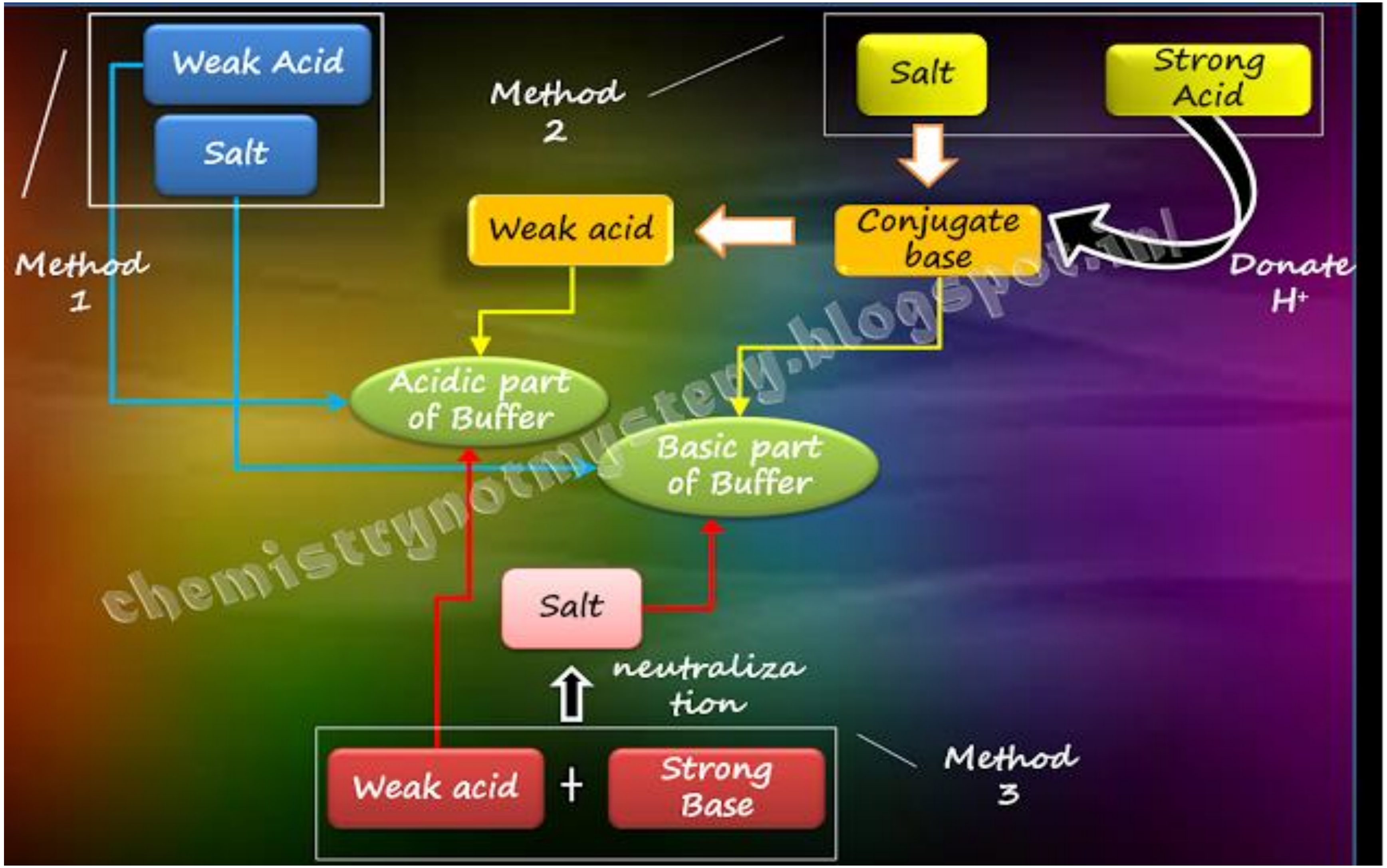
Titration of weak acids

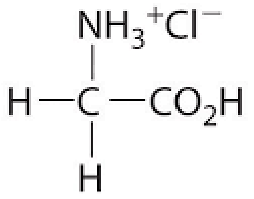
Methods To Prepare Buffer solutions



Titration of amino acids

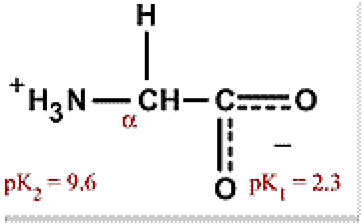
- Amino acids are weak polyprotic acids .
- Neutral amino acids are (gly, ala, threonine) are treated as diprotic acids .
- acidic amino acids (glu, asp,) are treated as triprotic acids .
- Basic amino acids (lys , arg , his) are treated as triprotic acids .
- pH_m is the pH at which the maximum total number of charges present.
- Glycine can be obtained in three forms :

a) Glycine hydrochloride

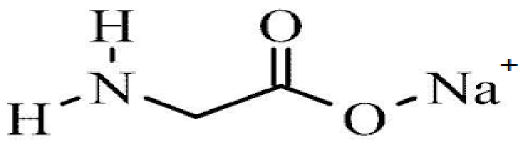


glycine hydrochloride

b) Isoelectric glycine



c)Sodium glycinate

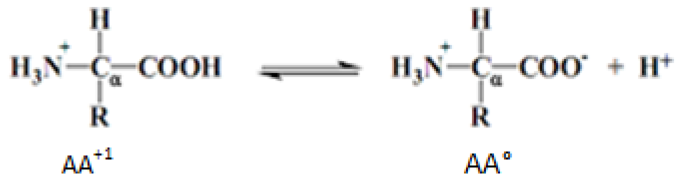


Titration of amino acids

- Example: Calculate the pH of a 0.1M solution of a) Glycine hydrochloride , b) Isoelectric glycine , c)Sodium glycinate

$K_{a1} = 4.57 \times 10^{-3}$

a) Glycine hydrochloride is a diprotic acid , the carboxylic group is a much stronger acid than the amino group , the pH of the solution is dependent exclusively by the extent the carboxyl group ionizes .



$K_{a1} = \frac{[AA^{\circ}][H^{+}]}{[AA^{+1}]}$, assume $y = [AA^{+1}]$ that ionizes .

Thus, $y = [H^{+}]$ produced, and $y = [AA^{\circ}]$ produced .

AA^{+1} remaining at equilibrium = $[AA^{+1}]$ original - $[AA^{+1}]$ that ionizes = $0.1 - y$

Thus, $K_{a1} = \frac{(y)(y)}{0.1 - y} = 4.57 \times 10^{-3}$

Titration of amino acids

Since amount of y (value of y) is stronger than that can be ignored ,

Thus $4.57 \times 10^{-4} - 4.57 \times 10^{-3}\ y = y^{2}$

$y^{2} + 4.57 \times 10^{-3}\ y - 4.57 \times 10^{-4} = 0.0$

$Y = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$, where $a = 1$, $b = 4.57 \times 10^{-3}$, $c = 4.57 \times 10^{-4}$

Thus $y = [H^{+}] = 1.92 \times 10^{-2}$.

pH = 1.72 .

What is the degree of ionization of glycine hydrochloride in this 0.1M solution ?

b) The pH of AA° is the pI (the pI is defined as that pH where the predominant ionic form is AA° , so net charge on the amivo acid is zero .)

So $pH = \frac{pK_{a1} + pKa_{2}}{2} = \frac{2.34 + 9.6}{2} = 5.97$

c)Sodium glycinate is a diprotic base ,

Both the unionized amino group and the carboxylate ion can accept a proton from water , but since the amino group is a much stronger base than the α-carboxylate group , the pH of the solution depends almost exclusively on the extent to which amino group ionizes .

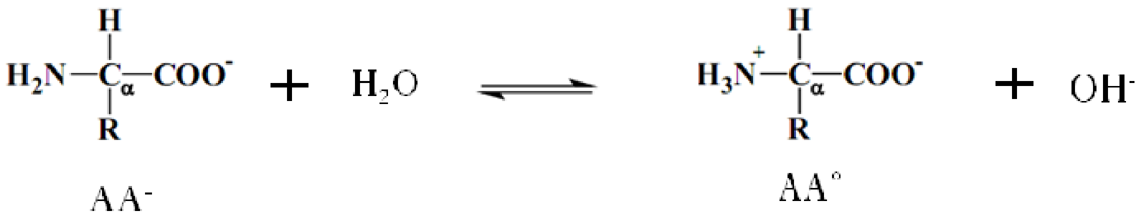
Titration of amino acids

For the amino group :

$$K_{b1} = \frac{K_w}{K_{a2}} = \frac{10^{-14}}{10^{-9.6}} = 3.98 \text{ x}10^{-5}$$

For carboxylate group ;

$$K_{b2} = \frac{K_w}{K_{a1}} = \frac{10^{-14}}{10^{-2.34}} = 2.19 \text{ x}10^{-12}$$



$$K_{b1} = \frac{[OH^-]\ \ [AA^\circ]}{[AA^{-1}]} = \frac{(y)\ (y)}{0.1 - (y)}$$

Because the concentration of sodium glycinate is much larger than K_{b1} thus y can be neglected from the dominator .

Titration of amino acids

$3.98 \times 10^{-5} = \frac{y^2}{0.1}$, so $y^2 = 3.98 \times 10^{-6}$

$y = \sqrt{3.98 \times 10{-6}}$

$y = 1.99 \times 10^{-3}$ M , $[OH^-] = 1.99 \times 10^{-3}$ M

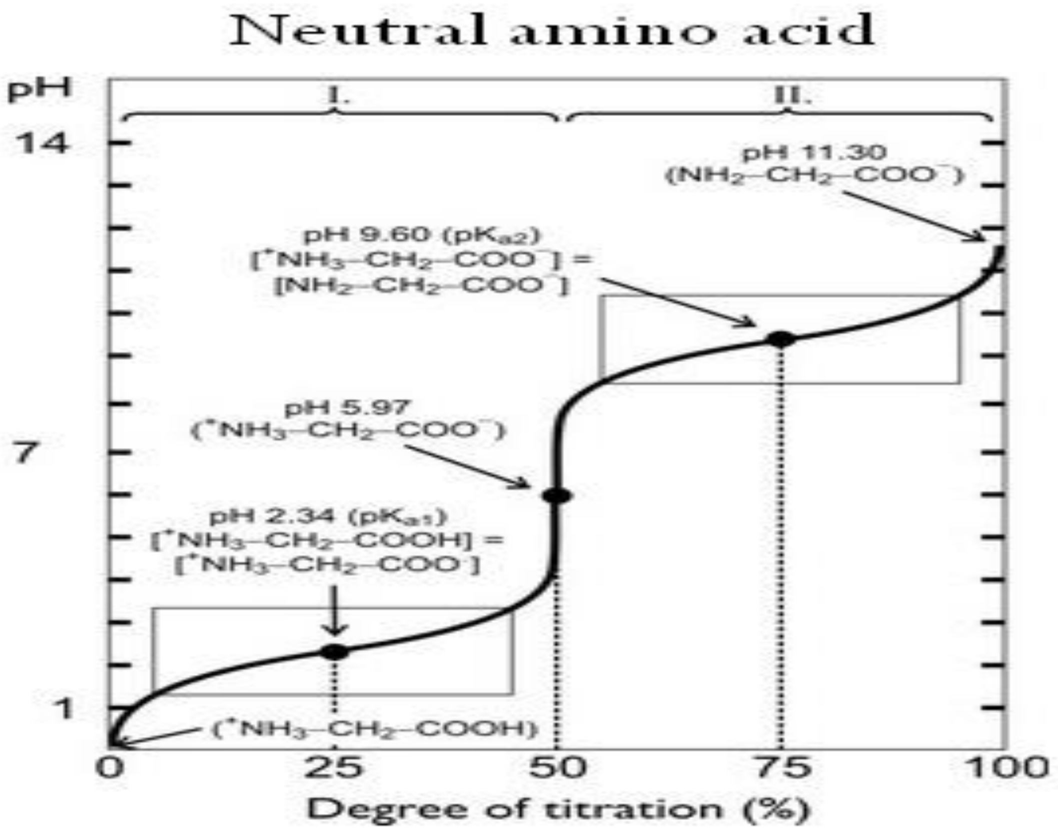
$[H^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10{-14}}{1.99 \times 10{-3}} = 5 \times 10^{-12}$ M

pH = $-\log[H^+] = 11.3$.

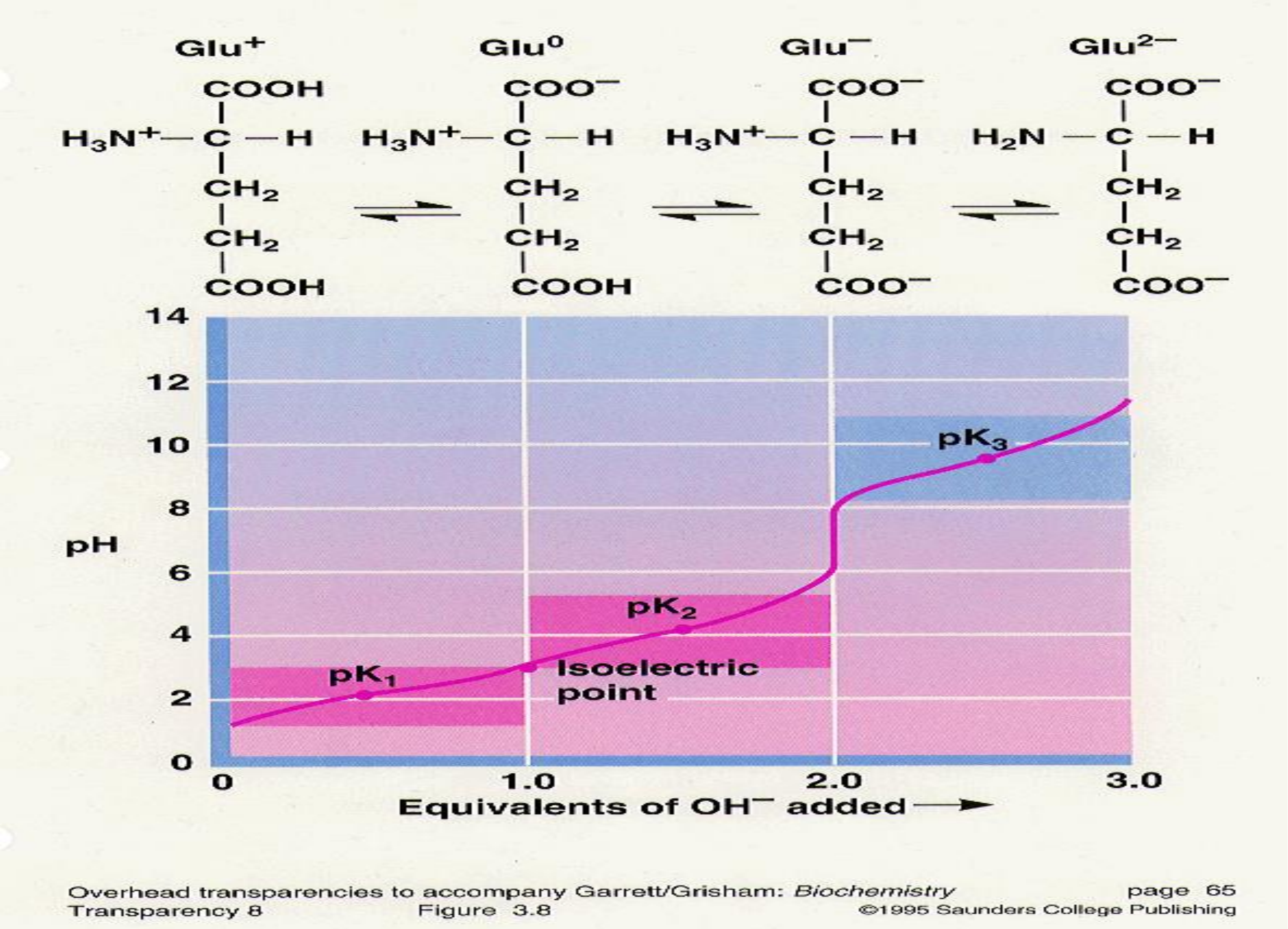
Titration Curve of Neutral Amino Acids

- Amino acids are titrated in exactly the same manner as diprotic and triprotic weak acids .

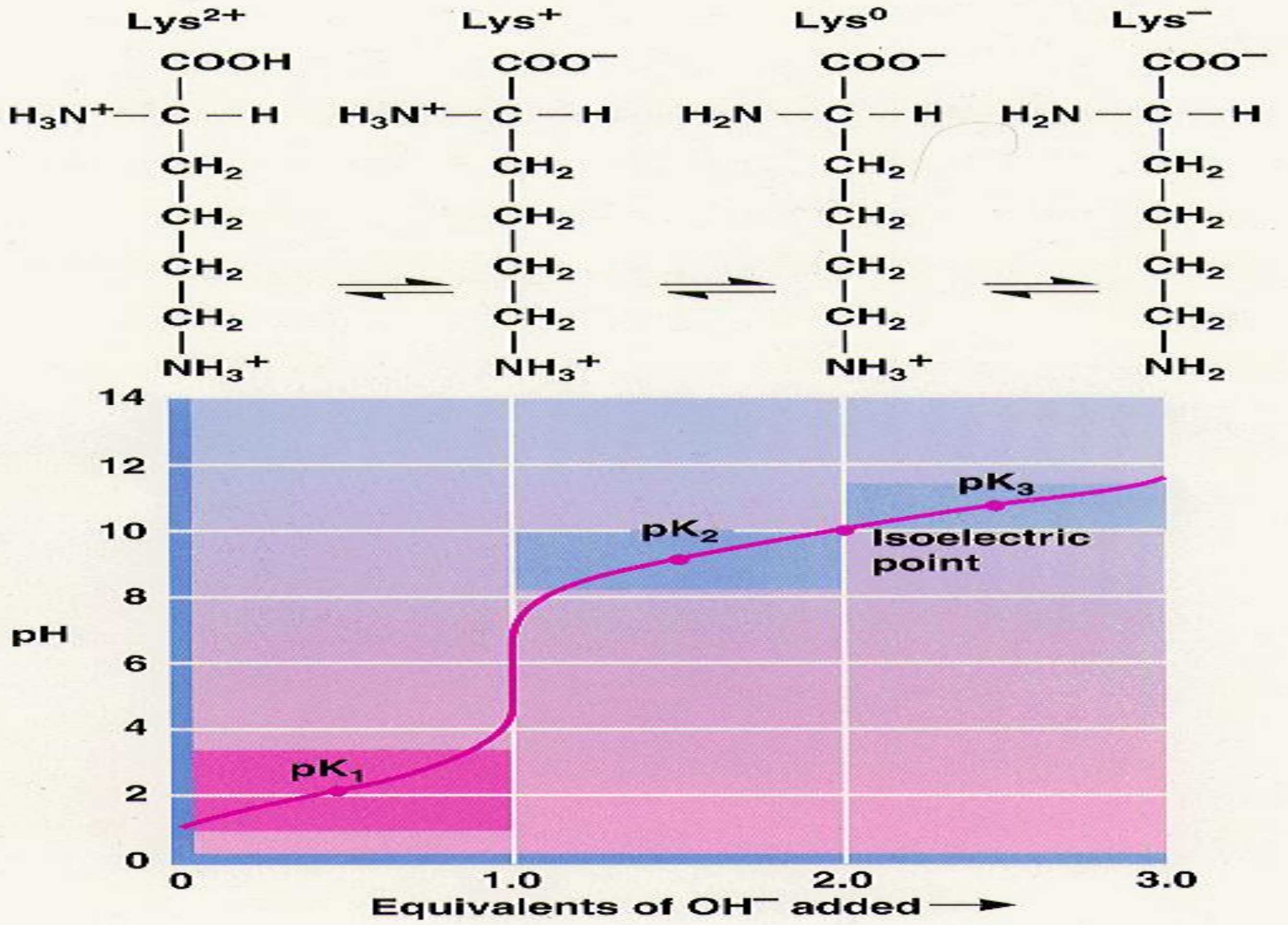
Neutral amino acid



Titration Curve of Acidic amino Acid (Glutamate)



Titration Curves of Lysine



Overhead transparencies to accompany Garrett/Grisham: *Biochemistry* page 65
Transparency 9 Figure 3.8

Titration Curves of Amino Acids

Information that can be 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- aminogroup), 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 .

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) .

In the case of triprotic amino acids , the pI is calculated from :

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

Titration Curves of Amino Acids

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

No of moles of weak acid or a.a

Calculate the first moles of OH by A= $\frac{no\ of\ mole\ of\ acid\ or\ a.a}{PKa1}$

Calculate the second moles of OH added B= No of moles of weak acid or a.a + A

Calculate the third moles of OH added C= No of moles of weak acid or a.a + B

How to Obtain a Titration Curves of Amino Acids

Sketch the pH curve for the titration of 100ml of 0.1M Glycine with KOH? Pka1=1.71, Pka2=9.6?

No of moles of a.a = M*V

= 0.1 * 0.1

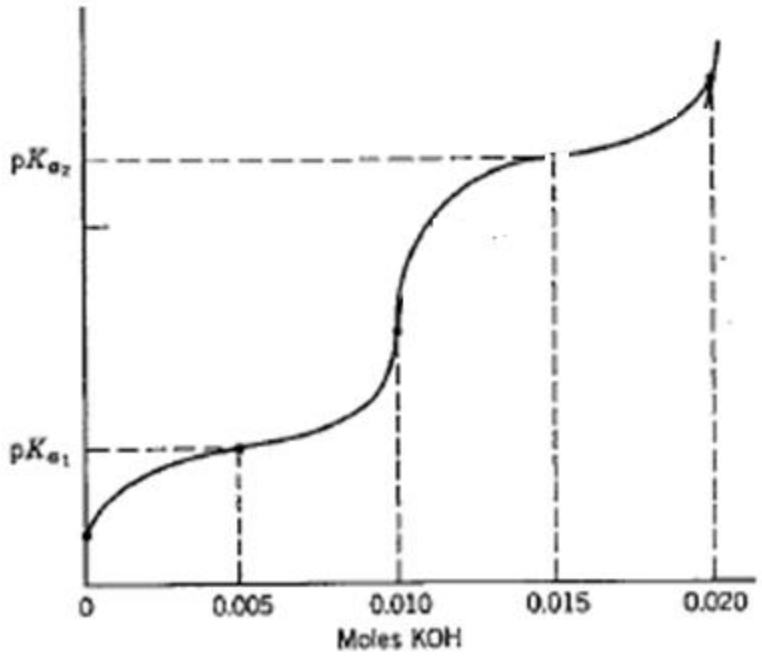
=0.01 mole

The first moles of OH by A= 0.01 / 1.71 = 0.005

The second moles of OH added B= 0.01 + 0.005 = 0.015

PI = (Pka1 + pka2)/ 2

=5.66



- Plot the titration curve of Aspartic acid it has a volume of 100ml and0.1M

When titrated with 0.1M KOH? Pka1=2.09, Pka2=3.86, Pka3=9.82?

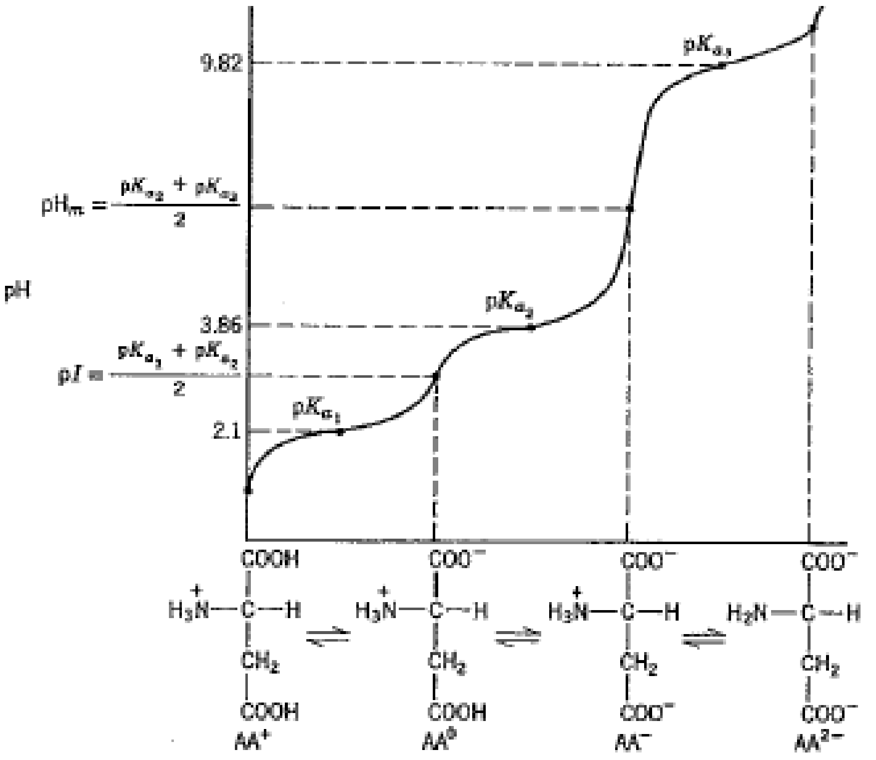


Figure 1-8 Titration curve of aspartic acid. For clarity, the vertical axis is not drawn to scale.

- Plot the titration curve of Lysine which has a volume of 200ml and 0.3M

When titrated with 0.1M NaOH? ? Pka1=2.18, Pka2=8.95, Pka3=10.35?

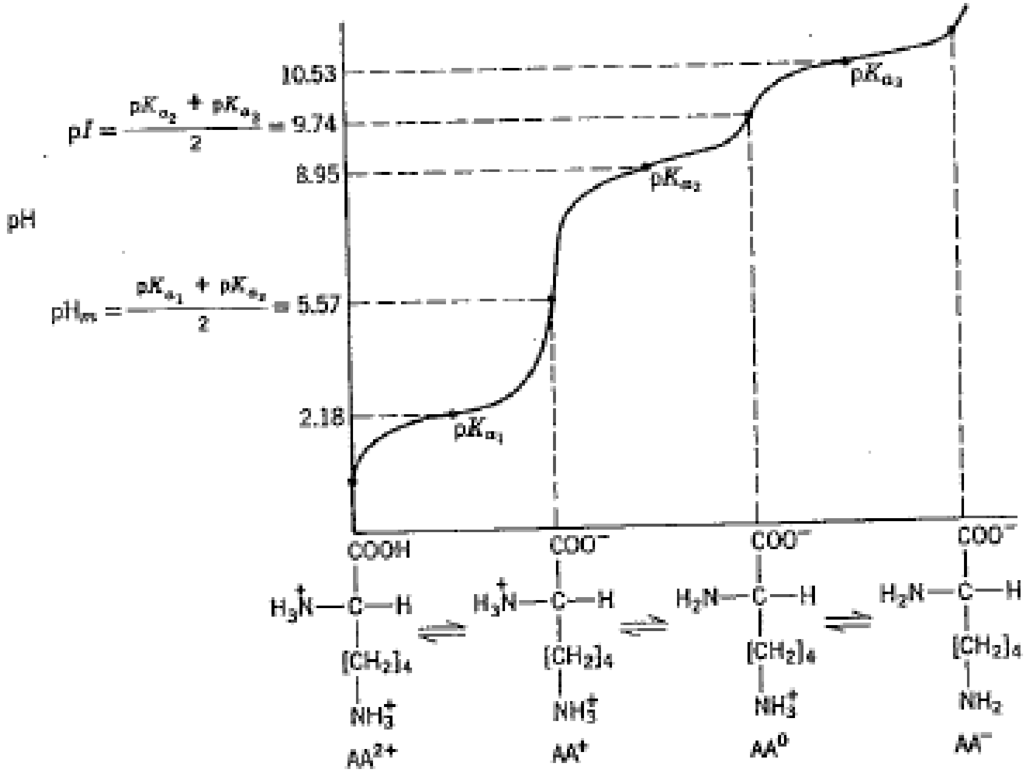


Figure 1-9 Titration curve of lysine. For clarity, the vertical axis is not drawn to scale.