Titration of Acid V/s Bases.

⇒ Selection of Indicators

- Near the equivalence of AB titration, the pH value of the soln changes steeply, and the pH range of this steep change depends on the nature of acid-base being titrated.
- The center of the steep change lies at pH 7 only when a SA and SB is titrated against each other.
- for any other titrn involving either WA or WB, the salt form undergoes hydrolysis
  ∴ it gives a pH value either >7 or <7.
- Selected indicator should be such that, it offers the colour change near vicinity of pH of the soln at the equivalence point.

⇒ ∴ the section of indicator must be :-

(i) the steep section of the titrn curve, at the equivalence point must enclose an interval of pH values at least as large as pH transition of an indicator.

(ii) The pH transition range of an indicator must coincide with the steep of the titrn curve.

(1) SA - SB

The pH at the equivalence point is 7 and slighly before the equ. pt. and after the equ. pt. the pH ranges b/w 3 to 11.
∴ that indicator should be used whose pH-value is within this range.

⇒ Phenolpthalein is the common indicator used whose :-

(i) pH range is within this
(iii) and its colour change is from colourless to pink colour, which can be usually visualize.

Step 1 Take 50 mL of 0.1 N HCl in conical flask and 0.1N NaOH in burette.

⇒ Before titration

When no base is added, there is only strong acid present in the conical flask.

∵ it is highly concentrated acid, so dissc^n of water is negligible.

∴ pH of sol^n is = $-\log [H_3O^+]$ coming from HCl

∴ $pH = -\log [0.1] \Rightarrow pH = 1$.

⇒ contribu^n of $[H_3O^+]$ coming from dissc^n of water is negligible.

Step 2 (A) Now, let 10 mL of NaOH is added to conical flask containing 50 mL of acid.

$$N_1V_1 = N_2V_2$$
$$0.1 \times 40 = N_2 \times 60$$
$$N_2 = 0.06$$

∴ pH of sol^n = $-\log [N_2] = -\log [6 \times 10^{-2}] = 1.23$

(B) 20 mL of NaOH is added

$$N_1V_1 = N_2V_2$$
$$0.1 \times 30 = N_2 \times 70$$
$$N_2 = 0.042$$
$$pH = -\log [42 \times 10^{-3}] = 1.38$$

(C) 30 mL of NaOH is added

$$N_1V_1 = N_2V_2$$
$$0.1 \times 20 = N_2 \times 80$$
$$N_2 = 0.025$$
$$pH = -\log [25 \times 10^{-3}] = 1.60$$

(D) 40 ml of NaOH is added

$N_1V_1 = N_2V_2$

$0.1 \times 10 = N_2 \times 90$

$N_2 = 0.0112$

$pH = -\log [0.0112] = 1.95$

Step 3 When 50 ml of NaOH is added, complete neutralization of acid takes place, and in the soln there is only NaCl and H_2O which has pH 7.

Step 4 After equivalence point.

when 10 ml of NaOH is added

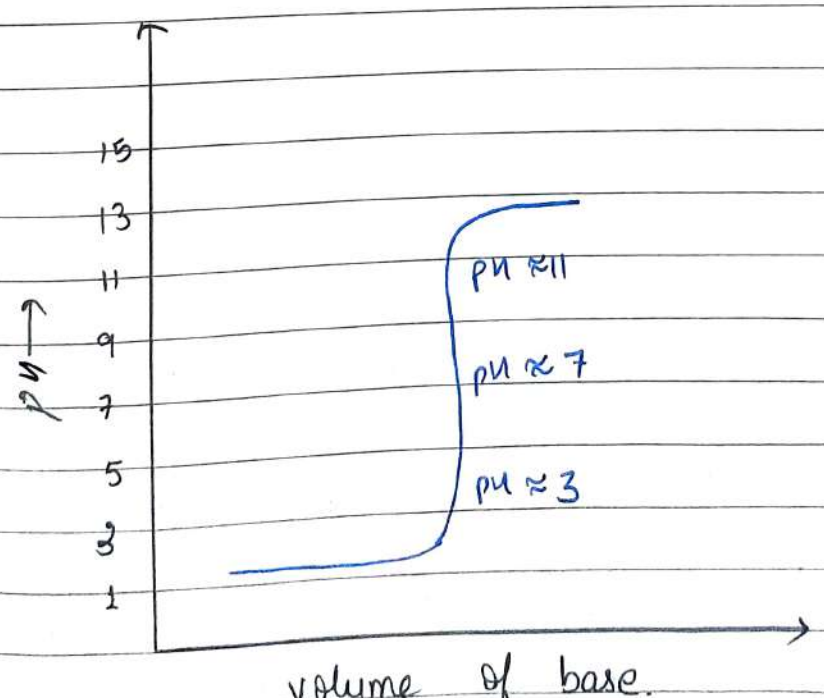
$N_1V_1 = N_2V_2$

$0.1 \times 10 = N_2 \times 110$

$N_2 = 0.009$

$p[OH] = -\log [9 \times 10^{-3}] = 2.05$

$pH = 11.95.$



(2)

WA - S.B

In burette we take NaOH and acetic acid in conical flask whose diss^n const $K_a = 1.75 \times 10^{-5}$ M. Normality of NaOH is 0.1 N and that of CH_3COOH is 0.1 N.

Step 1 before titration. (done on 10/8/19)

∵ pure acetic acid is present in ~~conif~~ conical flask and it is highly concentrated form.

∴ dissociation of monoprotic acid is given as.

$$[H_3O^+] = \sqrt{K_a [CH_3COOH]_0}$$

$$= \sqrt{1.75 \times 10^{-5}\ M \times 10^{-1}\ M}$$

$$= \sqrt{1.75 \times 10^{-6} M^2}$$

$$[H_3O^+] = 1.32 \times 10^{-3} M$$

$$pH = -\log [H_3O^+] = -\log [1.32 \times 10^{-3}] = 2.88$$

Step 2 Let us assume we have taken 25 mL of CH_3COOH in conical flask of 0.1 N and let us add 5 mL of NaOH from the burette.

→ Due to add^n of NaOH, CH_3COOH is forced to dissociate to give H^+ to neutralize the OH^- ions, due to this conc^n of CH_3COO^- is ↑sed.

→ These CH_3COO^- immediately combine with Na^+ to form CH_3COONa.

→ Now, in con. flask, ~~where~~ there is 5 mL of CH_3COONa and 20 mL of CH_3COOH So, it is a mixture of W.A and salt of its conj. base

ie it is a buffer soln.

Hence by using Henderson Hasselbalch eqn

ie. $pH = pKa + \log \frac{[salt]}{[Acid]}$

(A) conc^n of salt = $\frac{\text{No. of moles}}{\text{Litre}} = \frac{5\text{ ml of } 0.1N}{1000}$

$= 0.0005$ M

conc^n of acid = $\frac{\text{No. of moles}}{\text{Litre}} = \frac{20\text{ ml of } 0.1N}{1000} = 0.002M$

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

$= -\log (1.75 \times 10^{-5}) + \log \frac{[0.0005]}{[0.002]}$

$= 5 - 0.24 + \log [0.25] = 5 - 0.24 - 0.60$

$= 4.145$

(B) when 10 ml of NaOH is added it will form 10 ml of CH_3COONa and 15 ml of acetic acid ~~with~~ will remain in the conical flask.

$\therefore$ conc^n of salt = $\frac{0.1 \times 10}{1000} = 10^{-3}$ M

conc^n of acid = $\frac{0.1 \times 15}{1000} = 1.5 \times 10^{-3}$ M

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

$= -\log (1.75 \times 10^{-5}) + \log \frac{[10^{-3}]}{[1.5 \times 10^{-3}]}$

$= 5 - 0.24 + \log [0.667]$

$= 5 - 0.24 - 0.175$

$= 4.585$

(c) when 20 ml of NaOH is added it will form 20 ml of CH_3COONa and 5 ml of CH_3COOH remains in the con. flask.

$\therefore$ conc^n of salt $= \frac{0.1 \times 20}{1000} = 2 \times 10^{-3} M$

conc^n of acid $= \frac{0.1 \times 5}{1000} = 0.5 \times 10^{-3} M$

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

$= -\log (1.75 \times 10^{-5}) + \log \frac{[2 \times 10^{-3}]}{[0.5 \times 10^{-3}]}$

$= 5 - 0.24 + \log 4$

$= 5 - 0.24 + 0.603$

$= 5.36$

Step 3 at Equivalence point.

When 25 ml of NaOH is added to the conical flask there is CH_3COONa salt and water.

This salt undergoes hydrolysis.

$pH = \frac{1}{2} pKa + \frac{1}{2} pKw + \frac{1}{2} \log C$ (done on 17/8/19)

$\therefore pH = \frac{1}{2} (-\log(1.75 \times 10^{-5}) M - \frac{1}{2} \log(10^{-14}) \frac{M^2}{M} + \frac{1}{2} \log (0.1)$

$= 2.3725 + 7 - 0.5$

$pH = 8.8725$

Step 4 After equivalence point.

when we add 1 drop of NaOH after equ. pt, the colour of the sol^n turns pink, because whole the CH_3COOH is neutralized in the previous step and ∴ on add^n of single drop of NaOH, pheonolphthalein decomposes to react with NaOH drop and colour becomes pink.

Now, in the con. flask, there is 50 ml of salt and excess of NaOH.

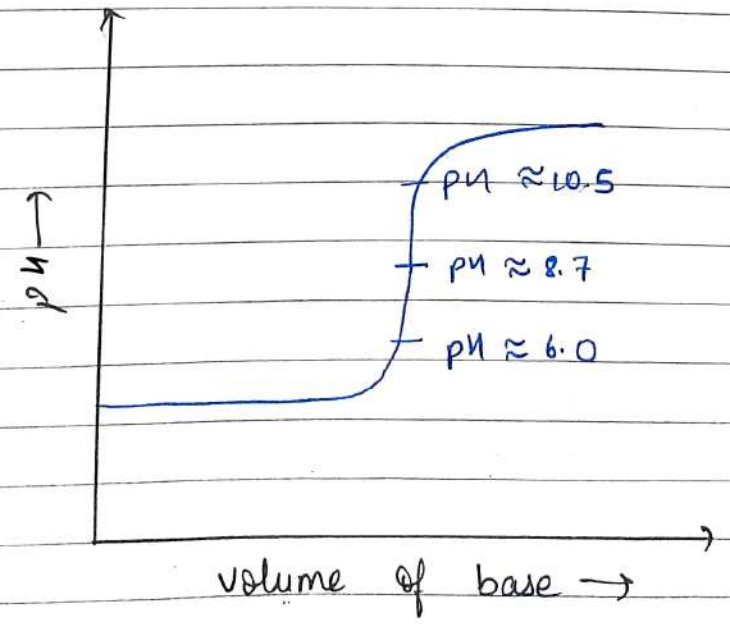
Let us suppose 3 ml of NaOH is added.

⇒ conc^n of OH^- is $= \frac{3}{55} = 0.0566$

$K_w = [OH^-][H^+]$

$[H^+] = K_w / [OH^-] = [17.66 \times 10^{-14}]$

$pH = 14 - \log[17.66] = 14 - 1.24 = 12.76.$



19/8/19

SA-WB

SA = HCl (burette)
WB = NH_4OH (con. flask)

Let us take 0.1 N NH_4OH and 0.1 N HCl, NH_4OH in Cf and HCl in burette, $K_b = 1.75 \times 10^{-5} M^2$

Step 1 Before Titration

25 ml of NH_4OH is taken in con. flask. ∵ it is a WB, so ⇌ exist b/w dissociated and undissociated species

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

this eqn is done on 19/8/19

$$[OH^-] = \sqrt{K_b \times [BOH]_i} = \sqrt{1.75 \times 10^{-5} \times 10^{-1} M^2} = 1.36 \times 10^{-3} M$$

$$\log [OH^-] = 3 - \log(1.36)$$
$$= 3 - 0.133$$
$$p(OH) = 2.867$$
$$pH = 14 - 2.867 = 11.133$$

Step 2 (A) Let 5 mL of ~~acetic~~ acid is added from burette into the con. flask. On add^n of HCl, 5 mL of it react with 5 mL NH_4OH to give NH_4Cl.

∵ in the C.f it is a mixture of W.B and salt of its conj. acid that is NH_4Cl, it is a buffer solution. Hence Henderson Hasenbalch equation is used

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

$$pOH = pKb + \log \frac{[salt]}{[base]}$$

$$[NH_4OH] = \frac{20}{1000} \times 0.1 = 0.002\ M$$

$$[NH_4Cl] = \frac{5}{1000} \times 0.1 = 0.0005\ M$$

$$pOH = -\log (1.75 \times 10^{-5}) + \log \frac{[0.002]}{[0.0005]} \frac{[5 \times 10^{-4}]}{[2 \times 10^{-3}]}$$

$$pOH = 4.745 - 0.602$$

$$pOH = 4.143$$

$$pH = 9.857$$

(B) Now, 15 mL of acid is added, so 15 mL of acid will react with 15 mL NH_4OH to given NH_4Cl.

$$[NH_4OH] = \frac{10}{1000} \times 0.1 = 0.001\ M$$

$$[NH_4Cl] = \frac{15}{1000} \times 0.1 = 0.0015\ M$$

$$pOH = -\log (1.75 \times 10^{-5}) + \log \frac{[0.0015]}{[0.001]}$$

$$pOH = 4.745 + 0.176 = 4.921$$

$$pH = 9.079$$

(C) When, 20 mL of acid is added

$$[NH_4OH] = \frac{5}{1000} \times 0.1 = 0.0005 \; ; [NH_4Cl] = \frac{20}{1000} \times 0.1 = 0.002$$

$$pOH = -\log (1.75 \times 10^{-5}) + \log \frac{[2 \times 10^{-3}]}{[5 \times 10^{-4}]}$$

$$pOH = 4.745 + \log 4 = 5.347$$

$$pH = 8.653$$

Step 3 At Equivalence Point

When 25 mL of HCl is added from the burette, whole of NH_4OH is used and there is only NH_4Cl salt and water, and the salt undergoes Hydrolysis. So, eq^n at equiv. point is.

$$pH = \frac{1}{2} pKw - \frac{1}{2} pKb - \frac{1}{2} \log C$$

$$pH = \frac{1}{2}(-\log 10^{-14}) - \frac{1}{2}(-\log(1.75 \times 10^{-5}) - \frac{1}{2} \log(10^{-1})$$

$$= 7 + 2.3725 + 0.5$$

$$pH = 9.87$$

Step 4 After equivalence Point.

Let 5 mL of HCl is added to con. flask containing 50 mL of salt and water. So the sol^n is acidic. Now, the sol^n contains 55 mL of volume.

$$N_1 V_1 = N_2 V_2$$

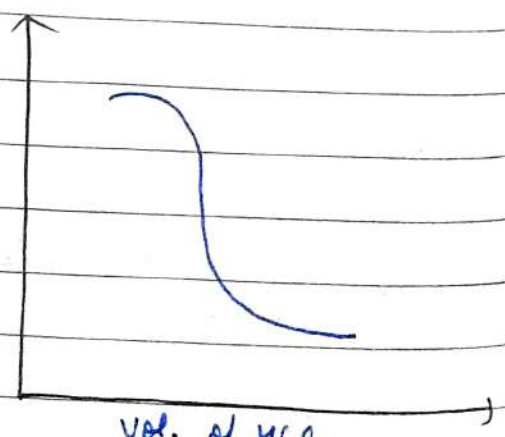
$$0.1\,N \times 5\,mL = N_2 \times 55\,mL$$

$$N_2 = \frac{0.1}{11} = 0.009\,N$$

∵ This normality of $[H^+]$ in solution

$$pH = -\log [0.009]\,N$$

$$pH = 2.04.$$



4. WA v/s WB

Since this titration is not feasible to give an exact equivalence point, so, it is not performed.

— x — x —

Solubility Product

When a sparingly soluble salt is dissolved in water, it dissociates slightly to give ions in the solution. Most of the salt is present in the undissociated form.

for eg $PbSO_4$, Silver chromate, $SrSO_4$,

$$PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}$$

$$K = \frac{[Pb^{2+}]\,[SO_4^{2-}]}{[PbSO_4]}$$

∵ most of the salt is present in undissociated form, so conc^n of $PbSO_4$ is const, ∴ it is multiplied with K.

$$K\,[PbSO_4] = Ksp = [Pb^{+2}]\,[SO_4^{-2}]$$

for eg. $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$$Ksp = [Ag^+]^2\,[CrO_4^{2-}]$$

When Na_2SO_4 sol^n is prepared, and now $PbSO_4$ is added to it, then solubility of $PbSO_4$ is further ~~is~~ suppressed due to presence of common ions ($[SO_4^{2-}]$). This is called ion effect.