# Ionic Equilibrium

1. INTRODUCTION

☞ Those compounds which can conduct electricity either in fused state or in solution state in any solvent are called Electrolytes.

☞ Compounds which contain ions in pure solid state and can conduct electricity in the pure liquid state are called True electrolytes e.g. NaCl, KCl etc.

☞ Compounds which do not conduct electricity in fused state but their solution in a solvent can conduct electricity are called potential electrolytes e.g. HCl, CH_3COOH, NaOH, NH_4OH etc.

There are two types of electrolytes –

(a) Strong Electrolytes : Compounds which completely ionised in aqueous solution and are good conductor of electricity e.g. HCl, H_2SO_4, HNO_3, NaOH, KOH, CH_3COONa, NH_4Cl etc. (α = 100%)

(b) Weak Electrolytes : Compounds which ionise partially in aqueous solution and are poor conductor of electricity e.g. CH_3COOH, HCN, NH_4OH, $Al(OH)_3$ etc. (α < 100%)

☞ Those compounds which do not conduct electricity either in fused state or their solution in any solvent are called Non Electrolytes.

2. ARRHENIUS THEORY

(1) When an electrolyte is dissolved in water it breaks into oppositely charged i.e. cations and anions this process is called ionisation.

(2) The solution is electrically neutral, so the number of positive charge is equal to the number of negative charge.

(3) Process of ionisation is reversible. An equilibrium is established between ionised and unionised electrolyte. Hence law of mass action can be applied to this equilibrium
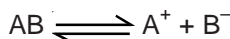
$$AB \rightleftharpoons A^+ + B^-$$

$$K_1 = \frac{[A^+][B^-]}{[AB]}$$

K_1 is called ionisation constant or dissociation constant.

(4) Electricity does not help in ionisation of electrolyte. It only causes migration of cation of cathod & anion to anode.

(5) The fraction of total amount of an electrolyte which gets ionised is called its degree of ionisation or degree of dissociation

$$\alpha = \frac{\text{No. of moles of electrolyte ionised}}{\text{Total no of moles before ionisation}}$$

(6) The equivalent conductance of a solution depends upon the number of ions and their charge in solution.

(7) The properties of solution governed by the ions present in the solution i.e. colour of solution.

(8) The colligative properties are effected by ionisation and depend upon number of cations and anions in the solution.

Note: (i) α is always less than 1

(ii) Degree of dissociation is assumed 100% at infinite dilution.

3. LIMITATIONS OF ARRHENIUS THEORY

(a)   Arrhenius explained the conductivity of ionic compound in aqueous solution or in presence of solvent only (i.e. presence of solvant is must) while ionic compounds in fused state form conductive liquids.

(b)   The increase of equivalent conductance for strong electrolytes is not due to increase in number of ions but due to the increase in ionic mobility with dilution.

Ionic mobility = speed of ions/potential gradient

(c)   Strong electrolytes do not obey Ostwald dilution law.

4. OSTWALD DILUTION LAW

Strong electrolytes are almost completely ionised, but the weak electrolytes are partially ionised. Therefore, Ostwald put forward the law for weak electrolytes.

Degree of ionisation can be determined by applying the law of mass action on dilute solutions of weak electrolytes. On the basis of that, equilibrium constant and ionisation constant can be determined.

Take an example of dissociation of a weak acid HA, which takes place as follows.

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

| 1 | 0 | 0 | Initial mole |
| $1 - \alpha$ | α | α | mole at equilibrium |
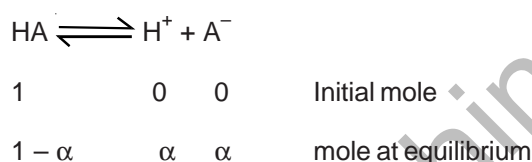
If volume is v, then

| $\dfrac{1-\alpha}{v}$ | $\dfrac{\alpha}{v}$ | $\dfrac{\alpha}{v}$ | concentration at equilibrium |

Therefore, $K_a = \dfrac{\left[H^+\right]\left[A^-\right]}{\left[HA\right]} = \dfrac{\alpha}{v} \times \dfrac{\alpha}{v} \times \dfrac{v}{1-\alpha}$

$$K_a = \dfrac{\alpha^2}{(1-\alpha)v}$$

K_a is called dissociation constant of the weak acid. Value of α is very low for weak electrolytes, thus $1 - \alpha = 1$. Then

$$K_a = \dfrac{\alpha^2}{v}$$

$$\alpha^2 = K_a \times v$$

$$\alpha \propto \sqrt{v} \text{ or } \alpha \propto \sqrt{\dfrac{1}{C}}$$

(a)   Therefore degree of ionisation of any substance is proportional to the square root of dilution. Thus degree of ionisation increases when dilution is increased. A substance tends to get completely ionised on infinite dilution.

(b)   Degree of ionisation increases on decreasing concentration.

$\Rightarrow$ Application of Dilution Law : Dissociation constant 'K' and molar conscentration 'c' of the electrolyte being known, 'α' can be calculated by using the relation.

☞ **Example :**

1. Ostwald dilution law may be applied to the solution of -

(1) HNO_3 (2) CH_3COOH (3) H_2SO_4 (4) HCl   **Ans. [2]**

2. Ostwald's dilution law is not applicable to strong electrolytes because –

(1) Strong electrolytes are completely ionised

(2) Strong electrolytes are volatile

(3) Strong electrolytes are unstable

(4) Strong electrolytes often contain metal ions   **Ans. [1]**

5. FACTORS RESPONSIBLE FOR DEGREE OF IONISATION

(1) **Dilution :**

When dilution is increased in a weak electrolyte, the degree of ionisation increases and at infinite dilution any substance gets almost completely ionised.

(2) **Temperature :**

Increase of temperature increases the degree of ionisation, and decrease of temperature decreases the degree of ionisation.

Kinetic energy of ions increases on increasing temperature and attractive forces between oppositely charged ions become less.

(3) **Nature of solute :** Ionic character of electrolyte increase than 'α' increase.e.g. strong acid and base is totally ionised.

(4) **Nature of Solvent :**

Degree of ionisation depends on the nature of solvent. Solvent molecules weakening the forces of attraction is called dielectric constant. Higher the polarity of the solvent molecule, more is its dielectric constant. Thus degree of ionisation of an electrolyte is high in a solvent of high dielectric constant.

Degree of ionisation of a compound in different solvents is different, because their dielectric constant are different.

(5) **presence of common ions :** The extent or degree of dissociation of an electrolyte is lowered in the presence of a strong electrolyte having a common ion.

☞ **Example :**

1. Degree of ionization increases with

(1) decreases in dilution   (2) decreases in temperature

(3) increase in temperature   (4) increase in concentration   **Ans. [3]**

2. Conductivity of an weak electrolyte solution with dilution -

(1) increase   (2) decrease   (3) no change   (4) none   **Ans. [1]**

3. Conductivity of strong electrolyte solution with dilution

(1) Increase   (2) Decrease

(3) First increase then decrease   (4) No change   **Ans. [2]**

6. IONIC PRODUCT OF WATER

Water is a weak electrolyte, which gets ionised to H^+ and OH^- to a very low extent.
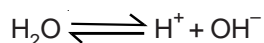
$$H_2O \rightleftharpoons H^+ + OH^-$$

According to law of mass action

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

Here K is called ionisation constant of water.

Therefore, $K[H_2O] = [H^+][OH^-]$

$$K_W = [H^+][OH^-] \qquad \text{Here} \qquad K_W = K[H_2O]$$

K_W is called ionic product of water.

In pure water, $\qquad\qquad [H^+] = [OH^-]$

$$\qquad\qquad\qquad 10^{-7} \quad 10^{-7}$$

Value of ionic product of water K_W is 1.0×10^{-14} at 25° C

Value of K_W depends on temperature. Value of K_w increases with increase in temperature and decreases with decrease in temperature.

Sp. Point :

Effect of Tempereature

$$T\uparrow \rightarrow K_w\uparrow$$
$$T\uparrow \rightarrow K\uparrow \qquad\qquad\qquad\qquad\qquad -\log[H^+] = pH$$
$$K_w = [H^+][OH^-] \qquad\qquad\qquad\qquad -\log[OH^-] = pOH$$
$$-\log K_w = -\log\big[[H^+][OH^-]\big] \qquad\qquad -\log K_w = pk_w$$
$$-\log K_w = -\log[H^+] - \log[OH^-]$$
$$pk_w = pH + pOH$$

Effect of tempreature on K_w

Temp.	K_w
0°C	0.3×10^{-14}
25°C	1×10^{-14}
50°C	5.3×10^{-14}
90°C	100×10^{-14}

On 25°C   **pH + pOH = 14**   ⟹ **7 Neutral pH**

On 90°C   **pH + pOH = 12**   ⟹ **6 Neutral pH**

For water increasing the temp. $\Rightarrow \alpha\uparrow$, $K_w\uparrow$, $K\uparrow$, $pH\downarrow$, $pOH\downarrow$

☞ **Example :**

1. K_w of H_2O is increased by -
(1) decreasing P
(2) increasing P
(3) increasing temp.
(4) addition of H^+

Ans. [3]

7. CLASSIFICATION OF SALTS

Salt : A substance which ionises in water to produce ions other than H^+ and OH^- is called a salt. Salts are produced by the neutralisation reaction.

(a) **Normal salt :**

In case the acid and base neutralise completely the salt formed is a normal salt. In case both acid and base are strong or weak, the salt is neutral, when the constituent acid is strong, the salt is acidic and when the constituent base is strong, the salt is alkaline.

Example : $NaCl$, Na_2HPO_3, Na_3PO_4, NaH_2PO_2 and KNO_3 .

(b) **Acidic salt :** If a polybasic acid (e.g., H_2SO_4, H_3PO_4, H_2SO_3 etc.) is neutralised partially by a base, the salt formed is acidic.

Examples : $NaHSO_3$, $NaHCO_3$, NaH_2PO_4, $Ca(H_2PO_4)_2$ etc.

(c) **Basic salt :** If a polyacidic base [e.g $Ba(OH)_2$, $Bi(OH)_3$,$Fe(OH)_3$ etc.] is neutralised partially by an acid, the salt formed is basic salt.

Example : $Mg(OH)Cl$, $Zn(OH)Cl$, $Al(OH)Cl_2$, $Pb(OH)NO_3$, $Ba(OH)Cl$, $Bi(OH)_2Cl$, $Ca(OH)Cl$, etc.

(d) **Mixed salt :** Salts formed by the simultaneous neutralisation of one acid by two bases or one base by two acids are called mixed salts.

Example : $NaKSO_4$, $ZnBrCl$, $Al(Cl_2)Br$, $Al(NO_3)Cl.Br$, $Ca(OCl)Cl$ etc.

(e) **Double salt :** A compound of two salts whose solution gives tests for all the constituent ions is called a double salt or lattice complex .

Example : $FeSO_4.(NH_4)_2SO_4.6H_2O$, $[K_2SO_4.Al_2(SO_4)_3.24H_2O]$

(f) **Complex salt :** A compound whose solution does not give tests for the constituent ions is called a complex salt, e.g., $K_4[Fe(CN)_6]$.

Strong Acid	Weak Acid	Strong Base	Weak Base
$HClO_4$	all $R-COOH$	$NaOH$	$LiOH$
H_2SO_4	$HCOOH$	KOH	$Be(OH)_2$
HNO_3	CH_3COOH	$RbOH$	$Mg(OH)_2$
HCl, HI, HBr	C_2H_5OH	$CsOH$	$Ca(OH)_2$
Picric Acid	H_2S	$Ba(OH)_2$	$Sr(OH)_2$
H_2PtCl_6	HCN		NH_4OH
H_2AuCl_6	H_2CO_3		$Zn(OH)_2$
	$\begin{matrix} COOH \\ | \\ COOH \end{matrix}$		$Al(OH)_3$
	H_3PO_4		$AgOH$
	H_3PO_3		
	H_2PO_3		
	$B(OH)_2$		

☞ **Example :**

1. Which one is not an basic salt

(1) COOH – COONa   (2) HCOONa   (3) $NaHSO_4$ (4) NaH_2PO_4 **Ans. [3]**

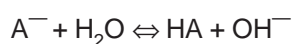## 8. HYDROLYSIS OF SALT OF WEAK ACID AND STRONG BASE

☞ Let AB be salt i.e. HA is weak acid and BOH is strong base.

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

After hydrolysis BOH will again get ionised to give B^+ and OH^- ions

$$BOH \Leftrightarrow B^+ + OH^-$$

Thus only A^- ions are hydrolysed to give weak acid HA & OH^- ions. This is known as Anionic Hydrolysis

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

$$K_h = \frac{[AH][OH^-]}{[A^-]} \qquad .....(1)$$

Weak acid HA further ionised partially and set a reversible equation formally to attain equilibrium
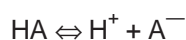
$$HA \Leftrightarrow H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad .....(2)$$

Eq. (1) and (2)

$$K_h = \frac{K_w}{K_a}$$

☞ As earlier, let C was the concentration (mole lit^{-1}) taken initially and 'h' be the degree of hydrolysis (mole ionised per mole of salt) then,

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

C   0   0   (initially)

C(1 – h)   Ch   Ch   (at equilibrium)

$$K_h = \frac{[AH][OH^-]}{[A^-]} = \frac{Ch.Ch}{C(1-h)} = \frac{Ch^2}{1-h}$$

if   h <<< 1 so 1 – h ≈ 1

$$\Rightarrow \qquad K_h = Ch^2 \quad \Rightarrow h = \sqrt{\frac{K_h}{C}}$$

$$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_W}{K_a.C}}$$

$$[OH^-] = Ch = C\sqrt{\frac{K_W}{K_a.C}} = \sqrt{\frac{K_W.C}{K_a}}$$

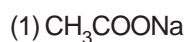$$pOH = \left[7 - \frac{1}{2}pK_a - \frac{1}{2}\log C\right] < 7$$

$$pH = 14 - pOH$$

$$pH = \left[7 + \frac{1}{2}pK_a + \frac{1}{2}\log C\right] > 7$$

☞ Solution will be basic

☞ Hydrolysis is anionic.

☞ P^H of solution is > 7.

☞ Red litmus change in to blue litmus.

☞ **Example :**

1. Which of the following salt how anionic hydrolysis

(1) CH_3COONa　　　(2) NaCl　　　(3) KCl　　　(4) All　　　**Ans. [1]**

9. HYDROLYSIS OF SALT OF A STRONG ACID AND A WEAK BASE

$[NH_4Cl, NH_4NO_3, (NH_4)_2SO_4]$

☞ Let AB be salt, HA is strong acid and BOH is weak base.

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

Only B^+ ion is hydrolysed so it is known as cationic hydrolysis.

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

$$K_h = \frac{[BOH][H^+]}{[B^+]} \qquad ....(1)$$

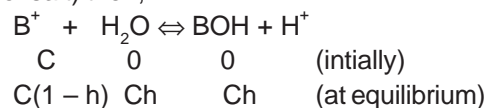☞ Weak base BOH further ionised partially and set a reversible equation formally to attain equilibrium
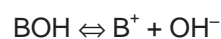
$$BOH \Leftrightarrow B^+ + OH^-$$

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad ....(2)$$

$$K_w = [H^+][OH^-] \qquad ....(3)$$

By eq. (1), (2) and (3)

$$K_h = \frac{K_w}{K_b}$$

☞ As earlier , let C was the concentration (mole lit^{-1}) taken initially and 'h' be the degree of hydrolysis (mole ionised per mole of salt) then,

$$B^+ \; + \; H_2O \Leftrightarrow BOH + H^+$$

$$\quad C \qquad 0 \qquad 0 \qquad \text{(intially)}$$

$$C(1-h) \quad Ch \qquad Ch \qquad \text{(at equilibrium)}$$

$$K_h = \frac{[BOH][H^+]}{[B^+]} = \frac{Ch.Ch}{C(1-h)}$$

$$K_h = \frac{Ch^2}{1-h}$$

if h <<< 1 so $1 - h \approx 1$

$$\Rightarrow \qquad K_h = Ch^2 \Rightarrow h = \sqrt{\frac{K_h}{C}}$$

$$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_W}{K_b.C}}$$

$$[H^+] = Ch = C\sqrt{\frac{K_w}{K_b \times C}} = \sqrt{\frac{K_w \times C}{K_b}}$$

$$pH = \left[7 - \frac{1}{2}pK_b - \frac{1}{2}\log C\right] < 7$$

Result :   Hydrolysis is cataionic
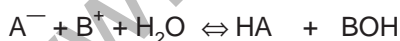
Nature of solution is acidic.

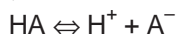pH of solution is less than 7.

Blue litmus change into red litmus.

10. HYDROLYSIS OF SALT OF A WEAK ACID AND A WEAK BASE

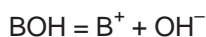☞ Let AB be salt i.e. HA and BOH both are weak acid and weak base respectively.

☞ Here both A$^-$ and B$^+$ ions will get hydrolysed because neither of HA and BOH are completely ionisable.

$$A^- + B^+ + H_2O \Leftrightarrow HA \; + \; BOH$$

$$K_h = \frac{[HA][BOH]}{[A^-][B^+]} \qquad \qquad .....(1)$$

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

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \qquad .....(2)$$

$$BOH = B^+ + OH^-$$

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad \qquad .....(3)$$

From equation (1), (2) & (3) we have

$$K_h = \frac{K_W}{K_a.K_b}$$

☞   Let degree of hydrolysis be h

$$A^- \quad + \quad B^+ \quad + \quad H_2O \quad \Leftrightarrow \quad AH \quad + \quad BOH$$

$$C \qquad\quad C \qquad\qquad\qquad\qquad 0 \qquad\qquad 0$$
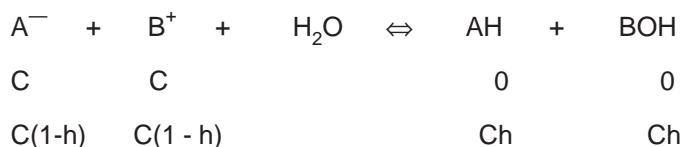
$$C(1-h) \quad C(1-h) \qquad\qquad Ch \qquad\quad Ch$$

$$K_h = \frac{Ch.Ch}{C(1-h).C(1-h)} = \frac{h^2}{(1-h)^2}$$

$$K_h = \frac{h^2}{(1-h)^2}$$

if $h <<< 1$

$$K_h = h^2 \Rightarrow h = \sqrt{K_h}$$

$$h = \sqrt{\frac{K_W}{K_a.K_b}}$$

☞   It is very important to note that here degree of hydrolysis is independent of concentration of salt taken initially. It just depends upon K_a and K_b.

☞   h increases on increasing temperature.

As,

$$HA \quad \Leftrightarrow \quad A^- + H^+$$

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

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

$$\Rightarrow \qquad [H^+] = K_a \cdot \sqrt{\frac{K_W}{K_a.K_b}} = \sqrt{\frac{K_W.K_a}{K_b}}$$

$$[H^+] = \left(\frac{K_w.K_a}{K_b}\right)^{½}$$

$$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

☞   **Conclusions :**

(i)

Condition	Behaviour of solution	P^H	Hydrolysis
$K_b > K_a$	basic	> 7	anionic
$K_a > K_b$	acidic	< 7	cataionic
$K_a = K_b$	neutral	= 7	neutral

☞   **Example :**

1.   Calculate the hydrolysis constant of analinium acetate if $K_a = 1 \times 10^{-5}$ and $K_b = 1 \times 10^{-10}$

(1) 1.24   (2) 10   (3) .1   (4) .01   **Ans. [1]**

## 11. HYDROLYSIS OF A SALT OF STRONG ACID & STRONG BASE

☞ Here HA and BOH both are strong acid and strong base respectively.

☞ As A^- will get hydrolysed to HA, HA will again get ionised in to A^- ions. The same thing happens with B^+ ions so hydrolysis of both A^- and B^+ ions is not possible.

☞ Also after coming into solution A^- and B^+ ions do not have tendency to react with each other they want to remain free so only A^- and B^+ are present in solution.

Result :

☞ The solution of such salts remain neutral, ie. pH = 7

☞ It is not a process of hydrolysis.

☞ No effect on litmus.

☞ **Example :**

1. Which salt is not hydrolysed in aqueous solution
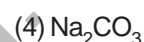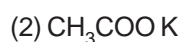
(1) $NaNO_3$ (2) $CH_3COO K$ (3) NH_4Cl (4) Na_2CO_3 **Ans. [1]**

12. SOLUBILITY & SOLUBILITY PRODUCT

❖ **Solubility :**

☞ At a constant temperature the mass of a solute present in 100g of solvent in its saturated solution is called its Solubility

☞ In numerical question, solubility of a substance is expressed in mole lit^{-1} it is number of moles of solute present in one litre of solvent in saturated solutions.

$$\text{Number of moles} = \frac{\text{amount in grams}}{\text{mol wt. in grams}}$$

$$\text{Solubility} = \frac{\text{Number of moles}}{\text{Litres of the solution}}$$

❖ **Solubility Product :**

Definition : Solubility product of a sparingly soluble electrolyte is equal to the product of ionic concentrations in a saturated solution at a given temperature.

☞ Let solubility of a compound A_xB_y be s mol lit^{-1} it means that if more than s moles are dissolved in solvent(one litre) only s moles will be soluble, rest will be insoluble following equilibrium is established.

| AB	⇔	AB	⇔	A^+	+	B^-
Insoluble		unionised solute		Ions		
Solute				(saturated solution)		
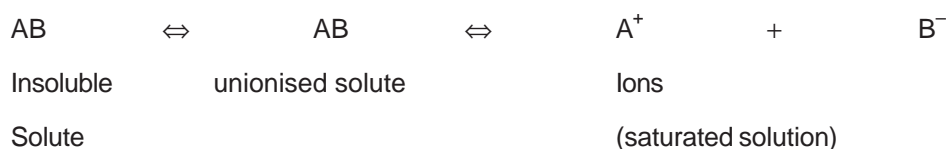
☞ K_{sp} increases with increase in temperature

(1) In a saturated solution $K_{sp} = [A^+][B^-]$

(2) In an unsaturated solution of AB, $K_{sp} > [A^+][B^-]$ i.e. more solute can be dissolved.

(3) In a super saturated solution $K_{sp} < [A^+][B^-]$ i.e precipitation will start to occur.

☞ Ionisation of compound A_xB_y may be shown as $A_xB_y \Leftrightarrow xA^{y+} + yB^{x-}$

$K_{sp} = [A^{y+}]^x[B^{x-}]^y$

☞ Let solubility of compound A_xB_y is s mol lit^{-1} equilibrium

$$A_xB_y \Leftrightarrow xA^{y+} + yB^{x-}$$
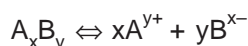
$$s \qquad xs \quad ys$$

$$K_{sp} = (xs)^x(ys)^y$$

$$K_{sp} = X^x y^Y s^{x+y}$$

(a) For AB type [ex. $AgCl$, $PbSO_4$, $BaSO_4$] $\qquad K_{sp} = s^2$

(b) For AB_2 or A_2B type [ex. $PbCl_2$, $CaCl_2$, Na_2SO_4, $Pb(NO_3)_2$] $\quad K_{sp} = 4s^3$

(c) For A_3B or AB_3 type [ex. $AlCl_3$, $FeCl_3$, Na_3PO_4] $\qquad K_{sp} = 27s^4$

(d) For A_3B_2 or A_2B_3 type [ex. $Al_2(SO_4)_3$, $Ba_3(PO_4)_2$] $\qquad K_{sp} = 108\, s^5$

☞ **Example :**

1. The amount of water needed to dissolve 1 gm of $BaSO_4$ [$K_{SP} = 1.0 \times 10^{-10}$] at 25^0C is

   (1) 830 litre   (2) 429 litre   (3) 210 litre   (4) None   **Ans. [2]**

2. If solubility of Ag_3PO_4 is C moles / litre, the K_{SP} is given by the expression

   (1) C^2 (2) $3C^2$ (3) $27C^4$ (4) $9C^4$ **Ans. [3]**

3. The solubility product of aluminium sulphate [$Al_2(SO_4)_3$] is given by the expression

   (1) $K_{sp} = [Al^{3+}]\, [SO_4^{2-}]$ (2) $K_{sp} = [Al^{3+}]^2\, [SO_4^{2-}]^3$

   (3) $K_{sp} = [Al^{3+}]\, [SO_4^{2-}]^3$ (4) $K_{sp} = [Al^{3+}]\, [SO_4^{2-}]^2$ **Ans. [2]**

4. Select the carbonate which is least soluble in water

   (1) $Fe\,CO_3\ K_{sp} = 2.0 \times 10^{-11}$ (2) $Pb\,CO_3\ K_{sp} = 1.0 \times 10^{-13}$

   (3) $Ca\,CO_3\ K_{sp} = 4.8 \times 10^{-9}$ (4) $Ba\,CO_3\ K_{sp} = 5.0 \times 10^{-6}$ **Ans. [2]**

13. APPLICATION OF K_{sp}

(1) In purification of common salt :

In a saturated solution of NaCl & impurities, by passing HCl gas through it increase the Cl^- ion concentration which shifts the equilibrium $NaCl \Leftrightarrow Na^+ + Cl^-$ to left & causes the precipitation of NaCl

(2) In preparation of $NaHCO_3$ by solvay method :

Precipitation of $NaHCO_3$ from it's saturated solution is done by eddition of NH_4HCO_3, HCO_3 as common ion.

(3) Predicting precipitation in ionic reaction :

Preciptation in an ionic reactions could be predicted by compairing K_{sp} to the ionic concentration product of ions

(4) Salting out action of soap :

When NaCl is added to saturated solution of soap (RCOONa) concentration of Na^+ increases & causes to precipitation of soap it is due to $[Na^+][RCOO^-] > K_{sp}$

(5) **In qualitative analysis :**

Qualitative analysis of mixtures is based on the principle of solubility product. Some important applications are as follows :

Group	Radiacal	Condition of Precipitate
Zero	NH_4^+, K^+, Na^+	dissolve 1,2 drop of CH_3COOH solution
Ist	Ag^{+2}, Pb^{+2}, Hg_2^{+2}	dissolve dil. HCl, precipited as Cl^{-1}
IInd	IIA = Cu^{+2}, Cd^{+2}, Bi^{+3}, Hg^{+2}, Pb^{+2}	presence of HCl in acidic medium precipited as S^{-2}
	IIB = As^{+3}, Sb^{+3}, Sn^{+2}, Sn^{+4}	dissolve H_2S
IIIrd	Fe^{+3}, Al^{+3}, Cr^{+3}	in presence of NH_4Cl dissolve NH_4OH precipited as OH^-
IV	Mn^{+2}, Ni^{+2} Co^{+2}, Zn^{+2}	precence of H_2S, in basic medium precipited as S^{-2}
V	Ba^{+2}, Sr^{+2}, Ca^{+2} (BSC)	presence of NH_4Cl dissolve $(NH_4)_2CO_3$, precipited as CO_3^{-2}
VI	Mg^{+2}	dissolve Na_24Po_4 precipited as HPo_4^{-2}

☞ **Example :**

1. An acidic solution containing Zn^{+2}, Cu^{+2}, Cd^{+2} & Ni^{+2} on passing H_2S gas which will give ppt

(1) Cu^{+2}, Cd^{+2} (2) Zn^{+2}, Ni^{+2}

(3) Cu^{+2}, Zn^{+2} (4) Zn^{+2}, Cd^{+2}, Cu^{+2}, Ni^{+2} **Ans. [1]**

2. The precipitation of soap by adding common salt is called

(1) saponification   (2) purification of soap

(3) salting out of soap   (4) 1 & 3 both   **Ans. [2]**

3. Addition of ammonium chromate to a ammonical solution containing Ba^{+2}, Sr^{+2}, Ca^{+2} resulting ppt. of-

(1) Ba^{+2} (2) Ba^{+2}, Sr^{+2} (3) Ba^{+2}, Sr^{+2}, Ca^{+2} (4) Sr^{+2}, Ca^{+2} **Ans. [4]**

4. Correct order of solubility product is –

(1) $CaCrO_4 > SrCrO_4 > BaCrO_4$ (2) $BaCrO_4 > SrCrO_4 > CaCrO_4$

(3) $CaCrO_4 > BaCrO_4 > SrCrO_4$ (4) $SrCrO_4 > BaCrO_4 > CaCrO_4$ **Ans. [1]**

☞ **Precipitation of II group radicals :** Group reagent is H_2S. In presence dilute HCl the ionic product of H_2S is suppressed due to common ion(H^+) and only ionic product of the sulphides of II radicals exceeds their solubility product and get precipitated.

II and IV precipitated $H_2S \rightleftharpoons 2H^+\downarrow + S^{-2}\downarrow$ common ion effect.

$$K_{spII} < [\quad][\quad] < K_{spIV}$$

☞ **Precipitation of IV group radicals :** Group reagent is H_2S in presence of NH_4OH. The presence of NH_4OH enhances the dissociation of H_2S. Thus due to high ionisation of H_2S the concentrations of S^{-2} ions increases and ionic product of sulphides of IV group radicals exceeds corresponding solubility product and get precipitated.

☞ **Precipitation of III group radicals :** Group reagent is NH_4OH in presence of NH_4Cl the presence of NH_4Cl suppresses the ionisation of NH_4OH, NH_4^+ as common ion. Thus the ionic product of hydroxides of III group radicals exceeds corresponding solubility products and get precipitated.

Solved Example :

Ex.1 Find out solubility of $AgCl_{(Ksp)}$ in solution of NaCl (conc. C)

Sol. $AgCl \rightleftharpoons Ag^+ + Cl^-$

First,   S   S   S

$K_{SP} = [Ag^+][Cl^-]$

$K_{SP} = S^2$

Later,

$AgCl \rightleftharpoons Ag^+ + Cl^-$ $NaCl \rightleftharpoons Na^+ + Cl^-$

S^1 $(S^1 + C)$ C   C

$K_{SP} = [S^1][S^1 + C]$

$K_{SP} = S^{1^2} + S^1C$

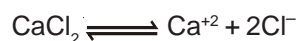$K_{SP} = S^1C$

$S^1 = \dfrac{K_{sp}}{C}$

Note : We take smallest power of S^1 and neglect the higher power.

Ex. 2 Find out solubility of KCl (K_{SP}) in solution of $CaCl_2$ (conc. C)

Sol. $KCl \rightleftharpoons K^+ + Cl^-$

  s   s   s

$K_{SP} = s^2$ $CaCl_2 \rightleftharpoons Ca^{+2} + 2Cl^-$

                                              C   C   2C

$KCl \rightleftharpoons K^+ + Cl^-$

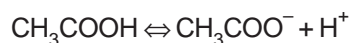s^1 $s^1 + 2C$

$K_{SP} = [s_1][s_1 + 2C]$

$K_{SP} = s_2^1 + 2s^1C$

$s^1 = \dfrac{K_{sp}}{2C}$

14. COMMON ION EFFECT

☞   If we consider ionisation of a weak electrolyte say, CH_3COOH, it ionises as :

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

$$K_a = \dfrac{\left[CH_3COO^-\right]\left[H^+\right]}{\left[CH_3COOH\right]}$$

☞ What do we mean by this equilibrium and this equilibrium constant ? A stage will come such that concentration of CH_3COOH, CH_3COO^- and H^+ will not get changed further, their concentrations on a definite mathematical calculation will give a constant called equilibrium constant which will remain constant at same temperature. It does not mean that reaction has stopped only concentration will remain same, ions will continue to change in molecule and molecule will continue to get ionised this is said to be Dynamic Equilibrium.

☞ Now suppose some how CH_3COO^- ions are added to the solution to increase CH_3COO^- ions concentration since mathematical calculation will tend to change itself to change that eq. constant, electrolyte (CH_3COOH) will do samething in order to keep K_a constant because it has to be a constant it will reduce its ionisation thus $[CH_3COOH]$ will increase, $[H^+]$ will decrease and K_a will remain constant.

☞ This is called Common ion Effect that if in a solution of weak electrolyte a solution of strong electrolyte with one of its common ion is added ionisation of weak electrolyte is suppressed.

15. APPLICATIONS OF COMMON ION EFFECT

☞ H_2S is used in presence of HCl as a group reagent for the analysis of second group. HNO_3 cannot be used because it oxidised H_2S to sulphur.

☞ NH_4OH and NH_4Cl are used as group reagent for the analysis of third group.

☞ Purification of common salt by passing HCl gas in a saturated solution of NaCl.

☞ Soap is precipitated from its solution by adding some NaCl.

☞ **Solubility of sparingly soluble in acids or bases :**

There are many salts of weak acids or weak bases which are almost insoluble in water but their solubility increases with decreasing P^H. The salts containing Carbonates, Phosphates, Fluorids acetates etc. are soluble at low P^H. The salts of weak bases similarly dissolve at higher P^H (low acidity) CaF_2 is insoluble in water but it goes into solution when some acid is added.

☞ **Example :**

1. Solubility of NaCl in heavy water is -

   (1) more than ordinary water   (2) less than ordinary water

   (3) same as ordinary water   (4) none of the above   **Ans. [1]**

2. The common ion effect is shown by which of the following sets of solutions –

   (1) $BaCl_2 + BaNO_3$ (2) NaCl + HCl   (3) $NH_4OH + NH_4Cl$ (4) None   **Ans. [3]**

Point to be remember :

1. type of write K_w

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

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

$$K_w = [H_3O^+]^2 = [H^+]^2 = [OH^-]^2$$

2. Conditon for isohydric for two weak acid

HA_1	HA_2
C_1	C_2
a_1	a_2
Ka_1	ka_2

$$[H^+] = \sqrt{Ka_1 C_1} \qquad\qquad [H^+] = \sqrt{Ka_2 C_2}$$

For isohydric :

$$[H^+]_1 = [H^+]_2$$

$$\sqrt{Ka_1 X C_1} = \sqrt{Ka_2 X C_2}$$

$$Ka_1 C_1 = Ka_2 C_2$$

Relative strength of two acid :

$$\frac{(acid)_1}{(acid)_2} = \frac{[H^+]_1}{[H^+]_2}$$

Strenth of two weak acid :

$$\frac{HA_1}{HA_2} = \frac{[H^+]_1}{[H^+]_2} = \frac{C_1\alpha_1}{C_2\alpha_2} = \sqrt{\frac{Ka_1 \times C_1}{Ka_2 \times C_2}} = \sqrt{\frac{Ka_1}{Ka_2}}$$

Ex. Strength of HCOOH [$Ka = 10^{-4}$] is how many times of HCN [$Ka = 10.6$] is ?

$$= \sqrt{\frac{Ka_1}{Ka_2}} = \sqrt{\frac{10^{-4}}{10^{-6}}} = 10 \text{ times}$$

❖ **Heat of neutrilisation :**

1. $S_A + S_B$ = Maximum heat

2. $S_A + W_B$ = Less

3. $W_A + W_B$ = Lessed

4. $H^+ + OH^- \longrightarrow H_2O + 13.6 \text{ Kcal}$

$\Rightarrow$ 13.6 × No. of Equivalent of water

Solved Example

Ex.1 What will be the value of K_w at 90ºC, if $[H^+]$ in pure water is 10^{-6} gram ion/litre?

(1) 10^{-10} (2) 10^{-16} (3) 1×10^{-12} (4) 2×10^{-6}

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

$[H^+]$ in pure water $= 10^{-6}$

$[OH^-] = 10^{-6}$

Therefore, $K_w = 10^{-12}$ **Ans. [3]**

Ex.2 Concentration of $[H^+]$ will decrease on mixing which of the following salts with the solution of acetic acid

(1) KCN   (2) NaCl   (3) NH_4Cl (4) $Al_2(SO_4)_3$

Sol. Solution of KCN is basic. Therefore, concentration of $[H^+]$ will decrease on mixing it with CH_3COOH and thus pH will increase.   **Ans.[1]**

Ex.3 Aqueous solution of $FeCl_3$

(1) turns blue litmus solution red   (2) turns red litmus solution blue

(3) decolourises litmus solution   (4) does not affect litmus solution

Sol. On dissolving $FeCl_3$ in water, it will give $Fe(OH)_3$, H^+ and Cl^-. Ionisation of $Fe(OH)_3$ will be low. Therefore, concentration of $[H^+]$ will be more than $[OH^-]$ in the solution, so the solution will be acidic and blue litmus solution will turn red.   **Ans.[1]**

Ex.4 When HCl gas is passed in saturated solution of common salt, then pure NaCl is precipitated, because

(1) Ionic product of Na^+ and Cl^- exceeds the solubility product of NaCl.

(2) HCl is highly soluble in water

(3) ionisation of NaCl is decreased due to chloride ions of HCl.

(4) HCl absorbs impurities.

Sol. Ionic product of Na^+ and Cl^- becomes more than the solubility product of NaCl.   **Ans.[1]**

Ex.5 Which of the following has maximum value of solubility product?

(1) $Fe(OH)_3$ (2) $Al(OH)_3$ (3) $Cr(OH)_3$ (4) $Zn(OH)_2$

Sol. In above, Fe Al and Cr are third group elements. Therefore, their solubility product is low, whereas Zn is of fourth group and therefore its solubility product is high.   **Ans.[4]**

Ex.6 Which of the following is true for aqueous solution of CH_3NH_2 of 0.1 M concentration

(1) $[OH^-] = 0.1M$ (2) pH = 0   (3) pH < 7   (4) pH > 7

Sol. CH_3NH_2 (an amine) is basic, therefore its pH will be greater than 7.   **Ans.[4]**

Ex.7 If pH of 0.1M acetic acid is 3.0, then dissociation constant of this acid will be

(1) 1×10^{-4} (2) 1×10^{-5} (3) 1×10^{-3} (4) 1×10^{-8}

Sol. $[H^+]$ 10^{-3}, pH = 3   C $= 10^{-1}$

$[H^+] = C.x$

$10^{-3} = 10^{-1} . x$

$x = \dfrac{10^{-3}}{10^{-1}} = 10^{-2}$, $K_a = Cx^2$

$K_a = Cx^2 = 10^{-1} \times 10^{-2} \times 10^{-2} = 10^{-5}$ **Ans.[2]**

Ex.8 Solution of which of the following will have maximum pH value?

(1) NaCl   (2) Na_2CO_3 (3) NH_4Cl (4) $NaHCO_3$

Sol. In above, Na_2CO_3 is most basic, therefore its pH value will be highest.   **Ans.[2]**

Ex.9 A precipitate will be obtained on mixing equal volume of which of the following solutions, if $K_{sp} = 1.8 \times 10^{-10}$?

(1) 10^{-4} M [Ag^+] and 10^{-4}M [Cl^-]   (2) 10^{-5} M [Ag^+] and 10^{-5}M [Cl^-]

(3) 10^{-6} M [Ag^+] and 10^{-6}M [Cl^-]   (4) 10^{-10} M [Ag^+] and 10^{-4}M [Cl^-]

Sol. Volume is increasing twice, therefore concentration will become half.

$$K_{sp} = [Ag^+][Cl^-]$$

Ionic product = $0.5 \times 10^{-4} . 10^{-4} \times 0.5 = 10^{-8} \times 0.25$

Solubility product = 1.8×10^{-10}

Ionic product > Solubility product, therefore precipitation will take place.   **Ans.[1]**

Ex.10 Which of the following are present in an aqueous solution of Na_2CO_3?

(1) H_2CO_3, Na^+, OH^- (2) H_2CO_3, OH^-

(3) CO_3^{-2} ion   (4) Na^+ and OH^- ion

Sol. $Na_2^+CO_3^- + 2H_2O \quad\quad 2Na^+ + 2OH^- + H_2CO_3$

$\quad\quad CO_3^{-2} + 2H_2O \quad\quad 2OH^- + H_2CO_3$ **Ans.[1]**

Ex.11 Why is NH_4Cl added before NH_4OH in qualitative analysis of third group ions?

(1) To increase concentration of OH^- (2) To decrease concentration of OH^-

(3) To make solution dilute   (4) For pure precipitation

Sol. To precipitate only the metal hydroxides of third group, NH_4Cl is added before NH_4OH in qualitative analysis, because the concentration of OH^- decreases due to common ion effect.   **Ans.[2]**

Ex.12 Why is the precipitate of calcium oxalate soluable in HCl.

Sol. H^+ of HCl converts $C_2O_4^{-2}$ to less ionised $H_2C_2O_4$, so the concentration of $C_2O_4^{-2}$ decreases and ionic product becomes less than solubility product. Therefore, it dissolve in HCl.   **Ans.[2]**

Ex.13 Zinc sulphide is precipitated on passing H_2S in the solution of zinc acetate, whereas no precipitate appears on passing H_2S in zinc chloride solution. Why?

Sol. $Zn(CH_3COO)_2 \quad\quad Zn^{+2} + 2CH_3COO^-$

$\quad\quad H_2S \quad\quad 2H^+ + S^{-2}$

On passing H_2S in zinc acetate, CH_3COOH is formed, due to which ionisation of H_2S increases and zinc sulphide gets precipitated. On passing H_2S in $ZnCl_2$, HCl and ZnS are formed and concentration of sulphide ion decreases so much that precipitation does not occur.   **Ans[2]**

Ex.14 What is the volume needed to make normality of the solution 3N, prepared by mixing 250 ml 6 M HCl and 350 ml 8M HNO_3?

(1) 833.3 ml   (2) 933.3 ml   (3) 1000 ml   (4) 500ml

Sol. $$N_1V_1 + N_2V_2 = N_3V_3$$
$$250 \times 6M + 350 \times 8 = 3N \times V_3$$
$$1500 + 280 = 3N \times V_3$$
$$V_3 = 1433.3 \text{ ml}$$

Volume $1433.3 - (250 + 350) = 833.3$ ml

Therefore, 833.3 ml water has to be mixed.   **Ans.[1]**

Ex.15 On dilution of a solution formed from CH_3COONH_4 and CH_3COOH,

(1) pH decreases   (2) pH increases   (3) pH remains unchanged   (4) None of the above

Sol. CH_3COONH_4 salt is made up of weak acid and weak base. Therefore, pH remains unchanged on diluting it, because it acts as an amphiresistant solution. **Ans.[3]**

Ex.16 Which of the following indicators is appropriate in the titration of NH_4OH and strong acid?

(1) Phenolphthalein   (2) Methyl orange   (3) Phenol red   (4) Litmus

Sol. In the titration of weak base and a strong acid, the resulting solution will be acidic. Therefore, methyl orgae is an appropriate indicator. **Ans.[2]**

Ex.17 What will be the mole fraction of acetone in the solution formed by 1.8 gram of water and 2.9 gram of acetone?

(1) $\dfrac{2}{3}$ (2) 2.9   (3) $\dfrac{1}{3}$ (4) $\dfrac{2.9}{4.7}$

Sol. 1.8g water = 0.1 g mole

2.9g acetone = $\dfrac{2.9}{58}$ = 0.05 g mole

Total mole = 1.5 g mole

Mole fraction of acetone = $\dfrac{0.05}{0.15}$ = $\dfrac{1}{3}$ **Ans.[3]**

Ex.18 Value of pK_a for acetic acid at 25^0C is 4.75, then what will be the pH value of the solution in which ratio of concentration of sodium acetate and acetic acid is 10?

(1) 3.75   (2) 4.75   (3) 5.75   (4) 10.0

Sol. pH = pK_a + log $\dfrac{[Salt]}{[Acid]}$ = 4.75 + log 10

pH = 5.75 **Ans.[3]**

Ex.19 Phenolphthalein gives which of the following colours in acidic medium.

(1) Pink   (2) Red   (3) No colour   (4) Violet

Sol. Phenolphthalein is colourless in acid medium because concentration of pH is low. **Ans.[3]**

Ex.20 If pK_a of acctic acid at 25^0C is 4.75, then determine the pH of that solution in which 0.02M sodium acetate and acetic acid are present?

(1) 4.75   (2) 3.75   (3) 5.75   (4) 2.75

Sol. [Salt] = [Acid]

pH = pK_a + log $\dfrac{[Salt]}{[Acid]}$

pH = 4.75 + log $\dfrac{0.02}{0.02}$

pH = 4.75 **Ans.[1]**

Ex.21 Which of the following ions are present in the solution of the monosodium salt of orthophosphoric acid?

(1) Na^+, PO_4^{-3}, $H_2PO_4^{-2}$, HPO_4^{-1} (2) Na^+, HPO_4^{-2}

(3) Na^+, $H_2PO_4^-$, HPO_4^{-2}, PO_4^{-3} (4) Na^+, HPO_4^{-2}, PO_4^{-3} **Ans.[2]**

Sol. Na^+ and undissociated $H_2PO_4^-$, HPO_4^{2}, PO_4^{-3} ions will be there, because H_3PO_4 dissociates in there steps.