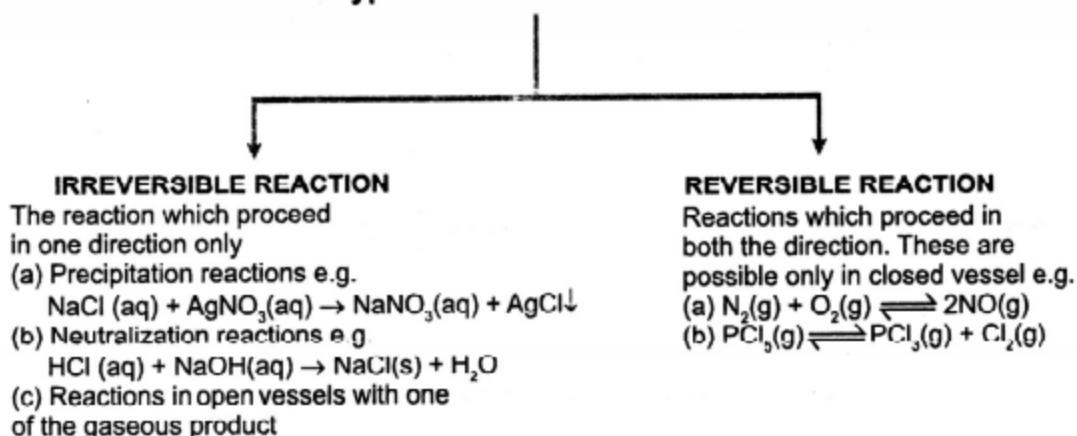


CHAPTER - 06

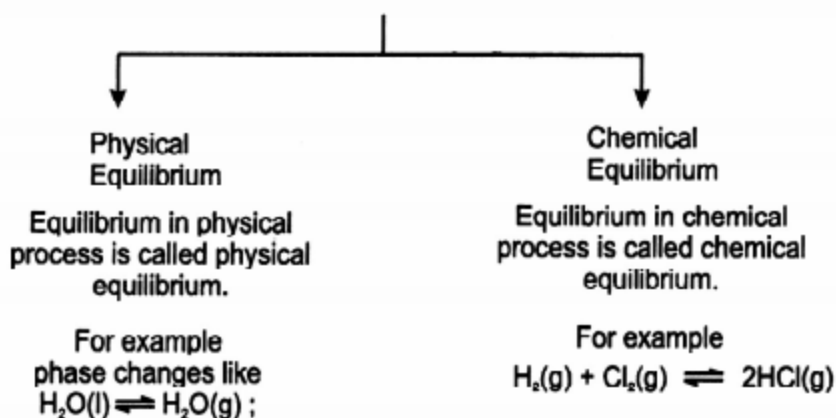
CHEMICAL AND IONIC EQUILIBRIUM

Equilibrium is a state in which there are no observable changes as time goes by. When a chemical reaction has reached the equilibrium state, the concentrations of reactants and products remain constant over time and there are no visible changes in the system. However, there is much activity at the molecular level because reactant molecules continue to form product molecules while product molecules react to yield reactant molecules. This dynamic situation is the subject of this chapter. Here we will discuss different types of equilibrium reactions, the meaning of the equilibrium constant and its relationship to the rate constant and factors that can effect a system at equilibrium.

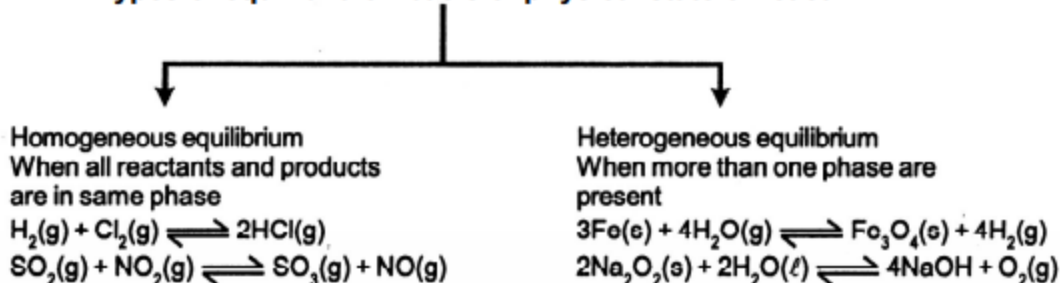
Types of chemical reactions



Types of equilibria on the basis of process



Types of equilibria on basis of physical state of react



Characteristics of chemical equilibrium :

- The nature and the properties of the equilibrium state are the same regardless of the direction from which it is achieved. It can be achieved in both directions.
- Equilibrium is dynamic in nature.
It means that at microscopic level reaction has not stopped. It appears that no change is occurring but both the opposing reactions are proceeding at the same rate. So there is no net change. Thus equilibrium is not static in nature.
- A catalyst can alter the rate of approach of equilibrium but does not change the state of equilibrium. By using catalyst, the equilibrium can be achieved in different (more/less) time, but the relative concentrations of reactants and products are same irrespective of the presence or absence of a catalyst.
- Equilibrium can be observed by constancy of some observable properties like colour, pressure, concentration, density, temperature, refractive index etc. which may be suitable in a given reaction.
- At equilibrium, free energy change $\Delta G = 0$
- Equilibrium state can be affected by altering factors like pressure, volume, concentration and temperature etc. (Le Chatelier's Principle).
- System moves toward an equilibrium state spontaneously even if it is disturbed. It will return to original state.

Law of mass action : [By Guldberg and Waage]

Rate at which a substance reacts \propto [Active Mass of the substance]

Ex. $aA + bB \longrightarrow \text{products}$

Rate of reaction $\propto [A]^a [B]^b$

Rate = $k [A]^a [B]^b$,

where k is the rate constant of the reaction.

Equilibrium constant (K) :

For a general reaction



Forward reaction rate $r_f = k_f [A]^a [B]^b$,

Backward reaction rate $r_b = k_b [C]^c [D]^d$,

At equilibrium $r_f = r_b$

$$k_f [A]_{eq}^a [B]_{eq}^b = k_b [C]_{eq}^c [D]_{eq}^d$$

The concentrations of reactants & products at equilibrium are related by

$$\frac{k_f}{k_b} = K_c = \frac{[C]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b}$$

- K_c is a constant and is called the **equilibrium constant in terms of concentration**, where all the concentrations are at equilibrium and are expressed in moles/litre.

- $K_p \rightarrow$ **Equilibrium constant in terms of partial pressure**. It is defined for the equilibrium reaction which contains at least one gaseous component.

e.g. $aA(g) + bB(g) \rightarrow cC(g) + dD(g)$

$$K_p = \frac{[P_C]_{eq}^c [P_D]_{eq}^d}{[P_A]_{eq}^a [P_B]_{eq}^b}$$

- **Relation between K_p & K_c**

$$PV = nRT \quad \text{or} \quad P = \frac{n}{V} RT$$

$$P = CRT \text{ where } C = \frac{n}{V} = (\text{moles per litre})$$

$$P_C = [C] RT ; \quad P_D = [D] RT ; \quad P_A = [A] RT ; \quad P_B = [B] RT$$

$$\Rightarrow K_p = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(c+d)-(a+b)}$$

$$K_p = K_c (RT)^{\Delta n}$$

$$1. \Delta n = 0 \quad K_p = K_c$$

$$2. \Delta n +ve \quad K_p > K_c$$

$$3. \Delta n -ve \quad K_p < K_c$$

Where $\Delta n_g = (c + d) - (a + b)$, calculation of Δn involves only gaseous components.

Units of Equilibrium Constants:

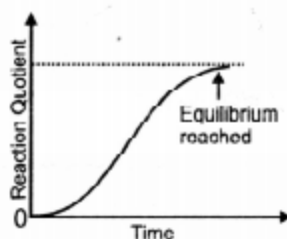
- Unit of K_p is $(\text{atm})^{\Delta n}$
- Unit of K_c is $(\text{mole/Lit})^{\Delta n} = (\text{conc.})^{\Delta n}$

Reaction Quotient (Q)

At each point in a reaction, we can write a ratio of concentration terms having the same form as the equilibrium constant expression. This ratio is called the reaction quotient denoted by symbol Q. It helps in predicting the direction of a reaction.

The expression $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ at any time during reaction is called reaction quotient. The concentrations

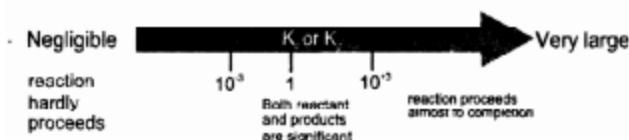
[C], [D], [A], [B] are not necessarily at equilibrium.



- The reaction quotient is a variable quantity with time.
- It helps in predicting the direction of a reaction.

If $Q > K_c$ reaction will proceed in backward direction until equilibrium is reached.

If $Q < K_c$ reaction will proceed in forward direction until equilibrium is established.



Note:

Case-I : If K is large ($K > 10^3$) then product concentration is very very larger than the reactant ($[\text{Product}] \gg [\text{Reactant}]$)
Hence concentration of reactant can be neglected with respect to the product. In this case, the reaction is product favourable and equilibrium will be more in forward direction than in backward direction.

Case-II : If K is very small ($K < 10^{-3}$)

$[\text{Product}] \ll [\text{Reactant}]$

Hence concentration of Product can be neglected as compared to the reactant.

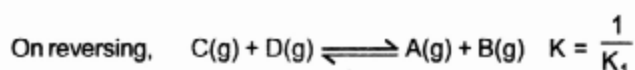
In this case, the reaction is reactant favourable.

Characteristics of equilibrium constant & factors affecting it :

- Equilibrium constant does not depend upon concentration of various reactants, presence of catalyst, direction from which equilibrium is reached
- The equilibrium constant does not give any idea about time taken to attain equilibrium.
- **K depends on the stoichiometry of the reaction.**

○ If two chemical reactions at equilibrium having equilibrium constants K_1 and K_2 are added then the resulting equation has equilibrium constant $K = K_1 \cdot K_2$

○ If the reaction having eq. constant K_1 is reversed then resulting equation has eq. constant $\frac{1}{K_1}$



○ If a chemical reaction having equilibrium constant K_1 is multiplied by a factor n then the resulting equation has equilibrium constant $K = (K_1)^n$, n can be fraction

- **Equilibrium constant is dependent only on the temperature.**

It means K_p and K_c will remain constant at constant temperature no matter how much changes are made in pressure, concentration, volume or catalyst.

- However if temperature is changed,

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]; \Delta H = \text{Enthalpy of reaction}$$

If $T_2 > T_1$, then $K_2 > K_1$ provided $\Delta H = +ve$ (endothermic reaction)

$K_2 < K_1$ if $\Delta H = -ve$ (exothermic reaction)

In the above equation, the unit of R and $\Delta H/T$ should be same.

- **Relation between equilibrium constant & standard free energy change.**

$$\Delta G^\circ = -2.303 RT \log K$$

Where ΔG° = standard free energy change, T = Absolute temperature, R = universal gas constant.

Heterogenous Equilibrium:

For pure solid and pure liquid, active mass is taken to be unity i.e. 1, as they remain constant throughout the reaction.



$$K_p = (P_{\text{CO}_2})_{\text{eq}}, K_c = [\text{CO}_2(g)]_{\text{eq}}$$

Degree of Dissociation (α) :

It is the fraction of one mole dissociated into the products.

(Defined for one mole of substance)

So, α = no. of moles dissociated / initial no. of moles taken

= fraction of moles dissociated out of 1 mole.

Note : % dissociation = $\alpha \times 100$

Observed molecular weight and Observed Vapour Density of the mixture

$$\text{Observed molecular weight of } A_n(g) = \frac{\text{molecular weight of } A_n(g)}{\text{total no. of moles at equilibrium}}$$

$$= \frac{aM_{th}}{a(1 + (n-1)\alpha)}$$

$$\therefore M_{obs} = \frac{M_{th}}{[1 + (n-1)\alpha]}$$

$$M_{mixture} = \frac{M_{A_n}}{[1 + (n-1)\alpha]}$$

$$\frac{D}{d} = 1 + (n-1)\alpha$$

$$\therefore \alpha = \frac{D-d}{(n-1)d} = \frac{M_T - M_0}{(n-1)M_0}$$

where M_T = Theoretical molecular wt. M_0 = observed molecular wt. or molecular wt. of the mixture at equilibrium.

Le Chatelier's Principle:

If a change is applied to the system at equilibrium, then equilibrium will be shifted in that direction in which it can minimise the effect of change applied and the equilibrium is established again under new conditions.

- **Effect of concentration :** If the concentration of a component is increased, reaction shifts in a direction which tends to decrease its concentration. e.g.

- **Effect of volume :**

- If volume is increased, pressure decreases hence reaction will shift in the direction in which pressure increases that is in the direction in which number of moles of gases increases and vice versa.
- If volume is increased then, for
 - $\Delta n_g > 0$ reaction will shift in the forward direction
 - $\Delta n_g < 0$ reaction will shift in the backward direction

- **Effect of pressure :**

On increasing pressure, equilibrium will shift in the direction in which pressure decreases i.e. no. of moles in the reaction decreases and vice versa.

$$\therefore P \propto \text{no. of moles}$$

- (i) For $\Delta n_g = 0 \rightarrow$ No. effects
- (ii) For $\Delta n_g > 0$

 $\Gamma \downarrow ; Q_p \downarrow ; (\text{Forward shift})$

$P \uparrow ; Q_p \uparrow ; (\text{Backward shift})$

- (iii) For $\Delta n < 0$, eq.

$P \uparrow ; Q_p \downarrow ;$ (Forward shift) ; $P \downarrow ; Q_p \uparrow ;$ (Backward shift)

- **Effect of catalyst :**

Due to catalyst, the state of equilibrium is not affected i.e. no shift will occur as catalyst lowers the activation energy of both the forward & reverse reaction by same amount, thus altering the forward & reverse rate equally and hence, the equilibrium will be attained faster i.e time taken to reach the equilibrium is less.

- **Effect of inert gas addition :**

- (i) **At constant volume :** Inert gas addition has no effect at constant volume

- (II) **At constant pressure :** If inert gas is added then to maintain the pressure constant, volume is increased. Hence equilibrium will shift in the direction in which larger no. of mole of gas is formed.

- (i) $\Delta n_g > 0$, reaction will shift in the forward direction
- (ii) $\Delta n_g < 0$, reaction will shift in the backward direction
- (iii) $\Delta n_g = 0$, no effect

- **Effect of temperature :**

- (ii) **Exothermic reaction** : The reaction in which heat is evolved

$T \uparrow \Rightarrow K' \text{ will decrease} \Rightarrow \text{backward}$

$T \downarrow \Rightarrow K$ will increase. \Rightarrow forward

- (ii) **Endothermic reaction : energy consumed.**

$T \uparrow \Rightarrow K \uparrow \Rightarrow \text{Forward}$; $T \downarrow \Rightarrow K \downarrow \Rightarrow \text{Backward}$

Application of le chatelier's principle : Practical equilibrium situations :

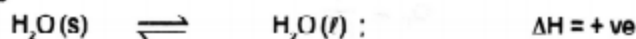
- **Formation of diamond :**



Density Low
Volume High

Formation of diamond is favourable at high pressure and high temperature

- **Melting of ice :**

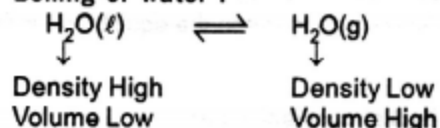


Density Low
Volume High

Density High
Volume Low

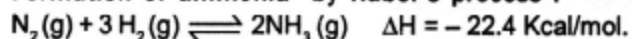
Melting of ice is favourable at high temperature and high pressure.

● **Boiling of water :**



On increasing pressure, equilibrium will shift in the direction in which volume is decreasing i.e. backward. Hence, on increasing pressure, the boiling point increases.

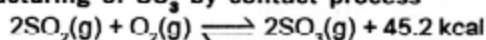
● **Formation of ammonia by Haber's process :**



(i) The reaction will shift in the forward direction at low temperature, but at very low temperature the rate of reaction becomes very low; thus moderate temperature is used for this reaction.

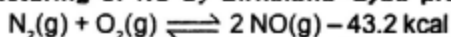
(ii) At high pressure, reaction will shift in forward direction to form more product.

● **Manufacturing of SO_3 by contact process**



High pressure (1.5 to 1.7 atm), Low temperature (500°C), Higher quantity of SO_2 and O_2 are favourable conditions for the formation of SO_3 .

● **Manufacturing of NO by Birkeland-Eyde process**



○ No effect on change of pressure

○ High temperature (1200°C to 2000°C), High concentration of N_2 and O_2 are favourable condition for the formation of NO.

Thermodynamics of Equilibrium :

$$\Delta G = \Delta G^\circ + 2.303 RT \log_{10} Q$$

where ΔG = Gibb's Free energy change

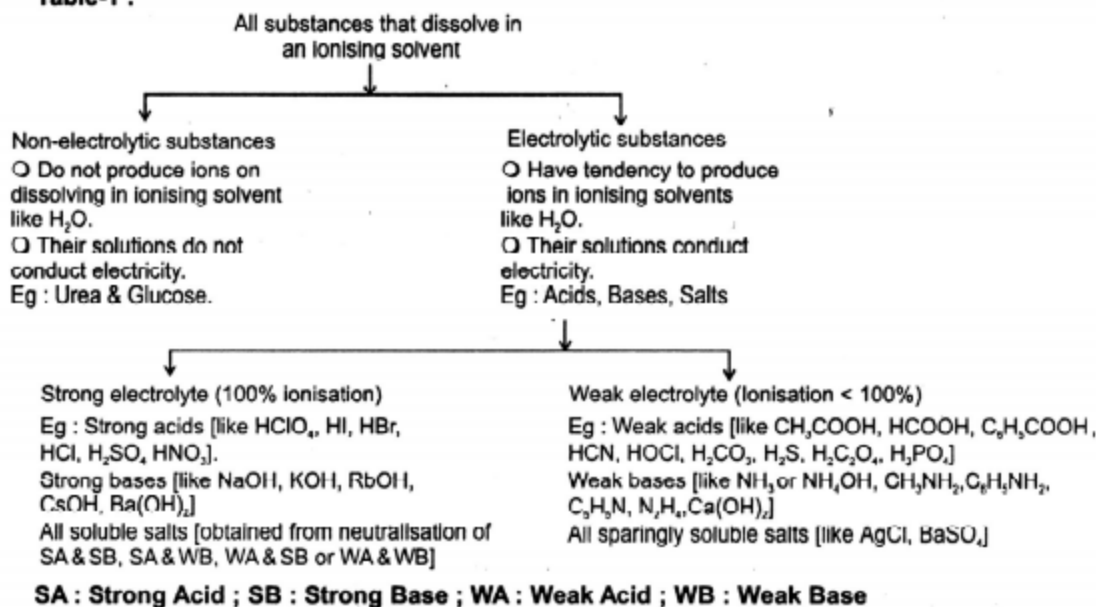
ΔG° = Standard Gibb's Free energy change

Q = reaction quotient

IONIC EQUILIBRIUM

Here we deal with the equilibria of species which are ionic in nature. Generally the concentration of H^+ and OH^- ions is of importance. Also the concentration of ions forming precipitates is focused upon. As like dissolves like, the solvent for production of these ions should be polar. It is generally water.

Table-1 :



Arrhenius Acid : Substance which gives H^+ ion from its own molecule on dissolving in an ionising solvent .
Eg : HCl , H_2SO_4 , CH_3COOH etc.

○ H_3BO_3 is not Arrhenius acid as it does not give H^+ from its own molecule.

○ H^+ ion in water is extremely hydrated (in form of H_3O^+ , $H_7O_2^+$, $H_9O_4^+$) due to its high charge density.

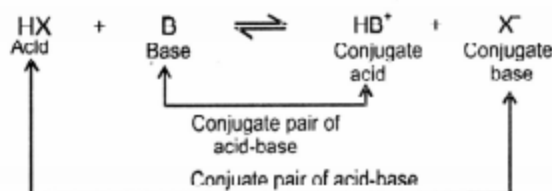
Arrhenius Base : Substance which gives OH^- ion from its own molecule on dissolving in an ionising solvent.
Eg : $NaOH$, $Ba(OH)_2$, NH_4OH etc.

Bronsted-Lowry concept (Conjugate acid-base concept / Protonic concept)

Bronsted Lowry Acid : Species which donate H^+ are Bronsted Lowry acids (H^+ donor).

Bronsted Lowry Base : Species which accept H^+ are Bronsted Lowry bases (H^+ acceptor).

Conjugated acid-base pairs : In a typical acid-base reaction,



○ Conjugate acid-base pair differ by only one proton (H^+).

Amphiprotic / Amphoteric Species : Species which can act as an acid as well as a base. eg : H_2O , NH_3 .

Lewis Concept (Electronic Concept)

Lewis Acid : An Lewis acid is a species which can accept an electron pair with the formation of coordinate bond.

Acid \leftarrow Electron pair donor \Rightarrow Acid : Electron pair acceptor.

eg : Electron deficient molecules : BF_3 , AlCl_3 , H_3BO_3 , BeCl_2

Cations : H^+ , Fe^{3+} , Na^+

Molecules with vacant orbitals : SiCl_4 , SO_2 .

Lewis Base : A Lewis base is a species which has a lone pair of electrons available for donation.

Base \rightarrow Electron pair acceptor \Rightarrow Base : Electron pair donor

eg : Molecules with donatable lone pairs : NH_3 , $\text{H}_2\ddot{\text{O}}$, $\text{CH}_3\ddot{\text{O}}\text{H}$

Ions : X^- , CN^- , OH^- .

PROPERTIES OF WATER :

Amphoteric Acid / Base Nature :

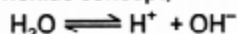
Water acts as an acid as well as base according to Arrhenius & Bronsted - Lowry theory, but according to Lewis concept it is a base, not an acid.



In pure water, $[\text{H}^+] = [\text{OH}^-]$, so it is always neutral

Ionic product of water :

According to arrhenius concept,



Ionic product of water is defined as :

$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} \text{ at } 25^\circ\text{C (experimental data)}$$

Degree of dissociation of water :

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \Rightarrow \alpha = \frac{\text{no. of moles dissociated}}{\text{no. of moles initially taken}} = \frac{10^{-7}}{55.55}$$

For any conjugate acid-base pair (HA & A^-) in aqueous solution :

$$\text{Now, } K_a \times K_b = K_w \Rightarrow \text{p}K_a + \text{p}K_b = \text{p}K_w = 14 \text{ (at } 25^\circ\text{C)}$$

ACIDITY AND pH SCALE :

- Acidic strength means the tendency of an acid to give H_3O^+ or H^+ ions in water.
So greater the tendency to give H^+ , more will be the acidic strength of the substance.
- Basic strength means the tendency of a base to give OH^- ions in water.
So greater the tendency to give OH^- ions, more will be basic strength of the substance.

The concentration of H^+ ions is written in a simplified form introduced by Sorenson known as pH scale.

$$\text{pH} = -\log [\text{H}^+] \text{ or } \text{pH} = \log \frac{1}{[\text{H}^+]} \text{ or } \text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$\text{pH} + \text{pOH} = \text{p}K_w = 14 \text{ (for an aqueous solution at } 25^\circ\text{C)}$$

pH can also be negative or greater than 14.

$$\text{Now, } \text{pH} = -\log [\text{H}^+] = 7 \text{ and } \text{pOH} = -\log [\text{OH}^-] = 7, \text{ for water at } 25^\circ\text{C (experimental)}$$

$$\left. \begin{array}{ll} \text{pH} = 7 = \text{pOH} & \Rightarrow \text{neutral} \\ \text{pH} < 7 \text{ or } \text{pOH} > 7 & \Rightarrow \text{acidic} \\ \text{pH} > 7 \text{ or } \text{pOH} < 7 & \Rightarrow \text{basic} \end{array} \right\} \text{at } 25^\circ\text{C only}$$

The value of α depends on :

- Nature of electrolyte :**
Strong electrolytes dissociate completely ($\alpha = 1$) whereas weak electrolytes dissociate partially. ($\alpha < 1$)
- Nature of solvent :**
A solvent having high value of dielectric constant will favour dissociation. (Generally polar solvents)
- Dilution :**
For weak electrolytes, degree of dissociation will increase with dilution (**Ostwald's dilution law**)
- Temperature :**
On increasing temperature, generally degree of dissociation increases. (for endothermic dissociations)
- Presence of other solute :**
When a substance is present in a solution, it may effect the dissociation of another substance. Generally, presence of common ion suppresses degree of dissociation of weak electrolyte. (**Common ion effect**).

A solvent is said to be showing levelling effect if various electrolytes (generally acids and bases) get completely dissociated in it and thus have the same strength.

A solvent is said to be showing differentiating effect if various acids and bases dissociate to different degrees in it and thus their relative strengths can be compared.

OSTWALD'S DILUTION LAW (FOR WEAK ELECTROLYTES)

$$K_{eq} = \alpha^2 C \Rightarrow \alpha = \sqrt{\frac{K_{eq}}{C}}$$

pH CALCULATIONS OF DIFFERENT TYPES OF SOLUTIONS:

Strong acid solution

- If $[H^+]_{\text{from strong acid}}$ is greater than 10^{-6} M. In this case, H^+ ions coming from water can be neglected.
- If $[H^+]_{\text{from strong acid}}$ is less than 10^{-6} M. In this case, H^+ ions coming from water cannot be neglected

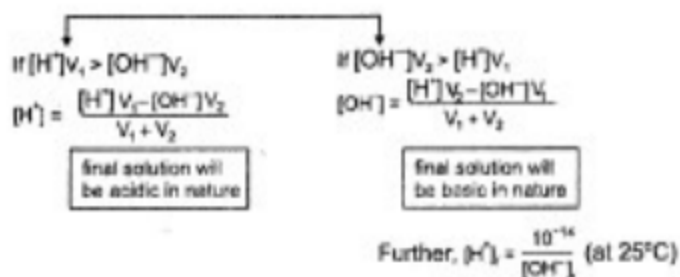
Mixture of two strong acids

$$[H^+]_f = \frac{[H^+]_1 V_1 + [H^+]_2 V_2}{V_1 + V_2}$$

Mixture of two strong bases

$$[OH^-]_f = \frac{[OH^-]_1 V_1 + [OH^-]_2 V_2}{V_1 + V_2}$$

Mixture of a strong acid and a strong base :



ISOHYDRIC SOLUTIONS :

If the concentration of the common ions in the solution of two electrolytes, for example H^+ ion concentration in two acid solutions HA_1 and HA_2 .

$$C_1\alpha_1 = C_2\alpha_2 \text{ (on equating the } H^+ \text{ concentrations from both acids).}$$

RELATIVE STRENGTH OF ACIDS AND BASES :

$$\frac{\text{Acid strength of } HA_1}{\text{Acid strength of } HA_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

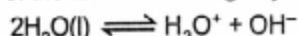
SALT HYDROLYSIS (REVERSE OF NEUTRALISATION)

Hydrolysis : The reaction of an ion with water in which either H_3O^+ or OH^- is produced, by dissociation of water molecule.



(A) Salt of strong acid and strong base

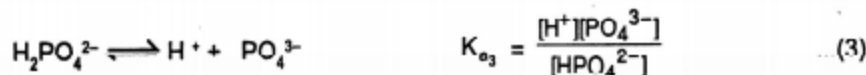
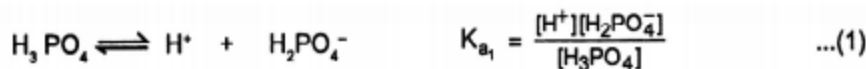
Neither of the ions will undergo hydrolysis, so the solution involves only the equilibrium of ionization of water.



Thus, the pH of solution will be 7 (neutral solution at $25^\circ C$).

Types of salt	Expression for K_h	Expression for h	Expression for pH
(i) Salt of weak acid and strong base	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\left(\frac{K_h}{C}\right)}$ ($h < 0.1$)	$pH = \frac{1}{2} [pK_w + pK_a + \log C]$
(ii) Salt of strong acid and weak base	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\left(\frac{K_h}{C}\right)}$ ($h < 0.1$)	$pH = \frac{1}{2} [pK_w - pK_b - \log C]$
(iii) Salt of weak acid and weak base	$K_h = \frac{K_w}{K_a K_b}$	$\frac{h}{1-h} = \sqrt{K_h}$	$pH = \frac{1}{2} [pK_w + pK_a - pK_b]$

For polyprotic acids like (H_2S , H_3PO_4 , H_2CO_3 , $H_2C_2O_4$), we already know that the dissociation always takes place in steps. Example : for H_3PO_4 ,



For all acids we always have $K_{a_1} \gg K_{a_2} \gg K_{a_3}$

BUFFER SOLUTION

Buffer solutions are those solutions which resist a change in pH upon addition of small amount of acid or base. This does not mean that the pH will not change, all it means is that the pH change would be less than the change that would have occurred had it not been a buffer.

1. Buffer of a weak acid and its salt with a strong base.

Eg : A solution containing CH_3COOH & CH_3COONa

2. Buffer of a weak base and its salt with a strong acid: Eg : A solution containing NH_4OH & NH_4Cl

3. Solution of salt of a weak acid and a weak base

Eg : A solution of $\text{CH}_3\text{COONH}_4$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Anion of Salt}]}{[\text{Acid}]}$$

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Cation of salt}]}{[\text{Base}]}$$

Buffer capacity : It is defined as the moles of a strong acid or strong base required to change the pH of 1L of a buffer by one unit.

INDICATORS: Indicators are the substances, which indicate the end-point of a titration generally by changing their colour.

$$\text{pH} = \text{pK}_{\text{in}} + \log \frac{[\text{In}^-]}{[\text{Hin}]}$$

SOLUBILITY(s) AND SOLUBILITY PRODUCT (K_{sp})

We will be dealing with the solubility of sparingly soluble salts in the following cases.

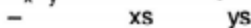
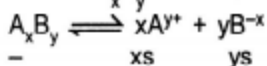
- (A) Simple solubility in H_2O
- (B) Condition for precipitation
- (C) Selective precipitation
- (D) Effect of common ions on solubility
- (E) Simultaneous solubility

Solubility product (K_{sp}) is a type of equilibrium constant, so will be dependent only on temperature for a particular salt.

Following examples will illustrate the different type of solubilities and the effects of different factors or situations on solubility of a salt.

(A) Simple solubility

Let salt A_xB_y be dissolved in water. Let its solubility in H_2O = 's' M. Then :



$$\text{F39: } \therefore K_{\text{sp}} = (xs)^x (ys)^y = x^x \cdot y^y \cdot (s)^{x+y}$$

For precipitation, ionic product (K_{sp}) should be greater than solubility product K_{sp}

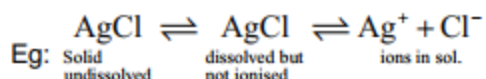
If a single solution has two or more ions both having tendency to precipitate with an ion of a reagent.

The ion whose salt has lesser concentration of ion of reagent for precipitation will form precipitate first

Because of the presence of common ion in solution, the solubility of the sparingly soluble salt generally decreases.

Solubility product (K_{sp}) : At constant temperature and pressure the saturated solution of a sparingly soluble salt has an

equilibrium between the excess of the solute and the ions furnished by it.



Applying law of mass action, $K = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$

or $K [\text{AgCl}] = [\text{Ag}^+] [\text{Cl}^-]$, $K_{sp} = [\text{Ag}^+] [\text{Cl}^-]$

The constant K_{sp} is known as solubility product. It is equal to the product of the concentration of ions in saturated solution.

When $K_{sp} > [\text{Ag}^+] [\text{Cl}^-]$ Solution not saturated

When $K_{sp} < [\text{Ag}^+] [\text{Cl}^-]$ Solution supersaturated and precipitation takes place

When $K_{sp} = [\text{Ag}^+] [\text{Cl}^-]$ Solution saturated

For general electrolyte $A_x B_y$, $K_{sp} = [A^{+y}]^x [B^{-x}]^y$

I. K_{sp} is independent of the source of ions.

II. Helps to know the solubility of electrolytes

III. Predicting ionic reactions

IV. Qualitative analysis

V. Purification of common salt, salting out of soap as Solvay ammonia soda process.

Relation between solubility product (K_{sp}) and solubility (S)

1. For binary electrolyte eg. AgCl , BaSO_4 , KI

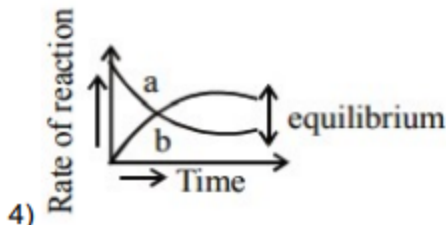
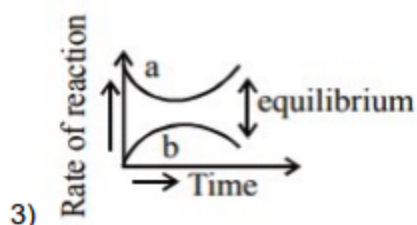
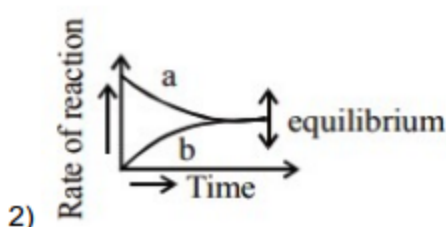
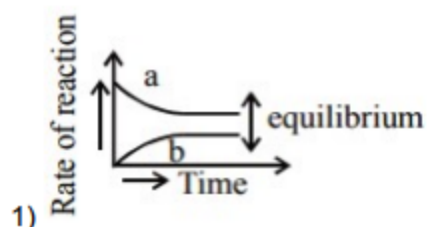
$$S = \sqrt{K_{sp}}$$

2. For ternary electrolyte eg. CaF_2 , PbI_2 , Hg_2Cl_2

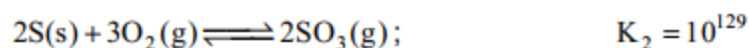
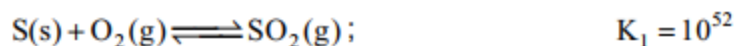
$$S = \left(\frac{K_{sp}}{4} \right)^{\frac{1}{3}}$$

PART-I (JEE MAIN)**SECTION-I- Straight objective type questions**

1. For the equilibrium $A \rightleftharpoons B$, the variation of the rate of the forward (a) and reverse (b) reaction with time is given by



2. For the following reactions, equilibrium constants are given:



The equilibrium constant for the reaction, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is

- 1) 10^{181} 2) 10^{154} 3) 10^{25} 4) 10^{77}
3. **Assertion:** An endothermic reaction $A \rightleftharpoons B$ will shift in the forward direction on increasing the temperature

Reason: Equilibrium constant for the above equilibrium decreases with increase in temperature.

In the light of the above statements, choose the correct option.

- 1) Both assertion and reason are true and reason is the correct explanation of assertion.
- 2) Both assertion and reason are true but reason is not the correct explanation of assertion.
- 3) Assertion is true but reason is false.
- 4) Assertion is false but reason is true.

4. The compounds A and B are mixed in equimolar proportion to form the products C and D as per the equation, $A + B \rightleftharpoons C + D$. At equilibrium, one third of A and B are consumed. The equilibrium constant for the reaction is

1) 0.5 2) 4.0 3) 2.5 4) 0.25

5. A mixture of 0.3 mol of H_2 and 0.3 mol of I_2 is allowed to react in a 10 litre evacuated flask at $500^\circ C$ according to the equation $H_2 + I_2 \rightleftharpoons 2HI$. The value of equilibrium constant is found to be 64. The amount of unreacted I_2 at equilibrium would be

1) 0.15 mol 2) 0.06 mol 3) 0.03 mol 4) 0.2 mol

6. For the following statements, the correct option is:

Assertion: The pH of water increases with increase in temperature.

Reason: The dissociation of water into H^+ and OH^- is an exothermic reaction.

- 1) Both assertion and reason are true and reason is the correct explanation of assertion.
- 2) Both assertion and reason are true but reason is not the correct explanation of assertion.
- 3) Assertion is true but reason is false.
- 4) Both assertion and reason are false

7. The pH value of 0.05 M $Ba(OH)_2$ solution is

1) 1 2) 12 3) 6 4) 13

8. The pH of a 0.01 M solution of acetic acid having degree of dissociation 12.5% is

1) 5.623 2) 2.903 3) 3.723 4) 4.509

9. The pH of a buffer solution that is 0.2 molar in CH_3COONa and 0.1 molar in CH_3COOH is (K_a for acetic acid = 2×10^{-5} ; $\log 2 = 0.3$)

1) 5 2) 6 3) 4 4) 3

10. NH_4Cl is an acidic salt, because

- 1) On hydrolysis, NH_4Cl gives NH_4OH and H^+ ions
- 2) It is a salt of weak acid and weak base
- 3) It is a salt of weak acid and strong base
- 4) On hydrolysis, NH_4Cl gives NH_4OH and OH^- ions

11. Consider the following statements
 (a) The pH of a mixture containing 400 mL of 0.1M H_2SO_4 and 400 mL of 0.1 M NaOH will be approximately 1.3
 (b) Extent of dissociation of CH_3COOH in the solution decreases on adding CH_3COONa into it.
 (c) A monobasic acid with $K_a = 10^{-5}$ has a pH = 5. The degree of dissociation of this acid is 50%.
 (d) Solubility of Ag_2CO_3 is higher in Na_2CO_3 solution than in pure water.
 The correct statements are:
 1) a, b and d 2) a, b and c 3) a and b 3) b and c
12. Solubility of PbI_2 in pure water is 0.005 M at 298 K. Then, the solubility product of PbI_2 at this temperature is
 1) 6.8×10^{-6} 2) 6.8×10^6 3) 2.2×10^{-9} 4) 5.0×10^{-7}
13. A solution contains chloride ions (Cl^-) and chromate ions (CrO_4^{2-}) in 0.1M and 0.001M concentration respectively. Solid AgNO_3 is gradually added to it. The salt that precipitates out first and the reason are (Given: $K_{sp}(\text{AgCl}) = 1.7 \times 10^{-10}$ and $K_{sp}(\text{Ag}_2\text{CrO}_4) = 1.9 \times 10^{-12}$)
 1) AgCl precipitates first because the amount of Ag^+ needed for precipitation is high
 2) Ag_2CrO_4 precipitates first because the amount of Ag^+ needed for precipitation is low
 3) AgCl precipitates first because the amount of Ag^+ needed for precipitation is low
 4) Ag_2CrO_4 precipitates first because the amount of Ag^+ needed for precipitation is high

SECTION-II - Numerical Type Questions

14. For the reaction $3\text{Fe}_{(s)} + 4\text{H}_2\text{O}_{(g)} \rightleftharpoons \text{Fe}_3\text{O}_{4(s)} + 4\text{H}_{2(g)}$, if $K_p = K_c (\text{RT})^x$, the value of $|x|$ is
15. How many of the following equilibria will shift in forward direction on the addition of an inert gas at constant pressure?
 1) $\text{COCl}_{2(g)} \rightleftharpoons \text{CO}_{(g)} + \text{Cl}_{2(g)}$ 2) $\text{CaCO}_{3(s)} \rightleftharpoons \text{CaO}_{(s)} + \text{CO}_{2(g)}$
 3) $2\text{H}_{2(g)} + \text{CO}_{(g)} \rightleftharpoons \text{CH}_3\text{OH}_{(g)}$ 4) $\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$
16. The pK_a of acetic acid and pK_b of ammonium hydroxide are 4.76 and 4.75 respectively. The pH of 0.1M solution of ammonium acetate will be

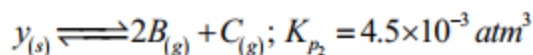
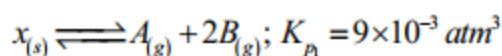
PART-II (JEE ADVANCED)

Section-III - Only one option correct type

17. Solubility product of $\text{Ni}(\text{OH})_2$ is 2×10^{-15} . The molar solubility of $\text{Ni}(\text{OH})_2$ in 0.1 M NaOH is about
 A) 1×10^{-15} B) 2×10^{-14} C) 2×10^{-13} D) 1×10^{-14}

18. If in the equilibrium, $\text{CaF}_{2(s)} \rightleftharpoons \text{Ca}^{+2}(\text{aq}) + 2\text{F}^{-}(\text{aq})$, the $[\text{Ca}^{+2}]$ is increased 4 times, then the fluoride ion concentration will
- A) Increase four times
B) Increase two times
C) Decrease to half of its original concentration
D) Decrease to one one-fourth of its original concentration

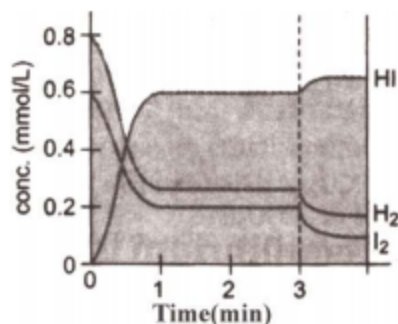
19. Two solid compounds x and y dissociates at a certain temperature as follows



The total pressure of gases over a mixture of x and y is

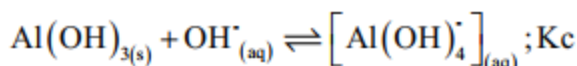
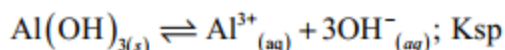
- A) 4.5 atm B) 0.85 atm C) 0.6 atm D) 0.45 atm
20. The pH of pure water at 25°C and 35°C are 7 and 6 respectively. The heat of formation of water from H^{+} and OH^{-} will be. (Given $R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$)
- A) + 84.551 kcal mol^{-1} B) -84.551 kcal mol^{-1}
C) +8.4551 kcal mol^{-1} D) -8.455 kcal mol^{-1}
21. Solid AgNO_3 is added to a solution which is 0.1 M in Cl^{-} and 0.1 M in CrO_4^{2-} . K_{sp} values for AgCl and Ag_2CrO_4 are 1.7×10^{-10} and 1.9×10^{-12} respectively. The concentration of Cl^{-} when Ag_2CrO_4 starts preprecipitating will be
- A) $3.9 \times 10^{-5} \text{ M}$ B) $2.9 \times 10^{-2} \text{ M}$ C) $3.9 \times 10^{-3} \text{ M}$ D) $1.9 \times 10^{-2} \text{ M}$
22. Which of the following mixtures will form a buffer solution when dissolved in 500 mL of water?
- A) 0.200 mol of aniline and 0.200 mol of HCl B) 0.200 mol of aniline and 0.400 mol of NaOH
C) 0.200 mol of NaCl and 0.100 mol of HCl D) 0.200 mol of aniline and 0.100 mol of HCl
23. pH of a buffer containing 0.01 M $(\text{NH}_4)_2\text{SO}_4$ and 0.02 M NH_4OH (pK_a of $\text{NH}_4^{+} = 9.26$) is
- A) $4.74 + \log 2$ B) $4.74 - \log 2$ C) $4.74 + \log 1$ D) $9.26 + \log 1$

24. Consider the following concentration vs time graph for the reaction, $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) + \text{Heat} \rightleftharpoons 2\text{HI}(\text{g})$



At the instant 3 min, what change was imposed on the equilibrium?

- A) Temperature was reduced
B) Temperature was increased
C) HI was added to the system
D) HI was removed from the system
25. Calcium lactate is a salt of weak organic acid and strong base represented as $\text{Ca}(\text{Lac})_2$. A aqueous mixture of $\text{Ca}(\text{Lac})_2$ contains 0.6 moles of the salt in 2 litre solution. pOH of solution is found to be 5.60. If 90% dissociation of the salt takes place, then what is pK_a of lactic acid?
- A) $2.8 - \log(0.54)$ B) $2.8 + \log(0.54)$ C) $2.8 + \log(0.27)$ D) $2.8 - \log(0.27)$
26. The salt $\text{Al}(\text{OH})_3$ is involved in the following two equilibria in the solution:



The correct expression for $[\text{OH}^-]$ at which solubility of the salt is minimum is

- A) $[\text{OH}^-] = \left(\frac{K_{sp}}{K_c} \right)^{1/3}$ B) $[\text{OH}^-] = \left(\frac{K_c}{K_{sp}} \right)^{1/4}$
C) $[\text{OH}^-] = \sqrt{\left(\frac{K_{sp}}{K_c} \right)^{1/4}}$ D) $[\text{OH}^-] = \left(\frac{3K_{sp}}{K_c} \right)^{1/4}$

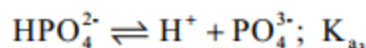
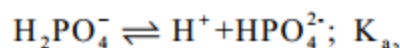
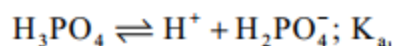
Section IV - One or more option correct type

27. Choose the correct statement(s):

(Use: $K_{sp}(\text{ZnS}) = 1.25 \times 10^{-22}$; $K_{a1} \times K_{a2}(\text{H}_2\text{S}) = 1 \times 10^{-21}$; $K_{sp}(\text{AB}) = 2 \times 10^{-10}$; $K_a(\text{HB}) = 1 \times 10^{-8}$; AOH is strong base)

- A) For acidified solution of 0.05 M Zn^{2+} saturated with 0.1 M H_2S , the minimum value of $[\text{H}^+]$ required to prevent the precipitation of ZnS is 0.2 M
B) For acidified solution of 0.05 M Zn^{2+} saturated with 0.1 M H_2S , the minimum value of $[\text{H}^+]$ required to prevent the precipitation of ZnS is 0.1 M
C) The molar solubility of AB at pH 3 is 4.47×10^{-3} M
D) The molar solubility of AB at pH 3 is 4.47×10^{-2} M

28. Consider the following dissociation equilibria of H_3PO_4 .



Choose the correct statement(s)

A) $K_{a_1} > K_{a_2} > K_{a_3}$

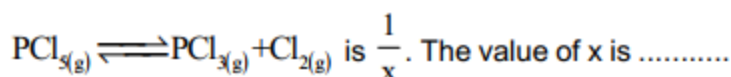
B) pH of aqueous NaH_2PO_4 is $\frac{pK_{a_2} + pK_{a_3}}{2}$

C) pH of a solution that is 0.1 M in Na_2HPO_4 and 0.2 M in NaH_2PO_4 is $pK_{a_2} - \log 2$

D) pH of an equimolar solution of Na_2HPO_4 and Na_3PO_4 is pK_{a_3}

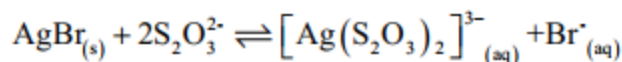
Section V - Numerical type questions

29. 5 moles of $\text{PCl}_{5(g)}$ and 1 mole of N_2 gas are placed in a closed vessel. At equilibrium $\text{PCl}_{5(g)}$ decomposes to an extent of 20% and the total pressure is found to be one atm. The K_p for the equilibrium



30. 20 mL of 0.1 M NH_4OH is mixed with 40 mL of 0.05 M HCl . The pH of the mixture will be
(use: K_b of $\text{NH}_4\text{OH} = 10^{-5}$; $\log 3 = 0.48$)

31. AgBr is involved in the following equilibrium when placed in aqueous $\text{Na}_2\text{S}_2\text{O}_3$.



The molar solubility of AgBr in 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ is $x \times 10^{-2}$. The value of x is

$$\left(\text{Given: } K_{sp}(\text{AgBr}) = 5 \times 10^{-13}, K_f([\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}) = 5 \times 10^{13} \right)$$

Section-VI - Matrix match type

32. Considering the titration of a weak monoprotic acid against a strong monoacidic base, match the pH of solution at different stages of titration.

Column-I (Percentage of titration completed)

Column-II (pH)

I) 0% (at the beginning of titration)

P) $7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$

II) 50%

Q) pK_a

III) 100%

R) $\frac{1}{2}pK_a - \frac{1}{2}\log C$

IV) 20%

S) $pK_a + \log \frac{1}{4}$

A) I \rightarrow P; II \rightarrow S; III \rightarrow R; IV \rightarrow Q

B) I \rightarrow R; II \rightarrow Q; III \rightarrow P; IV \rightarrow S

C) I \rightarrow R; II \rightarrow S; III \rightarrow P; IV \rightarrow Q

D) I \rightarrow P; II \rightarrow Q; III \rightarrow R; IV \rightarrow S