MARUDHAR KESARI JAIN COLLEGE FOR WOMEN

(AUTONOMOUS)

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PG Department of Chemistry

III B.Sc. Chemistry- semester- V

E-Notes

COURSENAME:PHYSICALCHEMISTRY-I	**CODE:FCH53**
UNIT-V ELECTROCHEMISTRY - II Applications of Conductometric Measurements - Determination of Degree of Dissociation of Weak Electrolytes, Ionic Product of water - Solubility Product of sparingly soluble salt - Conductometric Titrations - Concept of pH - Buffer solutions, Buffer action - Henderson equation - Applications of Buffer Solutions - Hydrolysis of Salts - Expressions for Hydrolysis Constant, Degree of Hydrolysis and pH of aqueous salt solutions.	
Learning Objective: To impart knowledge about variation of conductivity with dilution, measurement of conductivity and buffer solutions.	
Learning Outcome: To understand Electrochemistry and its application..	

ELECTROCHEMISTRY:

Electrochemistry is the study of electron movement in an oxidation or reduction reaction at a polarized electrode surface. Each analyte is oxidized or reduced at a specific potential and the current measured is proportional to concentration. This technique is a powerful methodology towards bioanalysis.

UNIT- V

Application of Conductometric measurements

1) Determination of degree of dissociation of weak electrolyte and dissociation constant
2) Determination of ionic product of water
3) Determination of solubility of sparingly soluble salts

1) Determination of degree of dissociation of weak electrolyte and dissociationconstant:

- Degree of dissociation is defined as the fraction of molecules undergo dissociation. It is given by

$$\alpha = \frac{\lambda_c}{\lambda_\infty}$$

- According to Kohlrausch's law

$$\lambda_\infty = \lambda^0_+ + \lambda^0_-$$

- From the degree of dissociation, the dissociation constant is determined usingthe expression,

$$\boxed{k_a = \frac{C\,\alpha^2}{(1-\alpha)}}$$

2) Determination of ionic product of water:

- Water is considered to be weak electrolyte and dissociated as follows

$$H_2O \rightleftharpoons [H^+] + [OH^-]$$

- For this the equilibrium constant is given as

$$\mathbf{k} = \frac{[H^+]+[OH^-]}{H_2O}$$

- Since water dissociates very slow, its concentration of undissociated watermay be taken as constant.

$[H^+] + [OH^-]$ = a constant k_w is a constant (or ionic product of water)k_w = $[H^+] + [OH^-]$

"The product of ionic concentration of H^+ and OH^- ions expressed in mol/lit isa constant at a given temperature, is known as ionic product of water."

k_W (Specific conductivity) can be determined by conductivity measurements,

The specific conductivity of water is $5.51\times 10^{-6}sm^{-1}$

The ionic conductance of H^+ is 349.8×10^{-4} sm^{-1}

OH^- is 198.5×10^{-4} sm^{-1}

For water,

$$\lambda_c = \frac{K \times 10^{-3}}{C}$$ **(in SI) where c is in gram equivalents/litre**

$$\lambda_c = \frac{5.51\times10^{-6}\times10^{-3}}{c}$$

$$\lambda_\infty = \lambda^0_{H^+} + \lambda^0_{OH}$$

$$= 349.8 \times10^{-4} + 198.5 \times10^{-4}$$

$$= 548.3 \times10^{-4}\ sm^2mol^{-1}$$

$\therefore$ Equivalent conductance $\lambda_c = \dfrac{K_w \times10^{-3}}{c}$ (in SI) where c is in gram equivalents/litre

Water may be considered as a dilute soln. of H^+ and OH^- in undissociated H_2O, therefore, λ_c will be taken as λ_∞

$$\lambda_\infty = \frac{K_w \times 10^{-3}}{c}$$

$$c = \frac{K_w \times 10^{-3}}{\lambda_\infty} \quad \text{where } c = [H^+] = [OH^-]$$

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

3) Determination of solubility of sparingly soluble salts:

1 A saturated solution of the sparingly soluble salt is prepared and its specific conductance is determined (k_{soln})

2 Let k_{H_2O} is specific conductance of pure water

k_{salt} is specific conductance of salt

∴ Specific conductance of salt is

$$(k_{salt}) = (k_{soln}) - k_{H_2O}$$

3 The molar conductance of the salt is

$$(\lambda_m) = \frac{k_{salt} \times c}{10^3}$$

Where c is concentration or solubility in moles/litre

4 Since the solubility is very low, it is assumed that the salt is completely ionized at infinite dilution, therefore λ_m is taken as λ_∞ (molar conductance at infinite dilution).

Thus,

$$\lambda_\infty = \frac{k_{salt} \times c}{10^3}$$

$$c = \frac{K_{salt} \times 10^{-3}}{\lambda_\infty} \quad [\because \lambda_\infty = \lambda^0_+ + \lambda^0_- \text{ (Kohlrausch's law)}]$$

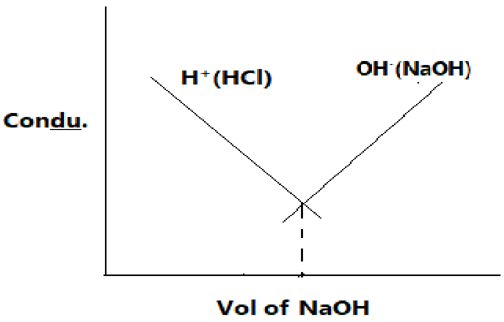
5 So the value of c (solubility) can be determined by knowing k and λ_∞ values.

CONDUCTOMETRIC TITRATIONS

- The determination of end- point of a titration using conductivity measurements isknown as conductometric titration.
- Its basic principle is that the equivalent conductivity of an electrolyte depends uponthe number of ions and their mobility.

Examples:

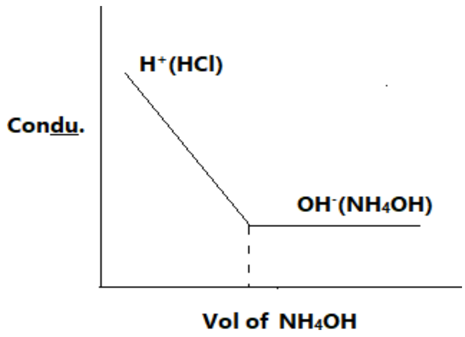
1) Strong acid Vs Strong Base
   [HCl] [NaOH]



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

i. At initial condu is high due to H^+ ion in HCl
ii. On gradual addition of NaOH, condu is decrease due to removal of H^+
iii. After end- point the condu is increased due to presence of OH^- from NaOH

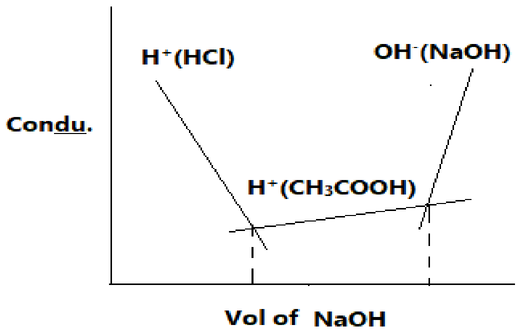
2) Strong acid Vs Weak Base
   [HCl] [NH_4OH]



$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$$

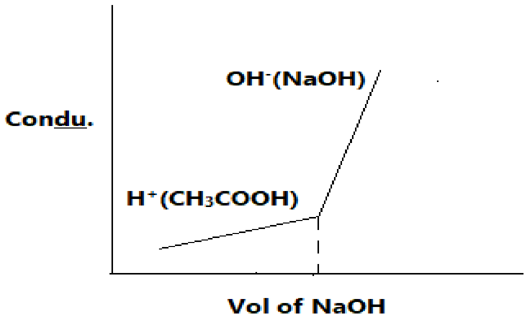
i. At initial condu is high due to H^+ ionfrom HCl
ii. On gradual addition of NH_4OH, condu is decreased due to removal of H^+
iii. After end-point the condu is study valuesince NH_4OH, gives less OH^- ions.

3) Weak acid Vs Strong Base
4) Mixture of acid Vs Strong Base
[CH_3COOH] [NaOH]



[HCl

$+CH_3COOH]$ $[NH_4OH]$



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

i. At initial, condu is less sinc CH_3COOH gives less H^+

ii. On gradual addition of NaOH, condu is slightly increase.

iii. After end-point the condu is increased rapidly due to excess of OH^- from NaOH

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

i. At initial condu is high due to H^+ion from HCl

ii. On gradual addition of NH_4OH, condu is decreased due to removal of H^+ and slightly increase in conductance since CH_3COOH gives less H^+

iii. After two end-points the condu is rapidly increased due to excess of of OH^- from NaOH

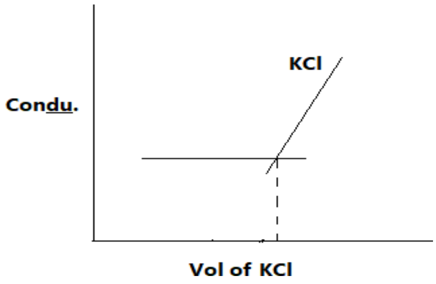
Advantages of conductometric titrations:

1) Colour solns. can be titrated which is not possible in ordinary titrations,
2) Very dilute solns. can be titrated,
3) Mixture of strong and weak acids can be titrated,
4) Need not be very careful near the end-point,
5) The results are very accurate.

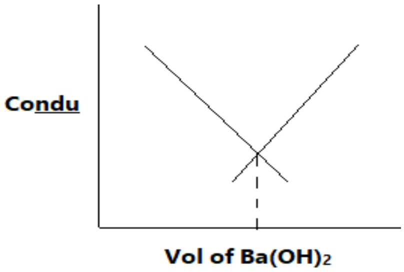
Precipitation titrations:

In some conductometric titrations the end-point is find out on precipitate formationis known as precipitation titration.

Eg: 1 KCl Vs $AgNO_3$



Eg:2 $MgSO_4$ Vs $Ba(OH)_2$ (double precipitation titration)



$KCl + AgNO_3 \longrightarrow AgCl + KNO_3$

i. In this reaction, one salt is replaced by another salt in equal amount, therefor e conductivity remains constant.

ii. After the end- point, a sharp incr ease in condu due to excess addition of burette solution.

$MgSO_4 + Ba(OH)_2 \longrightarrow Mg(OH)_2 + BaSO_4$

i. n this case, condu decr eases upto the end-point due to decr ease in the no. of ions.

ii. After the end- point, condu incr eases because of excess addition of $Ba(OH)_2$.

P^H concept

The P^H scale was intr oduced by Sor enson.

$$P^H = -\log_{10} [H^+]$$

$\therefore$ P^H is defined as “the negative logar ithm of base 10 of the hydr ogen ionconcentr ation” [moles lit^{-1}]

For neutr al soln. $[H^+] = [OH^-]$

$$= 1\times 10^{-7}$$

$$\therefore P^H = -\log_{10} [H^+]$$

$$= -\log_{10} [1\times 10^{-7}]$$

$$\boxed{\mathbf{P^H = 7}}$$

For acidic soln. $[H^+] > [OH^-]$

i.e., $[H^+] > 1\times 10^{-7}$

$$\boxed{\mathbf{P^H < 7}}$$

For basic soln. $[H^+] < [OH^-]$

i.e., $[H^+] < 1\times 10^{-7}$

$$\boxed{\mathbf{P^H > 7}}$$

Buffer solution:

- Solution that do not change their P^H by the addition of small amount of acid or basear e called buffer solutions.

  Ex:

  A mixture of weak acid and its salts (Acidic buffer)A mixture of weak base and its salts (Basic buffer)

Buffer action (or) activity

1) Mixture of weak acid and its salt [Eg: CH_3COOH and CH_3COONa]

   i. <u>Addition of HCl</u>

   $$CH_3COO^- + HCl \longrightarrow CH_3COOH + Cl^-$$

   ii. <u>Addition of NaOH</u>

   $$CH_3COOH + NaOH \longrightarrow CH_3COO^- + H_2O + Na^+$$

2) Mixture of weak base and its salts [Eg: NH4OH and NH4Cl]

   i. <u>Addn. of NaOH</u>

   $$NH_4^{\oplus} + NaOH \longrightarrow NH_4OH + Na^+$$

   ii. <u>Addn. of HCl</u>

   $$NH_4OH + HCl \longrightarrow NH_4^{\oplus} + H_2O + Cl^-$$

Buffer capacity:

- It is defined as the no. of moles of acid or base added to one litre of solution to change the P^H by unity.
- In mathematic we can write as

$$\text{Buffer capacity} = \frac{d_a}{d_{pH}}$$

Where d_a is no. of moles of acid or base added.

d_{pH} is change in P^H

Henderson's equation (Calculation of P^H)

1) Consider a buffer mixture of a weak acid HA and its salts NaA ,
2) The dissociation of the acid HA is

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

3) Apply the rate equation, we get the dissociation constant

$$k_a = \frac{[H^+][A^-]}{[HA]}$$

$$H^+ = \frac{k_a[HA]}{[A^-]}$$

Take $\log_{10}$ on both sides,

$$\log_{10}[H^+] = \log_{10} k_a + \log_{10}\frac{[HA]}{[A^-]}$$

Multiply by -1 on both sides,

$$-\log_{10}[H^+] = -\log_{10} k_a - \log_{10}\frac{[HA]}{[A^-]}$$

$$P^H = P^{ka} + \log_{10}\frac{[A^-]}{[HA]}$$

4) Since HA is a weak acid, the contribution of A^- from HA is negligee, ∴ $[A^-]$ conc. canbe taken as the conc. of salt itself.

III^{ry} [HA] is the conc. of the undissociated acid itself because it is weakly ionized,

$$P^H = P^{k}a + \log_{10} \frac{[salt]}{[acid]}$$

$$\boxed{P^H = P^{k_a} + \log_{10} \underline{[salt]}}$$

5) The above equ. is known as Henderson's equation,

6) similarly we can derive for the P^{OH} of a mixture of weak base and its salt

$$\boxed{P^{OH} = P^{k_a} + \log_{10} \underline{[salt]}}$$

Application of Buffer solution:

1 It has great importtant in biology, industries, research and medicines,

2 In Biology

i. Many biological fluids (like blood, milk) have definite P^H values,

ii. The P^H of the blood is 7.4 that maintained by amphoteric substance (Ex:plasma proteins) and buffer systems.

iii. There are two buffer system that maintained the blood P^H

1) $H_2CO_3 - HCO_3^{\ominus}$ 2) $H_2PO_4 - HPO_4^{\ominus}$

1) $H_3O^{\oplus} + HCO_3^{\ominus} \longrightarrow H_2CO_3 + H_2O$

$$H_2CO_3 \downarrow H_2O + CO_2$$

$OH^{\ominus} + H_2CO_3 \longrightarrow H_2O + HCO_3^{\ominus}$

3 In industrial

i. Manufacture and refining of sugar ,ii.

Purification of water,

iii. Tanning of leather,

iv. Manufacture of Milk products

v. Electroplating.

4 In the elimination of phosphate [Buffer mixture (CH_3COOH - CH_3COONH_4)]

5 Buffer solutions are used in the determination of dissociation constant of weak acidor base in the mixture.

HYDROLYSIS OF SALTSHydr

olysis:

It is defined as a reaction in which the anion and cation of dissolved salt reacts with H^+ and OH^- (used from water) to give acidity or alkalinity is called hydrolysis.

It may be consider as reverse combination or neutralization to give water,

$$H_2O \overset{K_h}{\rightleftharpoons} H^+ + OH^-$$

Hydrolysis constant:

The equilibrium constant of hydrolytic equilibrium is called hydrolysis constant. It is denoted by K_h

Degree of hydrolysis:

The fraction of total dissolved salt which undergo hydrolysis and attain equilibrium in solution is called degree of hydrolysis. The hydrated salt exist as weak acid or weak base.

Classification of Hydrolysis of Salt

It is classified into four types,

1) Salts of strong acid and strong base

2) Salts of weak acid and strong base

3) Salts of weak base and strong acid

4) Salts of weak acid and weak base

1) Salts of strong acid and strong base:

- These salts do not undergo hydrolysis.
- Consider KCl salt is dissolved in water, it gives K^+ and Cl^- have no tendency to react with H^+ and OH^- of water. This is because the possible products are almost completely dissociated into ions.

$$KCl + H_2O \longrightarrow KOH + HCl$$

- Consequently there is no change in H^+ and OH^-

2) Salts of weak acids and Strong base

Ex: CH_3COONa or CH_3COOK

When these salts dissolved in water, result alkaline solution.

Consider the hydrolysis of CH_3COONa

$$\underset{\text{(salt)}}{CH_3COONa} + HOH\,(H_2O) \longrightarrow \underset{\text{(weat acid)}}{CH_3COOH} + \underset{\text{(strong base)}}{\overset{+}{Na} + \overset{-}{O}H}$$

Thus, the solution of CH_3COONa consist of excess of OH^- than H^+ therefore the solution becomes alkaline.

Hydrolysis constant (K_h)

Consider the hydrolysis of any salt BA of weak acid HA and strong base BOHThe hydrolysis is due to the anion A^- of the weak acid.

$$\underset{\text{anion}}{\overset{-}{A}} + H_2O \xrightleftharpoons{K_h} \underset{\text{acid}}{HA} + \underset{\text{Free base}}{\overset{-}{O}H}$$

Apply the law of mass action (Oswald's dilution law) to above reaction andconcentration of H_2O taken as constant.

$$K_h = \frac{[HA]\,[OH^-]}{[A^-]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \square$$

The other equilibrium involved in this hydrolysis are,

$$H_2O \xrightleftharpoons{K_w} H^+ + OH^-$$

$$BOH \xrightleftharpoons{K_b} B^+ + OH^-$$

Apply the law of mass action

$$K_w = [H^+]\,[OH^-] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{②}$$

K_w is the dissociation constant or ionic product of water

$$K_a = \frac{[H^+][A^-]}{[HA]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{③}$$

K_a is the dissociation constant of acid (HA)Dividing ②

by ③

$$\frac{K_w}{K_a} = \frac{\cancel{[H^+]}[OH^-][HA]}{\cancel{[H^+]}[A^-]}$$

$$= \frac{[HA][OH^-]}{[A^-]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{④}$$

Comparing equation ④ with □

$$\boxed{\mathbf{K} \quad \underline{\mathbf{K}}}$$

Degree of hydrolysis:

Consider hydrolysis of salt 'BA' here C is mole/litre, x is degree of hydrolysis

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

	A^-	HA	OH^-
Initial concentration	C	0	0
At equilibrium	$C(1-x)$	Cx	Cx

$$K_h = \frac{[HA]\,[OH^-]}{[A^-]}$$

$$= \frac{Cx \cdot Cx}{C(1-x)}$$

$$K_h = \frac{Cx^2}{1-x}$$ if x is very small (1- x) is taken as unit.

$$K_h = Cx^2$$

$$x = \sqrt{\frac{K_h}{C}}$$ But $K_h = \frac{K_w}{K_a}$

$$\boxed{\therefore x = \sqrt{K}}$$

P^H of aqueous salt solutions (Hydrogen ion concentration)

	$\bar{A} + H_2O$	$\rightleftharpoons$	HA	$+\ \bar{O}H$
(Equillibrium concentration)	$C(1-x)$		Cx	Cx

$\therefore\ [OH^-] = Cx$

But $K_w = [H^+]\,[OH^-]$

$$[H^+] = \frac{K_w}{[OH^-]}$$

$$= \frac{K_w}{Cx}$$ But $x = \sqrt{\frac{K_w}{K_a}}$.

$$[H^+] = \frac{K_w}{C}\sqrt{\frac{K_a}{C\,K_w}}$$

$$[H^+]^{1/2} = \frac{K_w^2}{C^2}\left(\frac{K_a}{C^2 K_w}\right)$$

$$[H^+] = \sqrt{\frac{K_w \cdot K_a}{C}}$$

Taking logarithm on both sides

$$\log [H^+] = \frac{1}{2}\log K_w + \frac{1}{2}\log K_a - \frac{1}{2}\log C$$

Multiple by ⊖ on both sides

$$-\log [H^+] = -\frac{1}{2}\log K_w - \frac{1}{2}\log K_a + \frac{1}{2}\log C$$

$$P^H = \frac{1}{2}P^{K_w} + \frac{1}{2}P^{K_a} + \frac{1}{2}\log C$$

$$P^H = 7 + \frac{1}{2}P^{K_a} + \frac{1}{2}\log C$$

Fr om the above equation shows that the solution $P^H > 7$, Hence the solutionwill be alkaline.

3) Salts of Weak Base and Str ong Acid

Ex: NH_4Cl

When these salts dissolved in water, result acidic solution.Consider

the hydr olysis of NH_4Cl

$$\underset{\text{(salt)}}{NH_4Cl} + H_2O \rightleftharpoons \underset{\text{(weak base)}}{NH_4OH} + \underset{\text{(strong acid)}}{H^+ + Cl^-}$$

Thus, the solution of NH_4Cl contain excess of H^+ and OH^- consumed by NH^+,Hence the solution becomes acidic.

1. 3.1 Hydr olysis constant (K_h)

Consider the hydr olysis of any salt BA of weak base BOH and str ong base HAThe hydr olysis is due to cation B^+ of the weak base.

$$\underset{\text{(cation)}}{B^+} + H_2O \xrightleftharpoons{K_h} \underset{\text{(weakbase)}}{BOH} + \underset{\text{(Free acid)}}{H^+}$$

Apply the law of mass action (Oswald's dilution law) to above reaction and H_2Oconcentr ation is taken as constant.

$$K_h = \frac{[BOH]\,[H^+]}{[B^+]} \qquad \text{....................................}$$

The other equilibrium involved in this hydrolysis are,

$$H_2O \xrightleftharpoons{K_w} H^+ + OH^-$$

$$BOH \xrightleftharpoons{K_b} B^+ + OH^-$$

Applying law of mass action.

$$K_w = [H^+]\,[OH^-] \text{ ....} \quad ②$$

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \text{ ....} \quad ③$$

Dividing ② by ③

$$\frac{K_w}{K_a} = \frac{[H^+][OH^-][BOH]}{[B^+][OH^-]}$$

$$= \frac{[H^+][BOH]}{[B^+]}$$

Comparing equation ④ with ?

Degree of hy c

$$\boxed{K_h = \frac{K}{K}}$$

Consider hydrolysis of salt ‘BA’ here C is mole/litre, x is degree of hydrolysis

	$B^+ + H_2O$	$\rightleftharpoons$	BOH	$+ H^+$
Initial concentration	C		0	0
At equilibrium Conc,	C (1 - x)		C x	C x

$$K_h = \frac{[BOH]\,[H^+]}{[B^+]}$$

$$= \frac{Cx \,.\, Cx}{C(1-x)}$$

$$K_h = \frac{Cx^2}{1-x}$$ if x is very small (1- x) is taken as unit.

$K_h = Cx^2$

$x = \sqrt{\frac{K_h}{C}}$ But $K_h = \frac{K_w}{K_b}$

$$\boxed{\therefore x = \sqrt{K}}$$

P^H of aqueous salt solutions (Hydrogen ion concentration)

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

Equilibrium Conc, $C(1-x)$ Cx Cx

$[H^+] = Cx$

Sub. The value of x

$$[H^+] = c\sqrt{\frac{K_w}{K_b \cdot C}} \qquad \therefore x = \sqrt{\frac{K_w}{K_b \cdot}}$$

$$[H^+]^2 = c^2 \times \frac{K_w}{K_b \cdot C}$$

$$[H^+]^2 = \frac{K_w \cdot C}{K_b}$$

$$[H^+] = \sqrt{\frac{K_w \cdot}{C}}$$

Taking logarithm on both sides

$$\log [H^+] = \frac{1}{2}\log K_w + \frac{1}{2}\log C - \frac{1}{2}\log K_b$$

Multiple by ⊖ on both sides

$$-\log [H^+] = -\frac{1}{2}\log K_w - \frac{1}{2}\log C + \frac{1}{2}\log K_b$$

$$P^H = \frac{1}{2}P^{K_w} - \frac{1}{2}\log C - \frac{1}{2}P^{K_b}$$

$$P^H = 7 - \frac{1}{2}\log C - \frac{1}{2}P^{K_b}$$

From the above equation shows that the solution $P^H < 7$, Hence the solution will be acidic in nature.

4) Salts of Weak acid and Weak bases:

Ex: CH_3COONH_4

Hydrolysis constant

This kind of salts BA both cation and anion will undergo hydrolysis.

$$\overset{+}{B} + \overset{-}{A} + H_2O \overset{K_h}{\rightleftharpoons} \underset{\text{weak base}}{BOH} + \underset{\text{weak acid}}{HA}$$

Applying the law of mass action and concentration of water is constant.

$$K_h = \frac{[BOH]\,[HA]}{[B^+][A^-]}$$

The other equilibrium involved in this hydrolysis are,

$$HA \overset{K_a}{\rightleftharpoons} H^+ + A^- \quad ; \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

$$BOH \overset{K_b}{\rightleftharpoons} B^+ + OH^- \quad ; \quad K_b = \frac{[B^+][OH^-]}{[BOH]}$$

$$H_2O \overset{K_w}{\rightleftharpoons} H^+ + OH^- \quad ; \quad K_w = [H^+]\,[OH^-]$$

$$\frac{K_w}{K_a \cdot K_b} = \frac{\cancel{[H^+]}\cancel{[OH^-]}[HA][BOH]}{\cancel{[H^+]}[A^-][B^+]\cancel{[OH^-]}}$$

$$= \frac{[HA][BOH]}{[A^-][B^+]} \quad \therefore \; K_h = \frac{[BOH]\,[HA]}{[B^+][A^-]}$$

$$\boxed{\mathbf{\frac{K_w}{K_a.K}} \; =}$$

Degree of hydrolysis

Let 'C' moles/litre be concentration of salt and x is the degree of hydrolysis then,

	$\overset{+}{B}$	+ $\overset{-}{A}$	+ $H_2O \rightleftharpoons$	BOH	+ HA
Initial conc.	C	C		0	0
Equilibrium conc.	C (1 -x)	C (1 -x)		C x	C x

$$K_h = \frac{\cancel{C}x \cdot \cancel{C}x}{\cancel{C}(1-x)\ \cancel{C}(1-x)}$$

$$= \frac{x^2}{(1-x)^2}$$ Since x is small, it is negligible

$$K_h = x^2$$

$$\mathbf{x = \sqrt{K_h}}$$

$$\boxed{\mathbf{x = \sqrt{\frac{K_w}{K_a.K}}}}$$

P^H of aqueous salt solutions (Hydrogen ion concentration) Consider the hydrolysis of a salt of weak acid and weak base,

$$B^+ + A^- + H_2O \rightleftharpoons BOH + HA$$

Equilibrium conc.	$C(1-x)$	$C(1-x)$	Cx	Cx

H^+ion concentration determined from ionization of HA,

$$HA \overset{K_a}{\rightleftharpoons} H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$[H^+] = \frac{K_a [HA]}{[A^-]} \text{ ....}$$

$[HA] = Cx$ $[A^-] = C(1-x)$

Substituting in Equ.

$$[H^+] = K_a \cdot \frac{\cancel{C}x}{\cancel{C}(1-x)}$$

$$= \frac{K_a \cdot x}{1-x}$$ Since x is very small, it is negligible

$$[H^+] = K_a . x$$

$$= K_a \cdot \sqrt{\frac{\mathbf{K_w}}{\mathbf{K_a.}}}$$

$$[H^+]^2 = K_a^{2} \cdot \frac{K_w}{\cancel{K_a} \cdot K_b}$$

$$[H^+] = \sqrt{\frac{\mathbf{K_a \cdot K_w}}{\mathbf{K_b}}}$$

Taking log and multiply by -1

$$-\log [H^+] = -\log K_w^{\frac{1}{2}} - \log K_a^{\frac{1}{2}} - \log K_b^{\frac{1}{2}}$$

$$P^H = \frac{1}{2}P^{K_w} + \frac{1}{2}P^{K_a} - \frac{1}{2}P^{K_b}$$

$$P^H = 7 + \frac{1}{2}P^{K_a} - \frac{1}{2}P^{K_b}$$

Thus, the P^H of the solution depends on P^{K_a} and P^{K_b} values. If P^{K_a} and P^{K_b} are equal, then the $P^H = 7$. Hence the solution will be neutral.

PRACTICE QUESTIONS:

1. Evaluate the Applications of Conductometric Measurements
2. Explain Degree of Dissociation of Weak Electrolytes
3. Derive Henderson equation.
4. Discuss about Applications of Buffer Solutions
5. Give Expressions for Hydrolysis Constant

Reference Books :

1. Principles of Physical Chemistry - B. R. Puri, Sharma and Madan S. Pathania, 78 Vishnal Publishing Co., - 2013.
2. Text Book of Physical Chemistry - P. L. Soni, O. P. Dharmarha and U. N Dash - Sultan Chand & Co., - 2006.
3. Physical Chemistry - Negi and Anand - Eastern Wiley Pvt.Ltd..
4. Physical Chemistry - Negi and Anand - Eastern Wiley Pvt.Ltd..
5. Physical Chemistry - Kundu and Jain - S. Chand & Co.

Web source :

1. https://www.pdfdrive.com/modern-electrochemistry-e34333229.
2. http://xrayweb.chem.ou.edu/notes/symmetry.html.
3. http://www.uptti.ac.in/classroom-content/data/unit%20cell.pdf.