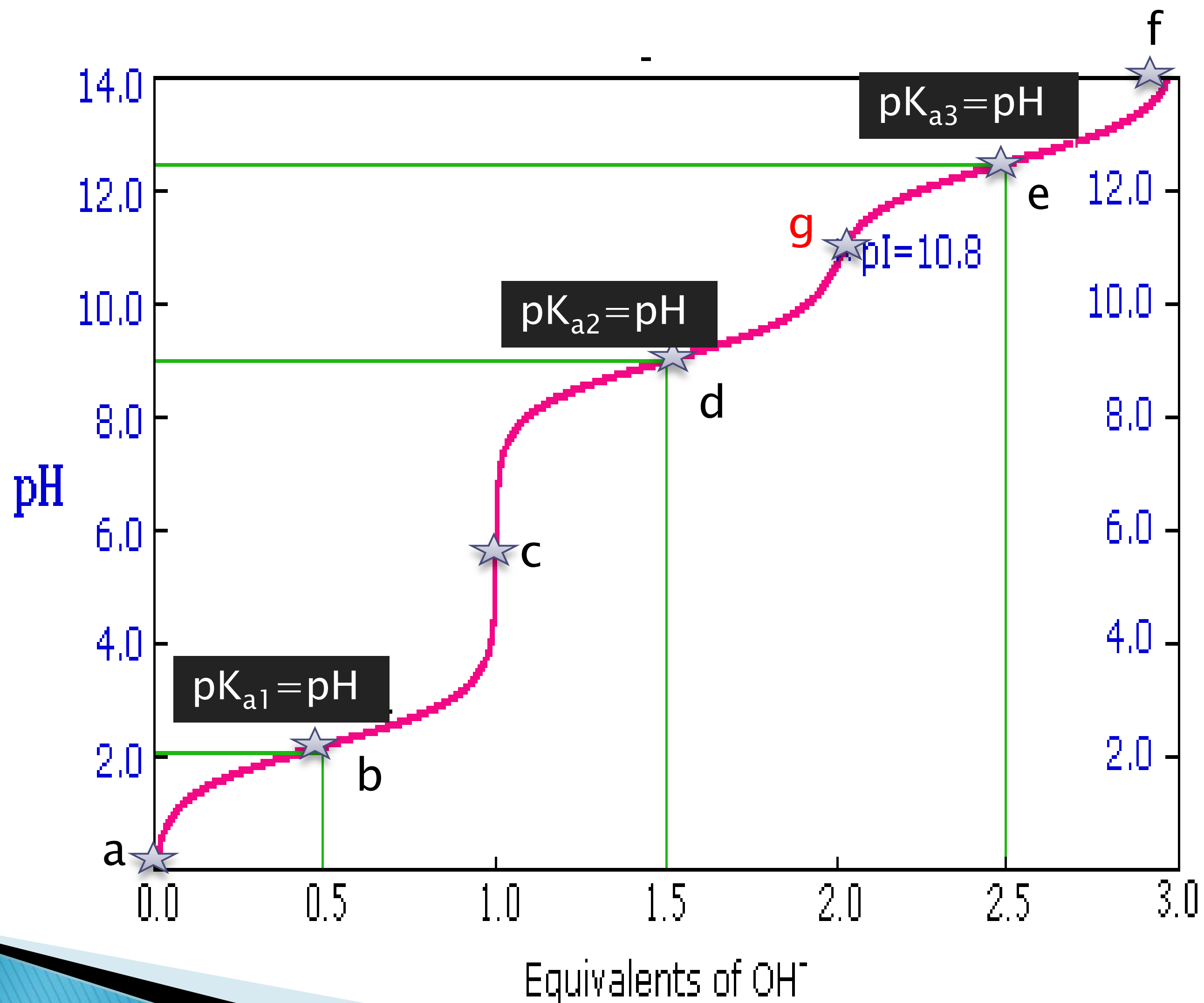
Titration curve cont’ed

Titration curve of lysine

- Lysine is a basic amino acid with an extra amino group in its side chain.
- pKa:
  - 1st α–COOH will be titrated first = 2.18
  - 2nd α –NH_3^+ will be titrated next = 8.95
  - 3rd R–NH_3^+ will be titrated last = 10.53
- We have three flat zones, i.e. three ionized groups.



Titration curve of lysine



Titration curve of lysine cont'ed

- **<u>At point a:</u>**
  - Before titration
  - $NH^{+}{}_{3}CH(CH_2)_4NH^{+}{}_{3}COOH$
  - The net charge = + 2
- **<u>At point b:</u>**
  - Pk_{a1} = pH
  - Here it has buffering capacity
  - $NH^{+}{}_{3}CH(CH_2)_4NH^{+}{}_{3}COOH = NH^{+}{}_{3}CH(CH_2)_4NH^{+}{}_{3}COO^{-}$
  - The net charge = +2 | +1 = + 1.5

Titration curve of lysine cont'ed

- **At point c:**
  - $NH^+_3CH(CH_2)_4NH^+_3COO^-$
  - All the α–COOH has been titrated.
  - The net charge = +1
- **At point d:**
  - Pk_{a2} = pH
  - Here it has buffering capacity
  - $NH^+_3CH(CH_2)_4NH^+_3COO^- = NH_2CH(CH_2)_4NH^+_3COO^-$
  - The net charge = +1 | 0 = + 0.5

Titration curve of lysine cont'ed

- **At point g:**
  - It is the Ip point
  - $NH_2CH(CH_2)_4NH^+{}_3COO^-$
  - The net charge = 0
  - Ip = pH, Ip = $(pKa_2+pKa_3)/2$
- **At point d:**
  - $NH_2(CH_2)_4NH^+{}_3COO^- = NH_2(CH_2)_4NH_2COO^-$
  - The net charge = 0 | −1 = − 0.5
  - Pk_{a3} = pH
  - Here it has buffering capacity

Titration curve of lysine cont'ed

- **At point f:**
  - End of titration
  - $NH_2(CH_2)_4NH_2COO^-$
  - The net charge = −1
  - All has been titrated.

Titration Curves of Amino Acids

Information obtained from a titration curve

1- The number of ionizable groups in that amino acid, which can be detected from the number of titration stages in the curve, (or the number of pK_a's or number of flat zones in the curve).

2- Whether the triprotic amino acid is basic or acidic, that can be detected from the pKa_2.

- If it's value is closer to the value of pKa_1 (that of the α-carboxyl group), then it is an acidic amino acid.
- If the value of it's pKa_2 is closer to the value of pKa_3 (that of the α-amino group), then it is basic amino acid.

3- The pK_a values of the amino acid can be obtained from the curve which is equal to the pH value at the mid-point.

Titration Curves of Amino Acids

4- The isoelectric point , pI for each amino acid can be obtained from the curve by detecting the point where the amino acid is all in the zwitterion form (net charge = 0.0) the pH at that point is the pI.

- Or it can be obtained mathematically from:

$$pI = \frac{pKa_1 + pKa_2}{2}$$ (in the case of a neutral amino acid)

$$pI = \frac{pKa_1 + pKa_2}{2}$$ (in the case of acidic amino acids)

$$pI = \frac{pKa_2 + pKa_3}{2}$$ (in the case of basic amino acids)

Titration Curves of Amino Acids

5- You can also determine from the curve the pH values at which the amino acid can act as a buffer. (the pH ranges ±1 from the pH value of each midpoint).

How to Obtain a Titration Curves of Amino Acids?

1- Calculate the no. of moles of weak acid or a.a

2- Calculate the first moles of OH^- by

A= no. of moles of acid or a.a / pK_{a1}

3- Calculate the second moles of OH^- added

B= No of moles of weak acid or a.a + A

4- Calculate the third moles of OH^- added

C= No of moles of weak acid or a.a + B

Example 1

- Sketch the pH curve for the titration of 100 ml of 0.1M glycine with KOH? $pk_{a1} = 1.71$, $pk_{a2} = 9.6$?

No. of moles of a.a = M × V

= 0.1 × 0.1

= 0.01 mole

The first moles of OH^-:

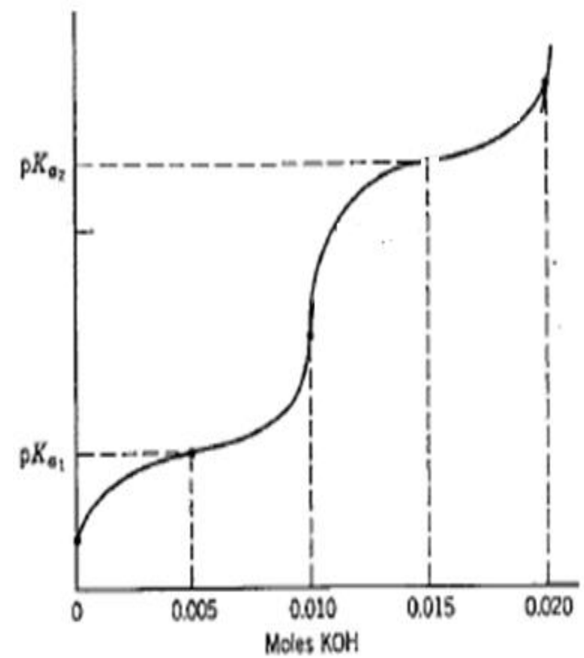
A = 0.01 / 1.71 = 0.005

The second moles of OH^- added:

B = 0.01 + 0.005 = 0.015

$PI = (pk_{a1} + pk_{a2}) / 2$

$= 5.66$



Example 2

- Plot the titration curve of aspartic acid it has a volume of 100 ml and 0.1M when titrated with 0.1M KOH? $pk_{a1} = 2.09$, $pk_{a2} = 3.86$, $pk_{a3} = 9.82$?

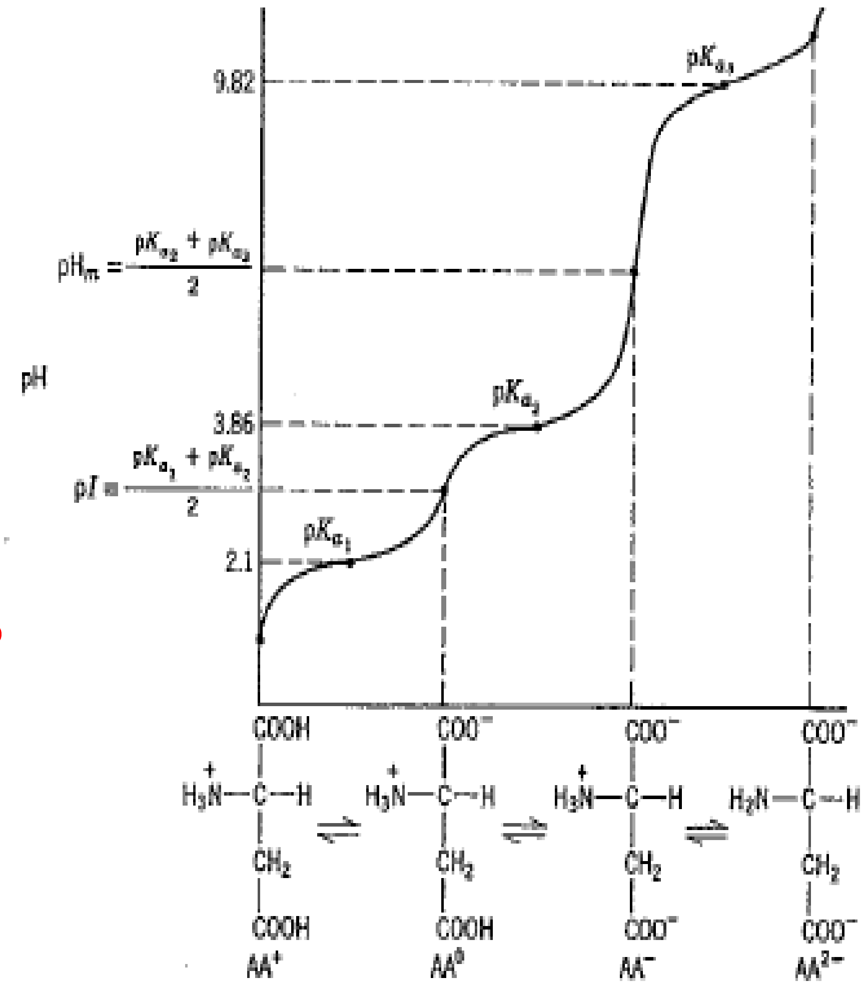


Figure 1-8 Titration curve of aspartic acid. For clarity, the vertical axis is not drawn to scale.

Example 3

- Plot the titration curve of lysine which has a volume of 200 ml and 0.3 M when titrated with 0.1M NaOH?
  $pk_{a1} = 2.18$, $pk_{a2} = 8.95$, $pk_{a3} = 10.35$?

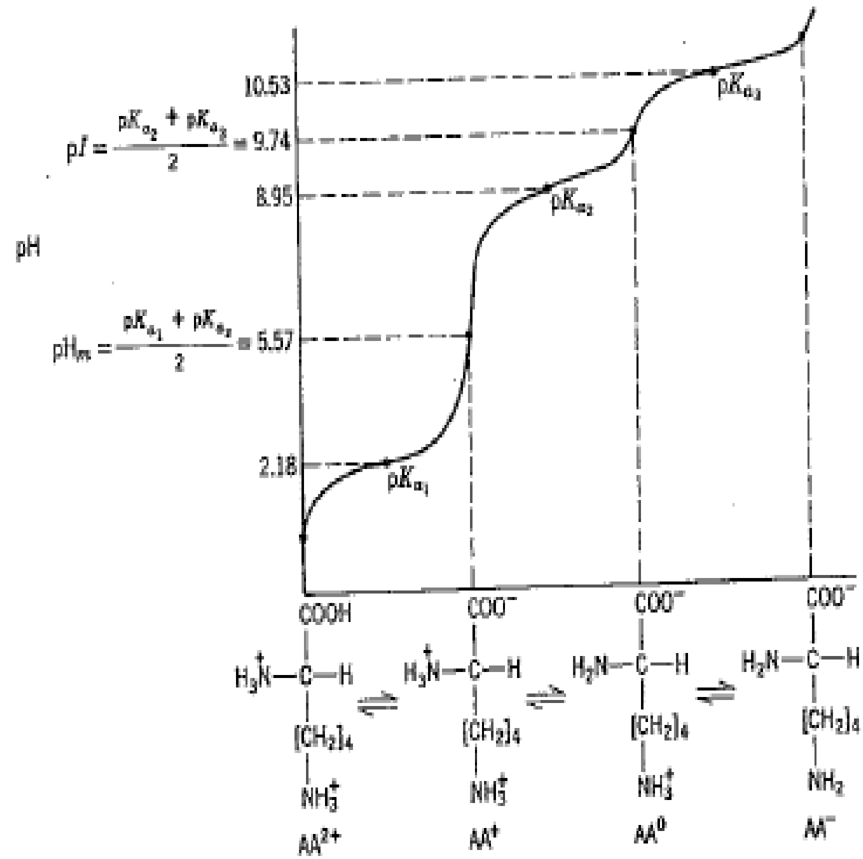


Figure 1-9 Titration curve of lysine. For clarity, the vertical axis is not drawn to scale.