Chapter Seven

Acid-Base Titration Curves

7 Acid-Base Titration Curves

They are also called ~~It is called also~~ neutralisation titration curves since H^+ that comes from acids or acidic solutions is neutralised with OH^- which comes from bases or basic solutions to form ~~from~~ a very slightly ionised water:

$$H^+ + OH^- \longrightarrow H_2O$$

__Titration :__ It is a the? gradual addition of titrant which is always standard solution to the titrand which is always the analyte (the solution under test or unknown), in the presence of a certain indicator. The titration is finished by the sudden change of indicator colour.

__Titrant :__ It is the solution which ~~is~~ contained in the burette and it is always the standard solution, but in some cases it refers to the analyte or unknown.

__Titrand :__ It is the solution which is always contained in a conical flask and it is always the analyte, but some times it refers to standard solution. The burette ~~and~~ pipette and volumetric flasks are used to measure and transfer the exact volumes of solutions. Beakers, conical flasks and cylinders are used to measure or transfer the approximate volumes of solutions.

In acid-base titrations, there is a change in $[H^+]$ concentration or pH of the solution by increasing or decreasing the pH of the solution until reaching equivalence point where a sudden change in pH is indicated by a sudden change in a certain acid-base indicator colour.

This chapter includes the majority? ~~most~~ of acid-base titrations involving strong acids with strong bases, weak acids with strong bases, strong acids with weak bases and weak acids with weak bases. The titrations are followed by calculation the pH during the process before addition of titrant and after addition of titrant till exceeding of equivalence point.

The data obtained are used to set up the titration curves and identifying the pH at equivalence point.

7.1 Titration of strong acid with strong base.

Example: 25ml of 0.1 M HCl solution is titrated with 0.1 M NaOH solution. Calculate the pH of this titration at the following stages:

(a) before addition of NaOH .

(b) after addition of NaOH till before the equivalence point.

(c) at equivalence point. (d) after equivalence point.

The solution:

(a) Before addition of NaOH:

$$\underset{0.1M}{HCl} \longrightarrow \underset{0.1M}{H^+} + \underset{0.1M}{Cl^-}$$

$pH = -\log[H^+] = -\log 10^{-1} = 1$

(b₁) After addition 15ml of NaOH: The added NaOH solution is reacted with an equivalent amount of HCl solution, i.e.

$(M\times V)_{HCl} = (M\times V)_{NaOH}$

$0.1\times V_{HCl} = 0.1\times 15$

$V_{HCl} = 15ml$ the volume of reacting acid.

unreacting acid = 25 – 15 = 10ml.

But this volume is present in total volume equals = 25 + 15 = 40ml.

$0.1\times 10 = 40\times M_{HCl}$

$$M_{HCl} = \frac{0.1\times 10}{40} = 0.025M$$

$$\underset{0.025M}{HCl} \longrightarrow \underset{0.025M}{H^+} + \underset{0.025M}{Cl^-}$$

$\therefore pH = -\log[H^+] = -\log 0.025 = 1.6$

(b_2) After addi~~tion~~ing 24ml of NaOH:

$0.1\times1 = 49\times M_{HCl}$

$$M_{HCl} = \frac{0.1\times1}{49} = 0.002M$$

$$\underset{0.002M}{HCl} \longrightarrow \underset{0.002M}{H^+} + \underset{0.002M}{Cl^-}$$

$\therefore pH = -\log[H^+] = -\log 0.002 = 2.7$

(c) After addi~~tion~~ing 25ml of NaOH:

$(M\times V)_{NaOH} = (M\times V)_{HCl}$

$25\times0.1 = 25\times0.1$

This is the equivalence point where 25ml of 0.1 M HCl is completely neutralised into NaCl: $HCl + NaOH \longrightarrow NaCl + H_2O$

NaCl is a salt derived from strong acid and strong base. It is completely ionised into Na^+ and Cl^-: $NaCl \longrightarrow Na^+ + Cl^-$

Any ion of this salt is ~~does~~ not subject to hydrolysis and the action of water molecules is to isolate Na^+ ions from Cl^- ions. Water is slightly ionised into H^+ and OH^-.

$H_2O \rightleftharpoons H^+ + OH^-$ or $2H_2O \rightleftharpoons H_3O^+ + OH^-$.

In this solution, $[H^+] = [OH^-] = 10^{-7}$ M . Therefore, pH = pOH = 7

(d) After addi~~tion~~ing 30ml of NaOH:

25ml of 0.1 M NaOH reacts with 25ml of 0.1 M HCl, which means that HCl is completely neutralised.

30 – 25 = 5ml Unreacted Volume ~~unreacting~~ of 0.1 M NaOH

Total volume = 30 + 25 = 55ml.

$$5\times0.1 = 55\times M_{NaOH}$$

$$M_{NaOH} = \frac{5\times0.1}{55} = 0.00091 = 9.1\times10^{-3}M$$

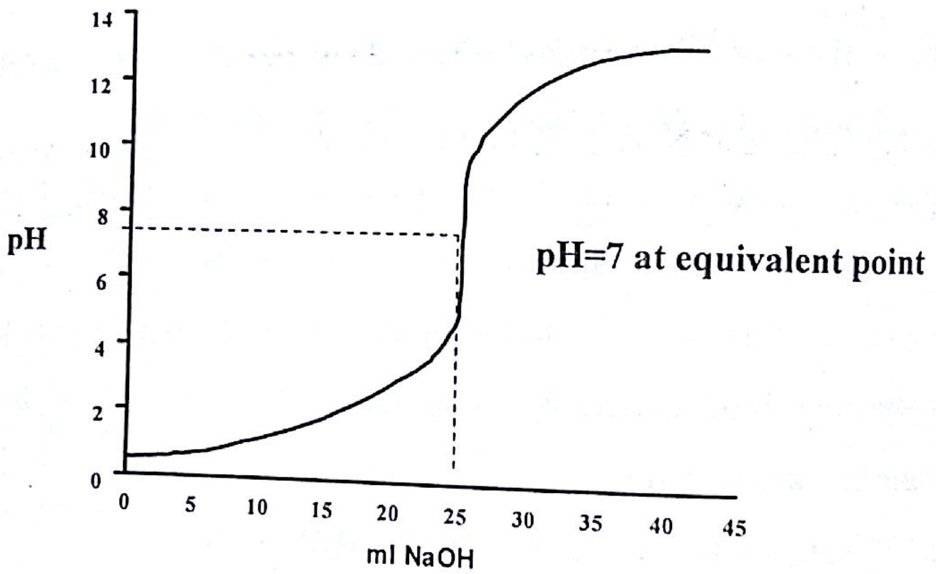
$$\underset{9.1\times10^{-3}M}{NaOH} \longrightarrow \underset{9.1\times10^{-3}M}{Na^{+}} + \underset{9.1\times10^{-3}M}{OH^{-}}$$

$$pOH = -\log[OH^{-}] = -\log 9.1\times10^{-3} = 2.04 \therefore pH = 14 - 2.04 = 11.96 \approx 12$$

Therefore, we get the following titration data:

ml NaOH	0	15	24	25	30
pH	1	1.6	2.6	7	12

A plot of pH values against ml of NaOH, ~~we get~~ gives the following curve which shows equivalence point at pH = 7 and the curve has S-shaped.



Fig(7-1): A titration curve of strong acid with strong base.

7.2 Titration of strong base with strong acid.

Example: 25ml of 0.1 M NaOH solution is titrated with 0.1 M HCl solution. Calculate the pH of this titration at the following stages:

(a) before the addition of 0.1 M HCl.

(b) after the addition of HCl till before the equivalence point.

(c) at equivalence point. (d) after equivalence point.

The solution:

the

(a) pH value before addition of HCl:

$$NaOH \longrightarrow Na^+ + OH^-$$

0.1M 0.1M 0.1M

$pOH = -\log[OH^-] = -\log 10^{-1} = 1$

$\therefore pH = 14 - 1 = 13$

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(b_1) After addition 15ml of HCl:

$(M\times V)_{NaOH} = (M\times V)_{HCl}$

$0.1\times V_{NaOH} = 0.1\times 15$

$\therefore V_{NaOH} = \frac{0.1\times 15}{0.1} = 15ml$ reacting volume of NaOH.

$\therefore$ Unreacting volume of NaOH = 25 – 15 = 10ml.

$\therefore$ Total volume = 25 + 15 = 40ml.

$10\times 0.1 = 40\times M_{NaOH}$

$M_{NaOH} = \frac{0.1\times 10}{40} = 0.025M$

$$NaOH \longrightarrow Na^+ + OH^-$$

0.025M 0.025M 0.025M

$-\log[OH^-]$

$pOH = \underline{-\log[H^+]} = -\log 0.025 = 1.6$

$\therefore pH = 14 - 1.6 = 12.4$

ing

(b_2) After addition 24ml of HCl solution:

$(M\times V)_{NaOH} = (M\times V)_{HCl}$

$0.1\times V_{NaOH} = 0.1\times 24$

$\therefore V_{NaOH} = \frac{0.1\times 24}{0.1} = 24ml$ reacting volume of NaOH.

Unreacting volume = 25 – 24 = 1ml. Total volume = 25 + 24 = 49 ml.

$$1\times0.1 = 49\times M_{NaOH}$$

$$M_{NaOH} = \frac{0.1\times1}{49} = 0.002M$$

$$\underset{0.002M}{NaOH} \longrightarrow \underset{0.002M}{Na^+} + \underset{0.002M}{OH^-}$$

$$pOH = -\log[OH^-] = -\log 0.002 = 2.7 \therefore pH = 14 - 2.7 = 11.3$$

(c) After addition 25ml of HCl:

$$(M\times V)_{NaOH} = (M\times V)_{HCl}$$

$$25\times0.1 = 25\times0.1$$

This is the equivalence point where 25ml of 0.1 M NaOH is completely altered into NaCl:

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

NaCl is a salt derived from strong acid and strong base. It is completely dissociated into Na^+ and Cl^- : $NaCl \longrightarrow Na^+ + Cl^-$

Any ion of this salt does not react with water (no hydrolysis) and the significance of water molecules is to isolate Na^+ ions from Cl^- ions. H_2O is slightly ionised into H^+ and OH^-.

$$H_2O \rightleftharpoons H^+ + OH^- \text{ or } 2H_2O \rightleftharpoons H_3O^+ + OH^-.$$

In this solution, $[H^+] = [OH^-] = 10^{-7}$ M. Therefore, $pH = pOH = 7$

(d) After addition 30ml of HCl:

25ml of 0.1 M HCl reacts with 25ml of 0.1 M NaOH, which means that NaOH is completely altered into NaCl.

$30 - 25 = 5$ml unreact~~ing~~ed volume of 0.1 M HCl $\longrightarrow$ Total volume $= 30 + 25 = 55$ml.

$$5\times0.1 = 55\times M_{HCl}$$

$$M_{HCl} = \frac{5\times0.1}{55} = 0.00091 = 9.1\times10^{-3}M$$

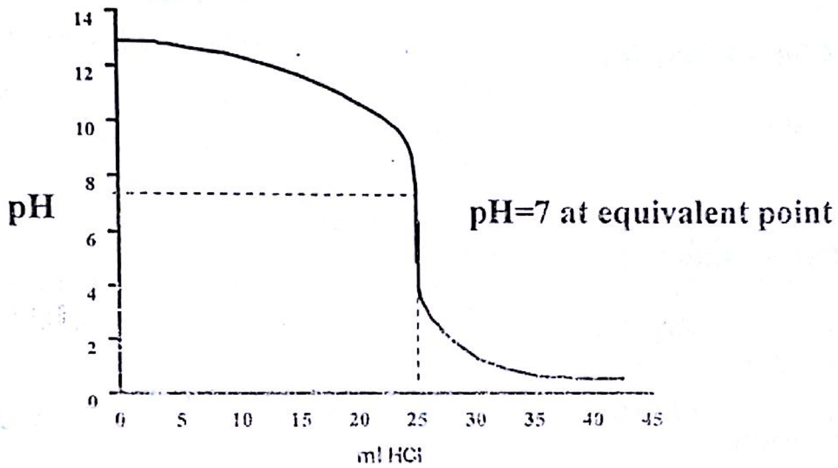
$$HCl \longrightarrow H^+ + Cl^-$$

$9.1\times10^{-3}M$ $9.1\times10^{-3}M$ $9.1\times10^{-3}M$ $\rightarrow$ $pH = -\log[H^+] = -\log 9.1\times10^{-3} = 2.04$

Therefore, we get the following titration data:

ml HCl	0	15	24	25	30
pH	13	12.4	11.3	7	2.04

A plot of pH values against ml of HCl, gives we get the following curve which shows equivalence point at pH = 7 and the curve is an inverse S-shaped.



Fig(7-2): A titration curve of strong base with strong acid.

7.3 Titration of weak acid with strong base.

Example: 25ml of 0.1 M CH_3COOH solution is titrated with 0.1 M NaOH solution. Calculate the pH of this titration at the following stages:

(a) before the addition of NaOH .

(b) after the addition of NaOH till before the equivalence point.

(c) at equivalence point. (d) after equivalence point.

The solution:

(a) pH value before the addition of NaOH:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \qquad K_a = 1.85\times10^{-5} \text{ at } 25^\circ C$$

CH_3COOH is a weak mono protic acid which dissociates partially into CH_3COO^- and H^+ ions which reaches an equilibrium steady state.

Therefore, the following relation is used to calculate the pH at this stage:

$$pH = 1/2pK_a - 1/2\log C_a \qquad pK_a = -\log K_a$$

$$= -\log 1.85\times10^{-5}$$

$$= -(-5+.026)$$

$$= -(-4.74) \longrightarrow = 4.74$$

$$= 1/2\times4.74 - 1/2\log 0.1$$

$$= 2.37 + 0.5 = 2.87$$

(b₁) After addition 15ml of NaOH:

$$(M\times V)_{CH_3COOH} = (M\times V)_{NaOH}$$

$$0.1\times V_{CH_3COOH} = 0.1\times15$$

V_{CH_3COOH} = 15ml reacting volume of acetic acid which is changed into its salt CH3COONa .

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

unreacting volume of $CH_3COOH = 25 - 15 = 10ml.$

Therefore, we have a buffer solution of CH_3COOH and its salt CH_3COONa.

Total volume = 15 + 25 = 40ml.

$$15\times0.1 = 40\times M_{CH_3COONa} \longrightarrow M_{CH_3COONa} = \frac{15\times0.1}{40} = 0.0375M$$

$$10\times0.1 = 40\times M_{CH_3COOH} \longrightarrow M_{CH_3COOH} = \frac{10\times0.1}{40} = 0.025M$$

$$pH = pK_a + \log\frac{[salt]}{[Acid]}$$

$$= 4.74 + \log\frac{0.0375}{0.025} = 4.74 + 0.1761 = 4.9161$$

(b₂) After addition 24ml of NaOH:

$$(0.1\times24)_{NaOH} = (0.1\times V)_{CH_3COOH}$$

V_{CH_3COOH} = 24ml reacting volume of acetic acid which is changed into its salt CH_3COONa .

unreacting volume of CH_3COOH = 25 −24= 1ml.

Total volume = 25 + 24 = 49ml.

$$24\times0.1 = 49\times M_{CH_3COONa} \longrightarrow M_{CH_3COONa} = \frac{24\times0.1}{49} = 0.049M$$

$$1\times0.1 = 49\times M_{CH_3COOH} \longrightarrow M_{CH_3COOH} = \frac{1\times0.1}{49} = 0.002M$$

Thus, we have buffer solution of CH_3COOH and its salt CH_3COONa .

$$pH = pK_a + \log\frac{[salt]}{[Acid]}$$

$$= 4.74 + \log\frac{0.049}{0.002} = 4.74 + 1.39 = 6.13$$

(c) After addition 25ml of 0.1 M NaOH:

$$(M\times V)_{CH_3COOH} = (M\times V)_{NaOH}$$

$$25\times0.1 = 25\times0.1$$

This is the equivalence point where all CH_3COOH is altered into its salt CH_3COONa. This is a salt which is derived from weak acid and strong base. The following relation is used to calculate the pH of this salt solution.

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log C_s$$

But total volume = 25 + 25 = 50ml

$$25\times0.1 = 50\times M_{CH_3COONa} \longrightarrow M_{CH_3COONa} = \frac{25\times0.1}{50} = 0.05M$$

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log C_s$$

$$= \frac{1}{2}\times 14 + \frac{1}{2}\times 4.74 + \frac{1}{2}\log 0.05 = 7 + 2.37 + 0.65 = 8.72$$

(d) After addi~~tion~~ing 30ml of 0.1 M NaOH:

At equivalence point, 25ml of CH_3COOH reacts with 25ml of NaOH to form CH_3COONa .

30 – 25 = 5ml of NaOH is added after equivalence point

Total volume = 30 + 25 = 55ml

$$5\times0.1 = 55\times M_{NaOH} \longrightarrow M_{NaOH} = \frac{5\times0.1}{55} = 9.1\times10^{-3}M$$

OH^- is obtained from the hydrolysis of CH_3COONa, but this concentration is very little compared with add~~ed~~ing 5ml of 0.1 M NaOH after equivalence point.

$$\underset{9.1\times10^{-3}M}{NaOH} \longrightarrow \underset{9.1\times10^{-3}M}{Na^+} + \underset{9.1\times10^{-3}M}{OH^-}$$

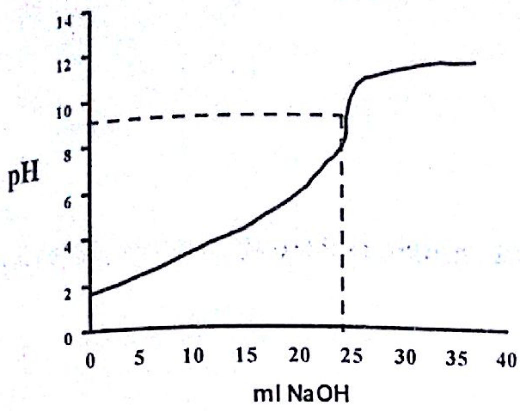
$pOH = -\log[OH^-] = -\log 9.1\times10^{-3} = 2.04 \therefore pH = 14 - 2.04 = 11.96 \approx 12$

Therefore, we get the following titration data:

ml NaOH	0	15	24	25	30
pH	2.87	4.92	6.13	8.72	12

A plot of pH values versus ml of NaOH, will give a titration curve showing equivalence point at pH = 8.72 which means that the equivalence point occurs at basic medium since sodium acetate is subject~~s~~ed to hydrolysis into CH_3COOH (weak acid) and strong base (NaOH).

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$



Equivalence point at pH = 8.72. Therefore, an indicator ~~which its~~ whose colour is changed in basic medium is used such as phenolphthalein.

Fig(7-3): **A titration curve of weak acid with strong base.**

7.4 Titration of weak base with strong acid.

Example: 25ml of ammonia (0.1 M) solution is titrated with 0.1 M HCl solution. Calculate the pH of this titration at the following stages:

(a) before the addition of 0.1 M HCl.

(b) after the addition of HCl till before the equivalence point.

(c) at equivalence point. (d) after equivalence point.

$K_{b\,NH_4OH} = 1.85\times10^{-5}$ at $25^{\circ}C$

The solution:

(a) before the addition of HCl:

$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$

Ammonia solution is weak mono hydroxyl group base.

$\therefore pOH = \frac{1}{2}pK_b - \frac{1}{2}\log C_b$

$pOH = \frac{1}{2}\times 4.74 - \frac{1}{2}\log 0.1$

$= 2.37 + 0.5 = 2.87$

$\therefore pH = 14 - 2.87 = 11.13$

(b_1) pH after addition 15ml of HCl:

$$(M\times V)_{HCl} = (M\times V)_{NH_3}$$

$$15\times0.1_{HCl} = 0.1\times V_{NH_3}$$

V_{NH_3} = 15ml reacting volume of ammonia which is changed into its salt NH_4Cl

$$NH_4OH + HCl \rightleftharpoons NH_4Cl + H_2O$$

unreacting volume of $NH_3 = 25 - 15 = 10ml$.

Therefore, we have buffer solution of the weak base and its salt NH_4Cl.

Total volume = 15 + 25 = 40ml.

$$15\times0.1 = 40\times M_{NH_4Cl} \longrightarrow M_{NH_4Cl} = \frac{15\times0.1}{40} = 0.0375M$$

10

$$15\times0.1 = 40\times M_{NH_4OH} \longrightarrow M_{NH_4OH} = \frac{10\times0.1}{40} = 0.025M$$

$$pOH = pK_b + \log\frac{[salt]}{[Base]}$$

$$= 4.74 + \log\frac{0.0375}{0.025} = 4.74 + 0.67 = 5.41$$

$$pH = 14 - 5.41 = 8.59$$

ل **(b_2) pH after addition 24ml of HCl:**

$$(24\times0.1)_{HCl} = (0.1\times V)_{NH_3}$$

V_{NH_3} = 24ml the reacting volume of ammonia .

unreacting volume of $NH_3 = 25 - 24 = 1ml$.

Therefore, we have 1ml of NH_4OH and 24ml of its salt NH_4Cl

$$NH_4OH + HCl \rightleftharpoons NH_4Cl + H_2O$$

Therefore, we have buffer solution of the weak base and its salt NH_4Cl.

Total volume = 24 + 25 = 49ml.

$$M_{NH_4Cl} = \frac{24\times0.1}{49} = 0.049M$$

$$M_{NH_4OH} = \frac{1\times0.1}{49} = 0.002M$$

$$pOH = pK_b + \log\frac{[salt]}{[Base]}$$

$$= 4.74 + \log\frac{0.049}{0.002} = 4.74 + 1.39 = 6.13 \quad \therefore pH = 14 - 6.13 = 7.87$$

(c) After addition 25ml of 0.1 M HCl:

$$(M\times V)_{HCl} = (M\times V)_{NH_3}$$

$$25\times0.1 = 25\times0.1$$

Therefore, all ammonia reacts completely with HCl to form the salt NH_4Cl which is derived from weak base and strong acid. This salt is subject~~s~~ed to hydrolysis to form weak base and strong acid. The solution then is anticipated to be at equivalence point. $NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$

Total volume = 25 + 25 = 50ml

$$25\times0.1 = 50\times M_{NH_4Cl} \longrightarrow M_{NH_4Cl} = \frac{25\times0.1}{50} = 0.05M$$

$$pH = \frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\log C_s$$

$$= \frac{1}{2}\times14 - \frac{1}{2}\times4.74 - \frac{1}{2}\log 0.05 = 7 - 2.37 \overset{+}{-} 0.65 = 5.28$$

(d) After addi~~tion~~ing 30ml of 0.1 M HCl:

25ml of HCl reacts with 25ml of NH_4OH to form NH_4Cl. ~~Unreacting~~ The unreacted Volume of 0.1 M HCl: = 30 – 25 = 5ml Total volume = 30 + 25 = 55ml

$$5\times0.1 = 55\times M_{HCl} \longrightarrow M_{HCl} = \frac{5\times0.1}{55} = 9.1\times10^{-3}M$$

$$\underset{9.1\times10^{-3}M}{HCl} \longrightarrow \underset{9.1\times10^{-3}M}{H^+} + \underset{9.1\times10^{-3}M}{Cl^-}$$

$pH = -\log[H^+] = -\log 9.1\times10^{-3} = 2.04$

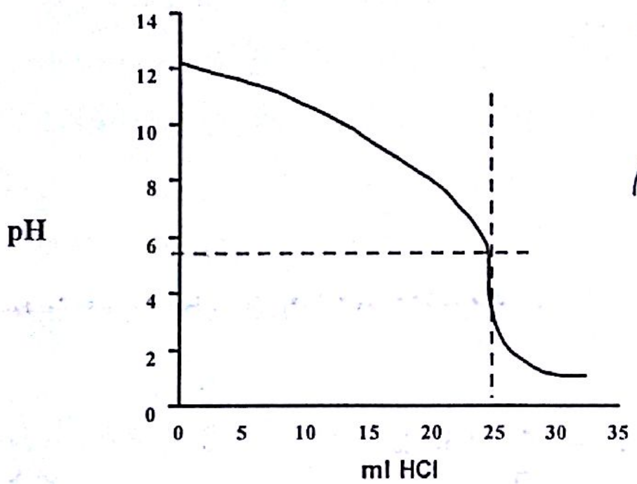
Therefore, we have collected the following titration data:

ml HCl	0	15	24	25	30
pH	11.13	8.95	7.87	5.28	2.04

It is worthing to note here that equivalence point occurs at pH = 5.28 which is acidic medium as a result of hydrolysis of NH_4Cl

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

Which gives weak base and strong acid. A plot of pH values against ml of HCl shows a titration curve of equivalence point at pH = 5.28 (acidic medium).



Equivalence point at pH =5.28. Therefore, a~~n~~ indicator chosen whose ~~which its~~ colour is changed in acidic medium is used such as methyl red or methyl orange.

Fig(7-4): A titration curve of weak base with strong acid.

7.5 Titration of weak acid with weak base.

Example: 25ml of 0.1 M CH_3COOH solution is titrated with 0.1 M NH_4OH solution. Calculate the pH of this titration at the following stages:

(a) before the addition of ammonia solution.

(b) after addition 15ml of 0.1 M ammonia solution.

(c) at equivalence point. (d) after addition 30ml of 0.1 M ammonia solution.

$K_{a\,CH_3COOH} = 1.85\times10^{-5}$ $\quad$ $K_{b\,NH_4OH} = 1.85\times10^{-5}$

$pK_a = 4.74$ $\quad$ $pK_b = 4.74$

The solution:

(a) before the addition of ammonia solution.

(a) pH value before the addition of 0.1 M NH_4OH:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$pH = \frac{1}{2}pK_a - \frac{1}{2}\log C_a$$

$$= \frac{1}{2}\times 4.74 - \frac{1}{2}\log 0.1 = 2.37 + \overset{0.5}{\underline{05}} = 2.87$$

(b_1) after addition 15ml of 0.1 M NH_4OH.

$(M\times V)_{NH_4OH} = (M\times V)_{CH_3COOH}$

$15\times0.1_{NH_4OH} = 0.1\times V_{CH_3COOH}$

$V_{CH3COOH}$ = 15ml reacting volume of CH_3COOH which is changed into CH_3COONH_4.

unreacting volume of CH_3COOH = 25 – 15 = 10ml.

Therefore, we have buffer solution of CH_3COOH and its salt CH_3COONH_4.

Total volume = 15 + 25 = 40ml.

$15\times0.1 = 40\times M_{CH_3COONH_4} \longrightarrow M_{CH_3COONH_4} = \frac{15\times0.1}{40} = 0.0375M$

$10\times0.1 = 40\times M_{CH_3COOH} \longrightarrow M_{CH_3COOH} = \frac{10\times0.1}{40} = 0.025M$

$$pH = pK_a + \log\frac{[salt]}{[Acid]}$$

$$= 4.74 + \log\frac{0.0375}{0.025} = 4.74 + 0.18 = 4.92$$

(b_2) after addition 24ml of 0.1 M NH_4OH.

$$(M\times V)_{NH_4OH} = (M\times V)_{CH_3COOH}$$

$$24\times 0.1_{NH_4OH} = 0.1\times V_{CH_3COOH}$$

$V_{CH3COOH}$ = 24ml reacting volume of CH_3COOH which is altered into CH_3COONH_4.

unreacting volume of CH_3COOH = 25 – 24 = 1ml.

Total volume = 24 + 25 = 49ml.

$$24\times 0.1 = 49\times M_{CH_3COONH_4} \longrightarrow M_{CH_3COONH_4} = \frac{24\times 0.1}{49} = 0.049M$$

$$1\times 0.1 = 49\times M_{CH_3COOH} \longrightarrow M_{CH_3COOH} = \frac{1\times 0.1}{49} = 0.002M$$

$$pH = pK_a + \log\frac{[salt]}{[Acid]} = 4.74 + \log\frac{0.049}{0.002} = 4.74 + 1.39 = 6.13$$

(c) pH at equivalence point (after addition 25ml of 0.1 M NH_4OH):

$$(M\times V)_{CH_3COOH} = (M\times V)_{NH_4OH}$$

$$25\times 0.1 = 25\times 0.1$$

Therefore, all CH_3COOH is changed into its salt CH_3COONH_4.

Total volume = 25 + 25 = 50ml

$$25\times 0.1 = 50\times M_{CH_3COONH_4} \longrightarrow M_{CH_3COONH_4} = \frac{25\times 0.1}{50} = 0.05M$$

CH_3COONH_4 is a salt derived from weak acid and weak base. The following relation is used to calculate its pH.

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b = \frac{1}{2}\times 14 + \frac{1}{2}\times 4.74 - \frac{1}{2}\times 4.74 = 7$$

(d) After addition 30ml of 0.1 M NH_4OH:

The reacting volume of NH_4OH = 25ml which reacts with 25ml of CH_3COOH to form CH_3COONH_4.

Unreacting volume of $NH_4OH = 30 - 25 = 5$ml.

Thus, we have another buffer solution which is NH_4OH and its salt.

Total volume = 30 + 25 = 55ml

$$25\times0.1 = 55\times M_{CH_3COONH_4} \longrightarrow M_{CH_3COONH_4} = \frac{25\times0.1}{55} = 0.045M$$

$$5\times0.1 = 55\times M_{NH_4OH} \longrightarrow M_{NH_4OH} = \frac{5\times0.1}{55} = 9\times10^{-3}M$$

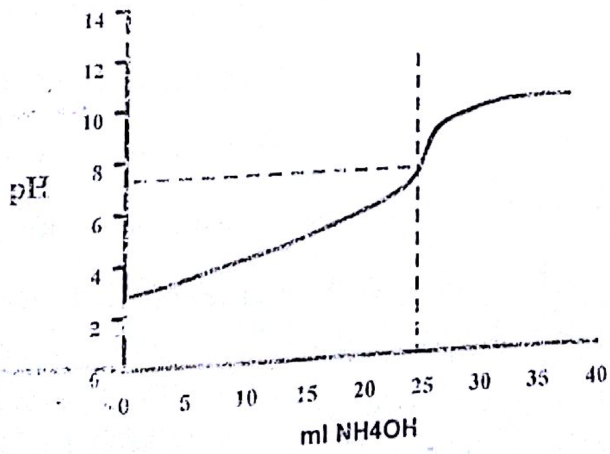
$$pOH = pK_b + \log\frac{[salt]}{[Base]} = 4.74 + \log\frac{0.045}{0.009} = 4.74 + 0.7 = 5.44$$

$\therefore$ pH = 14 – 5.44 = 8.56

Therefore, we get the following titration data:

ml NH_4OH	0	15	24	25	30
pH	2.87	4.92	6.13	7.0	8.56

A plot of pH values versus ml of NH_4OH, will give a titration curve showing equivalence point at pH = 7.0



Fig(7-5): A titration curve of weak acid with weak base.

It is clear from the above titration data and titration curve that:

1- pH at equivalence point equals 7.0 . This is a special case where $K_a = K_b$. But if $K_a > K_b$, the pH of solution is less than 7.0 . When $K_a < K_b$, the pH of solution is more than 7.0 , why ?

2- The change in pH around equivalence point is not sharp and is not clear. For example, the change in pH is less than one unit, when the volume increases from 24 to 25ml. Therefore, it is difficult to find a chemical indicator to identify the equivalence point. As a conclusion, another methods are used for this titration such as potentiometric titration.

7.6 Problems

1- Calculate the pH of a solution that contains 2.72 g of KH_2PO_4 and 3.48g of K_2HPO_4 in 100ml. pK_2 for phosphoric acid = 7.21 .

2- Calculate the weight of NH_4Cl that should be added to 100ml of 1 M NH_4OH to get pH = 9.3 . Consider no change in volume.

3- 50ml of 0.1 M HCl is titrated with 0.2 M NaOH. Calculate the pH in the following stages:

a) before the addition of NaOH.

b) after the addition of 15ml of the base.

c) after the addition of 25ml of NaOH.

d) after addition 40ml of the base.

e) plot the titration data to get the titration curve and locate the equivalence point.

4- 50ml of 0.1 M NaOH is titrated with 0.2 M HCl. Calculate the pH at the following stages:

a) before the addition of acid.

b) after addition 15ml of 0.1 M HCl.

c) after addition 25ml of the acid.

d) after addition 40ml of the acid.

e) plot the titration curve and locate the equivalence point.

5- 30ml of ammonia (0.1 M) is titrated with 0.1 M HCl. Calculate the pH at the following stages:

a) before the addition of HCl.

b) after addition 20ml of the acid.

c) after addition 30ml of the acid.

d) after addition 40ml of the acid.

e) plot the titration curve and locate the equivalence point.

6- Calculate the pH of titrat~~ion~~ing 25ml of 0.1 M acid with 0.1 M base after addit~~ion~~ing the following volumes of the corresponding base. 5ml, 12.5ml, 17.5ml and 30ml:

a) HCl with NaOH .

b) Benzoic acid with NaOH .

c) HCl with NH_4OH.

7- 20ml of acetic acid (0.1 M) is titrated with 0.1 M NaOH. Calculate the pH data at the following stages:

a) before the addition of base.

b) after addit~~ion~~ing 10ml of NaOH.

c) after addit~~ion~~ing 20ml of base.

d) after addit~~ion~~ing 25ml of the base.

e) plot the titration data to get the titration curve and locate the equivalence point.

f) Mention the indicator which is convenient in this titration.

8- 50ml of 0.1 M formic is titrated with 0.1 M KOH. Calculate the pH after the addition of the following volumes of KOH: (a) 20ml . (b) 40ml . (c) 50ml . (d) 60ml .

Table (6-2): Some acid base indicators.

Indicator	Its colour in acid medium	Its colour in basic medium	Extent of pH change
Cresol red	red	yellow	0.2 – 1.8
Cresol red	yellow	red	7.2 – 8.8
Methyl orange	red	yellow	2.9 – 4.0
Methyl red	red	yellow	4.2 – 6.2
Chlorophenol red	yellow	red	4.8 – 6.4
Bromothymol blue	yellow	blue	6.0 – 7.6
Phenol red	yellow	red	6.8 – 8.4
Phenolphthalein	colourless	red	8.3 – 10.0
Thymolphthalein	colourless	blue	9.4 – 10.5
Alizarin yellow	yellow	purple	10.1 – 12.1