Chapter Four :

Theory of neutralization :

Neutralization in acid-base solutions :

Electrolytes: electrolytes are solutes which ionize in a solvent to produce an electrically conducting medium. Or its ionizable substances which are gives positive ion and negative ionic the solvent .

Strong electrolytes : are ionized completely in the solvent .

Weak electrolytes : are only partially ionized in the solvent .

$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

HCl is a strong electrolyte which is completely ionized.

$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$

NH_3 is a weak electrolyte which is partially ionized.

Amphiprotic : is a term refers to substance because it exhibits both acidic and basic properties depending on the solute such as : water , methyl alcohol , ethyl alcohol .

$HNO_2 + H_2O \rightleftharpoons NO_2^- + H_3O^+$

acid base

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

base acid

Conjugate acids and basis :

After donating a proton by the acid , the species that remains is capable to accepting a proton to reform the original acid.

$acid1 \rightleftharpoons H^+ + base1$, $H2O \rightleftharpoons H^+ + OH^-$

acid conjugate base

$base2 + H^+ \rightleftharpoons acid2$, $NH_3^+ \rightleftharpoons OH^- + NH_4^+$

base conjugate acid

conjugate acid	conjugate base
HCN	CN^-
HCl	Cl^-
CH_3COOH	CH_3COO^-
NH_4^+	NH_3
H_2CO_3	HCO_3^-

Hydrogen ion exponent (pH) :

pH = power of hydrogen

$pH = -\log [H_3O^+]$ or $pH = +\log_{10} \frac{1}{[H3O+]}$

$[H_3O^+] = 10^{-pH}$

$pOH = -\log [OH^-]$ or $pOH = +\log_{10} \frac{1}{[OH]}$

$[OH^-] = 10^{-pOH}$

In neutral sol. $[H_3O^+] = [OH^-] \longrightarrow pH = 7$

In acidic sol. $[H_3O^+] > [OH^-] \longrightarrow pH > pOH$

In basic sol. $[H_3O^+] < [OH^-] \longrightarrow pH < pOH$

<u>Ionization constant of water (Kw) :</u>

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

$H^+ + H_2O \longrightarrow H_3O^+$

$H^+ + 2H_2O \longrightarrow H_5O_2^+$

$H^+ + 3H_2O \longrightarrow H_7O_3^+$

$H^+ + 4H_2O \longrightarrow H_9O_4^+$

$$K = \frac{[H3O][OH]}{[H2O]}$$

$Kw = [H_3O^+][OH^-]$

$10^{-14} = [H_3O^+][OH^-]$ (x –log)

$14 = pKw = pH + pOH$

$pH + pOH = 14$

<u>EX.</u> Calculate pH and pOH for each of :

a) 0.001M HCl

b) 0.001M NaOH

c) 0.001M NaCl

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

0.001 0 0

0 0.001 0.001

$[H^+] = 0.001M = 10^{-3}M$

$pH = -\log 10^{-3} = 3$

$pOH = 14 - 3 = 11$

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

0.001 0 0

0 0.001 0.001

$[OH^-] = 0.001M = 10^{-3}M$

$pOH = -\log 10^{-3} = 3$

$pH = 14 - 3 = 11$

$NaCl \longrightarrow Na^+ + Cl^-$

$[H_3O^+] = [OH^-] = 10^{-7}$

$pH = pOH = 7$

<u>Calculation of pH :</u>

1) **weak acid and base :**

a) <u>for weak acid :</u>

$HA \rightleftharpoons H_3O^+ + A^-$

$$Ka = \frac{[H_3O][A^-]}{[HA]}$$

$[HA] = Ca$

$[H_3O^+] = [A^-]$

$$Ka = \frac{[H3O]2}{[Ca\ ]}$$

$[H_3O^+] = \sqrt{KaCa}$

$pH = -\log [H_3O^+]$

b) for weak base :

$B + H_2O \rightleftharpoons BH^+ + OH^-$

$$Kb = \frac{[BH+][OH-]}{[B]}$$

$[B\ ] = Cb$

$[OH^-] = [BH^+]$

$$Kb = \frac{[OH-]2}{Cb}$$

$[OH^-] = \sqrt{KbCb}$

$pOH = -\log [\ OH^-\ ]$

$pH = 14 - pOH$

<u>EX.</u> Calculate pH for benzoic acid sol. , Ka= 6.3×10^{-5} , Ca= 6.1gm/L,

M.wt.= 122gm/mole ?

$pH = -\log [H_3O^+]$

$[H_3O^+] = \sqrt{KaCa}$

$$Ca = \frac{6.1\ gm/L}{122\ gm/mole} = 0.05\ mole/L$$

$[H_3O^+] = \sqrt{6.3x10 - 5 \text{ x } 0.05} =$

pH = - log =

2) **salts solutions :**

Salts can be classified into :

a) salt derived from strong acid and strong base, NaCl :

$NaCl \longrightarrow Na^+ + Cl^-$

$[H_3O^+] = [OH^-] = 10^{-7}$

pH = pOH = 7

b) salt derived from strong acid and weak base, NH_4Cl :

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

$Ka = \frac{[H3O][NH3]}{[NH4]}$

$[NH_4] = Cs$

$[H_3O^+] = [NH_3]$

$Ka = \frac{[H3O]2}{Cs}$

$[H_3O^+] = \sqrt{KaCs}$

Kw = KaKb

$[H_3O^+] = \sqrt{\frac{KaCs}{Kb}}$ (x –log)

pH = ½ (pKw – pKb – log Cs)

<u>EX.</u> Calculate pH for 0.2M of NH_4Cl sol. , pKb = 4.72 ?

pH = ½ (14 – 4.72 – log 0.2)

pH =

c) salt derived from weak acid and strong base, NaCN:

$NaCN \rightleftharpoons Na^+ + CN^-$

$Na^+ + H_2O \longrightarrow$ no ionized

$CN^- + H_2O \rightleftharpoons HCN + OH^-$

$Kb = \frac{[HCN][OH-]}{[CN]}$

[CN] = Cs

$[HCN] = [OH^-]$

$Kb = \frac{[OH-]2}{[CN]}$

$[OH^-]^2 = KbCN$

$[\frac{Kw}{H3O}]2 = \frac{Kw}{Ka} Cs$

$[H_3O^+]^2 = \frac{KwKa}{Cs}$ (x –log)

$[H_3O^+] = \sqrt{\frac{KwKa}{Cs}}$

pH = ½ (pKw + pKb + log Cs)

d) salt derived from weak acid and weak base, NH_4F :

$NH_4F \rightleftharpoons NH_4^+ + F^-$

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

$F^- + H_2O \rightleftharpoons HF^+ + OH^-$

$[H_3O^+] = \sqrt{\frac{KwKa}{Kb}}$

pH = ½ (pKw + pKa - pKb)

<u>Buffer solution :</u>

Buffer solution is defined as a solution that resist change in pH as a result of either dilution or addition of acid or base .

Buffer solution is a mixture of :

a) weak acid and its salt , $CH_3COOH + CH_3COONa$

b) weak base and its salt , $NH_3 + NH_4Cl$

<u>Q :</u> why buffer sol. resist the change in pH value in case of dilution or adding acid or base to sol. ?

1) When adding a strong acid , like HCl :

$HCl \longrightarrow H_3O^+ + Cl^-$

$CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$

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

$H_3O^+ + CH_3COO^- \rightleftharpoons CH_3COOH$

From the equation , pH value is not change or it change very little

because the hydronium ion from HCl react with CH_3COO^- to produce CH_3COOH that is ionized very little , therefor , pH not decrease .

2) When adding a strong base , like NaOH :

$CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$

$CH_3COONa \rightleftharpoons Na^+ + CH_3COO-$

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

$H_3O^+ + OH^- \rightleftharpoons H_2O$

OH^- from the base (NaOH) react with H_3O^+ from the acid to produce H_2O , and that lead to more dissociation of CH_3COONa to substitute the losses in H_3O^+ that mean , the sol. will resist the change in pH value when adding a strong base while the sol. still acidic (contain CH_3COOH molecules) nonionized .

EX. Calculate the pH change that takes place when 100ml of (a) 0.05M NaOH and (b) 0.05M HCl are added to 400ml of a buffer solution that is 0.2M in NH_3 and 0.3M in NH_4Cl ?

The initial pH of the solution is obtained assuming that :

$[NH_3] = M_{NH3} = 0.2$

$[NH_4^+] = M_{NH4Cl} = 0.3$

And substituting into the dissociation constant expression for NH_3

$$\frac{0.3\,[OH^-]}{0.2} = 1.76 \times 10^{-5}$$

$[OH^-] = 1.17 \times 10^{-5}$

$pH = 14 - (-\log 1.17 \times 10^{-5}) = 9.07$

a) addition of NaOH converts part of the NH_4^+ in the buffer to NH_3 :

$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$

The analytical concentrations of NH_3 and NH_4Cl then become :

$$M_{NH3} = \frac{400 \times 0.2 + 100 \times 0.05}{500} = \frac{85}{500} = 0.170$$

$$M_{NH4Cl} = \frac{400 \times 0.3 - 100 \times 0.05}{500} = \frac{115}{500} = 0.230$$

When substituted into the dissociation constant expression , these values yield :

$$[OH^-] = \frac{1.67 \times 10{-}5 \times 0.170}{0.230} = 1.30 \times 10^{-5}$$

$pH = 14 - (-\log 1.30 \times 10^{-5}) = 9.11$

and :

$\Delta\, pH = 9.11 - 9.07 = 0.04$

b) addition of HCl converts parts of the NH_3 to NH_4^+ ; thus :

$NH_3 + H_3O^+ \longrightarrow NH_4^+ + H_2O$

$$M_{NH3} = \frac{400 \times 0.2 - 100 \times 0.05}{500} = \frac{75}{500} = 0.150$$

$$M_{NH4Cl} = \frac{400 \times 0.3 + 100 \times 0.05}{500} = \frac{125}{500} = 0.250$$

$$[OH^-] = 1.76 \times 10^{-5} \times \frac{0.150}{0.250} = 1.06 \times 10^{-5}$$

$$pH = 14 - (-\log 1.06 \times 10^{-5}) = 9.02$$

$$\Delta pH = 9.02 - 9.07 = -0.05$$

It is of interest to contrast the behavior of an unbuffered solution with a pH 9.07 to the buffered ones just considered . it is readily shown that the additions of the same quantity of base would increase the pH to 12 – a pH change of 2.93 units . The addition of acid , on the other hand , would decrease the pH by slightly over 7 units .

Buffering capacity :

Buffering capacity depends on :

a) The ratio between concentration of both acid and base.

b) The total concentration of each acid and salt.

Maximum buffering capacity can observed when pH = pKa (ratio of salt to acid is equal to 1.0)

Calculation of pH for buffer solution :

1) weak acid and its salt , ($CH_3COOH + CH_3COONa$)

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^- \quad \ldots\ldots\ldots\ldots(1)$$

$$Ka = \frac{[H][CH3COO-]}{[CH3COOH]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

$$[H^+] = Ka \frac{[H][CH3COOH]}{[CH3COO-]} \quad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

$$CH_3COONa \rightleftharpoons Na^+ + CH_3COO^- \quad \ldots\ldots\ldots(4)$$

From equation (1) :

$[CH_3COOH] = [CH_3COOH] - [H^+]$

$[CH_3COO^-] = [H^+]$

From equation (4) :

$[CH_3COO^-] = [Na^+]$

$[CH_3COO^-] = [CH_3COOH] + [H^+]$

$[CH_3COO^-] = [H^+]$

Substitution in equation (3) :

$$[H^+] = Ka \frac{[CH3COOH]-[H]}{[CH3COONa]+[H]}$$

Because of the value of $[H^+]$ is very small , then it can be negligible .

$$[H^+] = Ka \frac{[CH3COOH]}{[CH3COONa]}$$

$$[H^+] = Ka \frac{Ca}{Cs} \qquad (x - \log)$$

$$pH = pKa + \log \frac{Cs}{Ca}$$ …… Henderson- Hasselbach

2) weak base and its salt , ($NH_3 + NH_4Cl$)

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ ……(1)

$$Kb = \frac{[OH][NH4+]}{[NH3]}$$ ……..(2)

$$[OH] = Kb \frac{[NH3]}{[NH4+]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^- \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

From equation (1) :

$[NH_3] = [NH_3] - [OH^-]$

$[OH^-] = [NH_4^+]$

From equation (4) :

$[NH_4Cl] = [NH_4^+]$

$[NH_4^+] = [NH_4Cl] + [OH^-]$

Substitution in equation (3) :

$$[OH^-] = Kb \frac{[NH3]-[OH-]}{[NH4+]+[OH-]}$$

$$[OH^-] = Kb \frac{Cb}{Cs} \quad (x - \log)$$

$$pH = pKb + \log \frac{Cs}{Cb}$$

<u>EX.</u> Calculate pH for a solution prepared by adding 10ml of 0.1M acetic acid to 20ml of 0.1M sodium acetate , Ka = 1.75×10^{-5} ?

we should calculate the conc. of acid and salt , final vol. = 30ml

for CH_3COOH :

M1V1 = M2V2

0.1m.mole x 10ml = M2 x 30ml

M2(HOAc) = 0.033 m.mole / ml

For CH_3COONa (OAc-) :

M1V1 = M2V2

0.1 m.mole x 20ml = M(OAc-) x 30ml

M(OAc-) = 0.067 m.mole/ml

$$pH = pKa + \log \frac{Cs}{Ca}$$

$$pH = 4.67 + \log \frac{0.067}{0.033}$$

pH= 4.67 + log 2

pH = 5.06

<u>EX.</u> Calculate the vol. of concentrated ammonia and weight of ammonia chloride (NH_4Cl) that is needing to prepare 100ml of buffer sol.

with pH = 10 salt conc. = 0.2M , pkb = 4.67 ?

we need to prepare 100ml of 0.02M of NH_4Cl :

m.moles NH_4Cl = 0.2m.mole/ml x 100ml = 20 m.moles

mg(NH_4Cl) = 20m.moles x 53.5 mg/m.mole = 107 x 10^{-3} mg

thus , we need 107 mg of NH_4Cl

we can calculate the conc. of NH_3 from :

pOH = pKw – pH

pOH = 14 – 10 = 4

$$pOH = pKb + \log \frac{Cs}{Cb}$$

$$4 = 4.67 + \log \frac{0.2 \text{ m.mole/ml}}{[NH3]}$$

$$\log \frac{0.2 \text{ m.mole/ml}}{[NH3]} = -0.67 \qquad (x - \log)$$

$$\log \frac{0.2 \text{ m.mole/ml}}{[NH3]} = 10^{-0.67} \longrightarrow 10^{-1} \times 10^{0.24} = 1.7 \times 10^{-1} = 0.17$$

$$[NH_3] = \frac{0.2}{0.17} = 1.2 \text{ m.mole/ml}$$

<u>Acid – Base indicators :</u>

Acid-base indicators are weak organic acids or bases , most of indicators have two colors , one is appear in acidic medium and the other is appear in basic medium (that means, the indicator will change its color when acid or base were adding to sol.) .

We can symbolize to the typical reaction of an acid-base indicator as follows :

$$H_2O + HIn \rightleftharpoons H_3O^+ + In^-$$

acid color base color

$$In^- + H_2O \rightleftharpoons InH^+ + OH^-$$

base color acid color

Where : HIn = acidic indicator

In = basic indicator

$$Ka = \frac{[H3O][In-]}{[In]} \quad \ldots\ldots\ldots\ldots(1)$$

$$[H_3O^+] = \frac{Ka\,[HIn]}{[In-]}$$

$$Kb = \frac{[InH+][OH-]}{[In]} \quad \ldots\ldots\ldots\ldots(2)$$

The best indicator is the indicator whose change its color in equivalent point .

The change in color of indicator can observed in the region where the ratio various from a tenfold excess of one form to other , therefore, acidic color can be observed when :

$$\frac{[In]}{[HIn]} \leq \frac{1}{10}$$

And the basic color when :

$$\frac{[In]}{[HIn]} \geq \frac{10}{1}$$

Some indicators requires smaller ratio changes and others longer.

If equation (1) is multiplying by (- log) , then :

$$[H_3O^+] = \frac{Ka\,[HIn]}{[In-]} \qquad (x - \log)$$

$$pH = pKa - \log \frac{[In-]}{[HIn]}$$

when $\frac{[In-]}{[HIn]} = \frac{1}{10}$ or $\frac{10}{1}$

$$pH = pKa - \log \frac{1}{10}$$

$$pH = pKa - 1$$

and ,

$$pH = pKa + \log \frac{10}{1}$$

$$pH = pKa + 1$$

ΔpH = pH basic – pH acidic = (pKa+1) – (pKa – 1) = 2

That means , when we assume that pKa = 5 , the change in color of indicator occur when the pH value variant from (5-1) to (5+1) e.g. (4-6).

Some important Acid-Base indicators

Common name	transition range,pH	acid color	base color
Methyl yellow	2.9 – 4.0	red	yellow
Methyl orange	3.1 – 4.4	red	orange
Bromocresol green	3.8 – 5.4	yellow	blue
Methyl red	4.2 – 6.3	red	yellow
Bromothymol blue	6.2 – 7.6	yellow	blue
Phenol red	6.8 – 8.4	yellow	red
Phenolphthalein	8.3 – 10.0	colorless	purple
Thymolphthalein	9.3 – 10.5	colorless	blue

Types of acid-base indicators :

The table above shows many acid-base indicators that are used in analytical routine work .two common indicators are described in the following paragraphs:

1) **phthaline indicators :** the best known phthaline indicator is ***phenolphthalein*** **,** it is organic weak acid , colorless in acidic sol. and exhibit a variety of colors in alkaline media .

Significant concentrations for color ion is appear in the pH range between 8.0 and 9.8 .

2) **Azo indicators :** most azo indicators exhibit a color range from red to yellow with increasing basicity . the best known azo indicators is ***methyl orange*** , it is a weak base has sulphonic group SO_3H and dimethylamin .

Choice of indicators for titration of acid and base :

End point detection in a neutralization titration based upon the change in color of indicator in equivalent point .

The selection of an appropriate indicator require knowledge the pH changes which occurs throughout titration. Thus, we need to know how neutralization titration curves are derived .

For any sol. to know the pH change throughout titration , it must be plotte titration curve that show the pH change according to the amount of acid or base that will be adding to the sol.

There are two methods to detect titration curves :

1) Calculated method : in this method , pH values are calculated from amount of acid or base that was added to the sol.

2) Practical method : in this method , pH values can be calculate by using an instrumental called " pH- meter ".

The advantages of titration curve are :

1) Detect the end point of titration .

2) Choice the suitable indicator for titration .

1) **<u>Titration of strong acid with strong base :</u>**

This type can be expressed by titration of 50ml of 0.1N HCl with 50ml of 0.1N NaOH :

a) before adding the base :

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

0.1 0.1 0.1

$pH = - \log [H^+] = - \log 0.1$

$pH = 1$

b) after adding 10ml of NaOH :

$HCl + NaOH \longrightarrow NaCl + H_2O$

(50x0.1)	**(10x0.1)**	**0**
5	1	0
4	0	1

$[H_3O^+] = \frac{4}{60} = 0.066$

$pH = - \log 0.066 = 1.18$

c) when adding 50ml of NaOH :

$HCl + NaOH \longrightarrow NaCl + H_2O$

(50x0.1)	**(50x0.1)**	**0**
5	5	0
0	0	5

$[H_3O^+] = [OH^-] = 10^{-14}$

$[H_3O^+]^2 = 10^{-14}$

$[H_3O^+] = 10^{-7}$

$pH = -\log 10^{-7} = 7$

d) after adding excess of NaOH (60ml) :

$HCl + NaOH \longrightarrow NaCl + H_2O$

(50x0.1)	**(60x0.1)**	**0**
5	6	0
0	1	5

$[OH^-] = \frac{1}{(50+60)ml} = 0.009$

$pOH = -\log 0.009 = 5$

$pH = 14 - 5 = 9$

The figure shows that the range of pH change at equivalent point is 4 -10 , therefore , both of ph.ph and M.O can be use successfully.

2) **<u>Titration of strong base with a strong acid :</u>**

(gives as H.W for students) .

3) **<u>Titration of weak acid with a strong base :</u>**

100ml of 0.1N CH_3COOH with 100ml of 0.1N NaOH , Ka = $1x10^{-5}$.

a) before adding NaOH :

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

$$[H_3O^+] = \sqrt{KaCa} = \sqrt{10-5 \times 10-1} = 10^{-3}$$

$$pH = -\log 10^{-3} = 3$$

b) after adding 10ml NaOH :

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

(100x0.1)	**(10x0.1)**	**0**
10	1	0
9	0	1

<u>Note</u> : the product from this reaction is weak acid and it's salt , therefore , it is buffer sol. :

$$pH = pKa + \log \frac{Cs}{Ca}$$

$$pH = 5 + \log \frac{1}{9}$$

$$pH = 4.05$$

c) when adding 50ml of NaOH :

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

(100x0.1)	**(50x0.1)**	**0**
10	5	0
5	0	5

$$pH = pKa + \log \frac{Cs}{Ca}$$

$$pH = 5 + \log \frac{5}{5}$$

pH = 5

d) when adding 80ml of NaOH :

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

(100x0.1)	**(80x0.1)**	**0**
10	8	0
2	0	8

$$pH = pKa + \log \frac{Cs}{Ca}$$

$$pH = 5 + \log \frac{8}{2}$$

pH = 5.6

e) at end point , when adding 100ml of NaOH :

at end point m.mole of NaOH = m.mole of CH_3COOH

$$Cs = \frac{10}{100+100} = \frac{10}{200} = 0.05N$$

Because of the salt is derived from weak acid and strong base , therefore,

$$pH = \frac{1}{2}(pKw + pKa + \log Cs)$$

$$pH = \frac{1}{2}(14 + 5 + \log 0.05)$$

pH = 8.85

f) when adding 120ml of NaOH :

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

(100x0.1)	**(120x0.1)**	**0**
10	12	0
0	2	8

$$[OH^-] = \frac{2}{100+120} = \frac{2}{220} = 9.1x10^{-3}$$

$$pOH = -\log [OH^-] = -\log 9.1x10^{-3} = 2.04$$

pH = 14 – 2.04 = 11.96

<u>Note 1 :</u> Effect of concentration :

The concentration of analyte and reagent are affects on neutralization titration curves. For example:

The titration of acid or base with 0.1M (curve A) shows that pH change at equivalence point region is large , while the titration with 0.001M shows that the pH change is less but still pronounced (curve B) .

<u>Note 2 :</u> Effect of acid :

Figure below shows the effect of acid conc. measured in Ka value on neutralization curves . at equivalence point region, when Ka is decreased the range of pH change is decrease too. and the titration can be done if Ka = 10^{-6} or more. while when Ka $<$ 10^{-6} the titration cannot be done, because it cannot using any types of indicators .