Acid Base Titrations

Chemical reaction between an acid and a base takes place, this reaction is based on the principle of neutralization.

$$H^+ + OH^- \rightleftharpoons H_2O \quad \text{(Neutralization of ions)}$$

Acidimetry an standard acid solution used for determining strength of alkali / base.

Alkalimetry an standard soln of base used for determining strength of acid.

This titration is used for determination of salts like
- Na_2CO_3
- $Na_2B_4O_7$

Advantages of acid-base titrations

- Reaction between acid base is quite fast & instaneous.
- Rxn will be single without any side rxns.
- Rxn will always reach to the completion.
- " " " be stoichometric (means reactant and pdts as per rxns are same)

Theory-1 Acid base titrations

Arrhenius Theory

Acid is any subs which ionize (partially or completely) in water or aq medium to give H^+ ions

$$HCl + H_2O \rightleftharpoons H^+ + Cl^-$$

$$CH_3COOH + H_2O \rightleftharpoons H^+ + CH_3COO^-$$

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Base is any sub^s which ionize in water or aq med to give OH^- ions.

$NaOH + H_2O \leftrightharpoons Na^+ + OH^- (aq)$

$KOH + H_2O \leftrightharpoons K^+ + OH^-$

Neutralisation Rxn

Acid + Base $\leftrightharpoons$ Salt + H_2O

Adv- This concept explain behaviour of acid base practically.

Limitations

- Defined for aq. med only
- Fails to explain stability of H^+
- Not explain conjugate acid base theory.
- " define acid / base which doesn't contains H^+/OH^- ions.

Theory - 2 Brownsted - Lowry Theory

Acc. to this theory

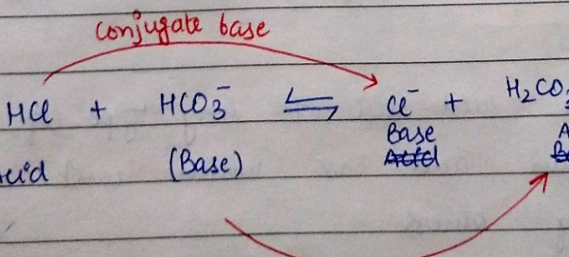
Acid → ~~which~~ sub^s / species that gives or donate proton in any type of solvent

eg H_2SO_4, HCl, CH_3COOH etc., HSO_4^-, HCO_3^-

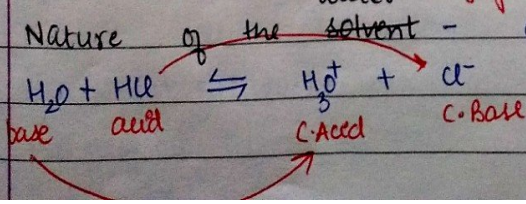
Base those species which ~~gives~~ accept proton in any type of solvent.

Eg ~~OH^+~~ OH^-, Cl^-, Br^-, I^-, HSO_4^-, HCO_3^-

Conjugate Acid - Base Concept (will always be tnt)



Nature of the ~~solvent~~ water - amphiprotic → sometimes acidic or basic.



Advantage
Explain stability of proton

Limitations
Don't explain acid base where proton is not.

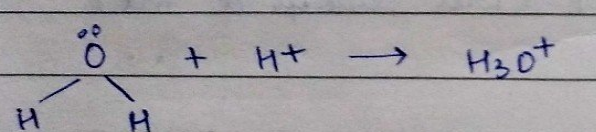
Theory-3 Lewis Theory

Base these species which can donate the lone pair of electrons. Lewis base are nucleophile
eg NH_3, SO_4^{2-}, F^-, Cl^-, I^-, CN^-

Acid species which accept lone pair of electron
Lewis acid are electrophile.
Eg NH_4^+, $AlCl_3$, BCl_3

Octet Rule atoms of main group element have tendency to combine in such a way that each atom has complete electrons in valence shell.

Nature of water it's lewis base



Adv - • define acid base w/o any type of solvent
• explain acid base which can't describe by others.

Strong Acid vs Strong Base Curves

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$HCl + NaOH \rightarrow NaCl + H_2O$

Consider titration b/w 1N of 100ml HCl with 1N NaOH soln.

1N HCl in conical flask

$pH = -\log[H^+]$, $H^+ = 1N$

$= -\log[1] = -\log\frac{1}{1} = \log 1 = 0$

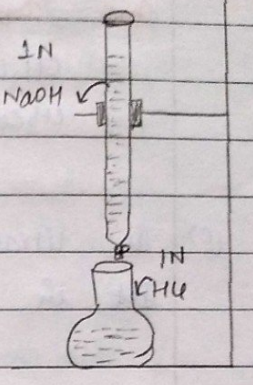
→ After addn of 1N NaOH (1ml)

Total vol = 100 + 1 = 101 ml

remain HCl = 99 ml

$H^+ = \frac{99}{101}$; $pH = -\log\left[\frac{99}{101}\right]$

$= +\log\frac{101}{99} = \log 1.020$



$pH = 0.0086$

→ After addn 50 ml of 1N NaOH soln

Total vol = 150 ml

Remain HCl = $\frac{50}{150}$ ⇒ $pH = -\log\frac{50}{150}$

$pH = \log\frac{150}{50} = \log 3 = 0.4771$

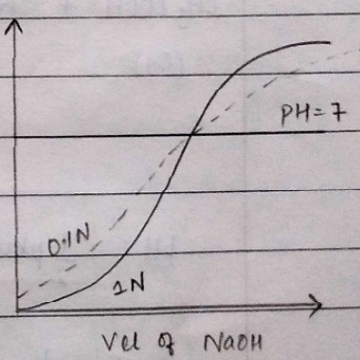
→ After addn 99.9 ml of 1N NaOH

Total vol = 199.9

Rem HCl = 0.1 ml

$pH = -\log\frac{0.1}{199.9} = \log\frac{199.9}{0.1}$

$pH = \log 1999 = 3.3008$ Acidic



→ After addn of 100 ml 1N NaOH, the pH will sharply change to 7

→ After addn 100.1 ml 1N NaOH soln

Total vol = 100 + 100.1 = 200.1

Rem NaOH = 100.1 − 100 = 0.1 ml

$pOH = -\log\frac{0.1}{200.1}$, $\log\frac{2001}{1} = 3.3012$

$pH = pKw - pOH$

$= 14 - 3.3012$

$= 10.698$

Basic

Weak Acid Strong Base

$CH_3COOH + NOH \rightarrow CH_3COONa + H_2O$

(a) H^+ ion concen" is small at the start of titration, so pH will be higher.

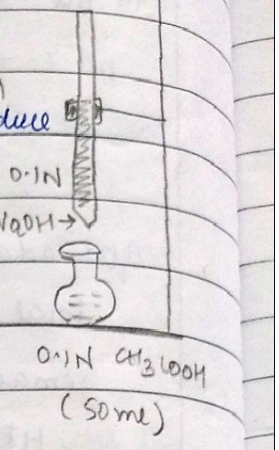
$CH_3COOH = [H^+] = 1.34 \times 10^{-3}$, $pH = -\log 1.34 \times 10^{-3} = -\log 10^{-3} - \log 1.34$

$= 3 - 0.1271 = 2.8729$

(b) When 0.1N NaOH alkali is added it produce the salt which give common ion effect and dissocin of weak acid further ↓.

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

$CH_3COONa \rightarrow CH_3COO^- + Na^+$



(c) In titration b/w SA - SB at equivalence pH = 7

But in this equivalence pH will be more than 7.

$$pH = \frac{1}{2} pKw + \frac{1}{2} pKa + \frac{1}{2} \log C$$

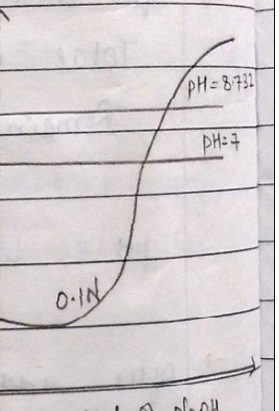
→ 50 ml of 0.1N CH_3COOH } 100 ml

50 ml of 0.1N NaOH

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

(0.1) (0.1) (0.1) → for 50ml

$C = 0.05$ → for 100ml



Initial pH is higher and at equivalence also pH is higher

$$pH = \frac{1}{2} pKw + \frac{1}{2} pKa + \frac{1}{2} \log C$$

$= \frac{1}{2} \times 14 + (\frac{1}{2} \times 4.7447) + \frac{1}{2} \log 0.05$

$= 7 + 2.3724 + (-\frac{1}{2} \times 1.3)$

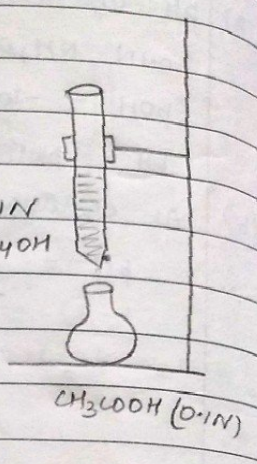
$= 7 + 2.372 - 0.65$

$= 8.7224$ at equivalence pt.

Weak acid vs weak Base

$CH_3COOH + NH_4OH \longrightarrow CH_3COONH_4 + H_2O$

Let's consider titration of 50 ml 0.1N CH_3COOH with 0.1N NH_4OH



$CH_3COOH = H^+ = 1.34 \times 10^{-3}$ m

(0.1N) $pH = -\log 1.34 \times 10^{-3} = 2.8729$

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

$CH_3COONH_4 \longrightarrow CH_3COO^- + NH_4^+$

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

Conc. of H^+ & OH^- will further ↓ due to common ion effect

$CH_3COONH_4 + H_2O \longrightarrow CH_3COOH + NH_4OH$

Inflection of pH at equivalence pt will be less.

If we use dil soln then sharp end pt. can't be reached.

$pH = \frac{1}{2} pKw + \frac{1}{2} pKa - \frac{1}{2} Kb$

$= 7 + \frac{1}{2} \times 4.7447 - \frac{1}{2} \times 4.7447$

$pH = 7$

$Ka = 1.8 \times 10^{-5}$

$Kb = 1.8 \times 10^{-5}$

$pKa = -\log 1.8 \times 10^{-5}$

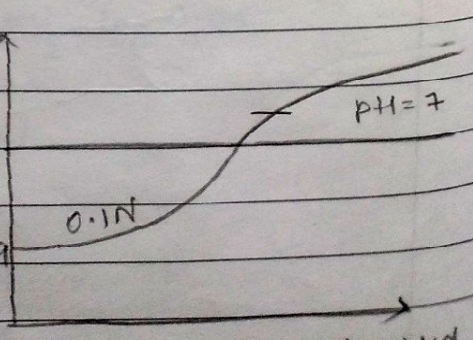
$= 4.7447$

$pKb = 4.7447$

If $Ka = Kb$ $pH = 7$

$Ka > Kb$ = $pH > 7$

$Ka < Kb$ = $pH < 7$



mix indicator is used to detect end point.