

# BRUSH UP for NEET/JEE 2020

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Unit  
2

Electrochemistry | Chemical Kinetics | Surface Chemistry

## Electrochemistry

### ELECTROCHEMISTRY

- Electrochemistry is the study of relationship between electrical energy and chemical energy, produced in a redox reaction, and how one can be converted into another.
- Conductors are substances which allow the passage of current whereas insulators do not allow electric current to pass through them.
- Electrolytes are the aqueous solutions of compounds which conduct electricity and are decomposed to their ions by the passage of current.
- A compound whose aqueous solution does not conduct electricity, is called non-electrolyte.
- Electrolysis is a chemical reaction brought about by the passage of electric current through an electrolyte.
- Electrochemical cell is a device in which the free energy of physical or chemical process is converted into electrical energy.

### FARADAY'S LAWS OF ELECTROLYSIS

- **First law of electrolysis** : Amount of substance deposited or liberated at an electrode is directly proportional to amount of charge passed (utilized)

through the electrolyte.

$$W \propto Q$$

$$W = ZQ = Z \times I \times t$$

$Z$  = Electrochemical equivalent

- **Second law of electrolysis** : When same amount of charge is passed through different electrolytic solutions connected in series then mass of substances deposited or dissolved at anode or cathode are in ratio of their equivalent mass. *i.e.*,  
 $W_1/W_2 = E_1/E_2$

### GALVANIC CELL

This cell converts chemical energy produced in a redox reaction into electrical energy. Galvanic cell is made up of two half cells *i.e.*, anodic and cathodic. Oxidation takes place at anode and reduction at cathode. It is also known as voltaic cell. In this zinc rod act as anode, immersed in  $ZnSO_4$  solution and copper rod act as cathode, immersed in  $CuSO_4$  solution. Two rods are connected by a wire and two solutions are connected by a salt bridge.

- **Anode half cell reaction** :  
 $Zn_{(s)} \rightarrow Zn_{(aq)}^{2+} + 2e^-$  (oxidation)
- **Cathode half cell reaction** :  
 $Cu_{(aq)}^{2+} + 2e^- \rightarrow Cu_{(s)}$  (reduction)
- **Overall process** :  $Zn_{(s)} + Cu_{(aq)}^{2+} \rightarrow Cu_{(s)} + Zn_{(aq)}^{2+}$

In galvanic cell like Daniell cell; electrons flow from anode (zinc rod) to the cathode (copper rod) through external circuit. Zinc dissolves as  $Zn^{2+}$  in solution and  $Cu^{2+}$  ion, in the cathode cell picks up two electron and deposited at copper rod.

- **Electrode potential** : The electrical potential difference set up between the metal and its ions in the solution is called electrode potential or the tendency of an electrode to lose or gain electrons when it is in contact with solution of its own ions.
- **Standard electrode potential** : At the unity concentration of electrode and temperature  $25^{\circ}C$ , the potential of the electrode is termed as standard electrode potential ( $E_{cell}^{\circ}$ ).  
The standard electrode potential of hydrogen electrode is zero. So, it is used as reference electrode.
- **Electromotive force (emf)** : The difference between the electrode potentials of the two half cells is known as cell potential or cell voltage. It is called emf of the cell if no current is drawn from the cell.
- The arrangement of all the electrodes in order of their increasing standard reduction potentials, called electrochemical series.  
Reduction potential = -oxidation potential
- Substances with stronger reducing power are placed above hydrogen and those with weaker reducing power are placed below hydrogen.
- **Applications of electrochemical series** :
  - It is useful in predicting the relative strengths of oxidising and reducing agents.
  - Reactivity of an element can be predicted.
  - It is useful to predict whether a metal will

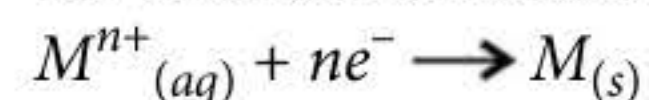
liberate hydrogen gas from an acid or not.

- To predict feasibility of a redox reaction by calculating standard EMF of cell :

$$E_{cell}^{\circ} = E_R^{\circ} - E_L^{\circ}$$

## NERNST EQUATION

- For a reduction reaction,



$$E_{cell} = E_{cell}^{\circ} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}_{(aq)}]}$$

At  $T = 298\text{ K}$ ;  $R = 8.314\text{ J K}^{-1}\text{ mole}^{-1}$  and  $F = 96500\text{ C}$ , we get

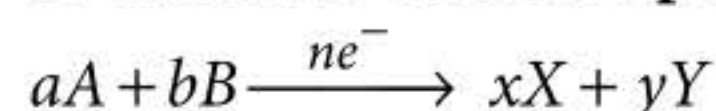
$$E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}_{(aq)}]}$$

- For concentration cell,

$$E_{cell} = \frac{0.0591}{n} \log \frac{C_2}{C_1} ; \text{ where } C_2 > C_1$$

- **Applications of Nernst equation** :

- **To calculate electrode potential of a cell** :



$$E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{n} \log \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

- **To calculate equilibrium constant** :

At equilibrium,  $E_{cell} = 0$

$$E_{cell}^{\circ} = \frac{0.0591}{n} \log K_c \text{ at } 298\text{ K}$$

- **Relation between cell potential and Gibbs' energy change** :

$$\Delta G^{\circ} = -nFE_{cell}^{\circ} ; \Delta G^{\circ} = -2.303 RT \log K_c$$

## SOME COMMERCIAL CELLS

	Dry cell	Lead storage battery	Fuel cell
<b>Anode</b>	Zinc	Lead	Porous carbon containing catalysts ( $H_2$ passed)
<b>Cathode</b>	Graphite	Lead dioxide	Porous carbon containing catalysts ( $O_2$ passed)
<b>Electrolyte</b>	$MnO_2 + C$ (touching cathode) $NH_4Cl + ZnCl_2$ (touching anode)	$H_2SO_4$ (38%)	Conc. aqueous KOH/NaOH
<b>Anode reaction</b>	$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^{-}$	$Pb_{(s)} + SO_4^{2-}_{(aq)} \longrightarrow PbSO_{4(s)} + 2e^{-}$	$H_{2(g)} + 2OH^{-}_{(aq)} \longrightarrow 2H_2O_{(l)} + 2e^{-}$
<b>Cathode reaction</b>	$2MnO_{2(s)} + 2NH_4^{+}_{(aq)} + 2e^{-} \longrightarrow Mn_2O_{3(s)} + H_2O_{(l)} + 2NH_{3(g)}$	$PbO_{2(s)} + SO_4^{2-}_{(aq)} + 4H^{+}_{(aq)} + 2e^{-} \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)}$	$O_{2(g)} + 2H_2O_{(l)} + 4e^{-} \longrightarrow 4OH^{-}_{(aq)}$

## PEEP INTO PREVIOUS YEARS

1. For the cell reaction :
- $$2\text{Fe}^{3+}_{(aq)} + 2\text{I}^{-}_{(aq)} \longrightarrow 2\text{Fe}^{2+}_{(aq)} + \text{I}_{2(aq)}$$
- $E^{\circ}_{\text{cell}} = 0.24 \text{ V}$  at 298 K. The standard Gibbs' energy ( $\Delta_r G^{\circ}$ ) of the cell reaction is  
[Given that Faraday constant,  $F = 96500 \text{ C mol}^{-1}$ ]
- (a)  $23.16 \text{ kJ mol}^{-1}$       (b)  $-46.32 \text{ kJ mol}^{-1}$   
(c)  $-23.16 \text{ kJ mol}^{-1}$       (d)  $46.32 \text{ kJ mol}^{-1}$   
(NEET 2019)

2. For the following cell,  
 $\text{Zn}_{(s)} | \text{ZnSO}_4(aq) || \text{CuSO}_4(aq) | \text{Cu}_{(s)}$   
 when the concentration of  $\text{Zn}^{2+}$  is 10 times the concentration of  $\text{Cu}^{2+}$ , the expression for  $\Delta G$  (in  $\text{J mol}^{-1}$ ) is  
 [F is Faraday constant; R is gas constant; T is temperature;  $E^{\circ}_{\text{cell}} = 1.1 \text{ V}$ ]
- (a)  $2.303 RT - 2.2F$       (b)  $-2.2F$   
(c)  $2.303 RT + 1.1F$       (d)  $1.1F$   
(JEE Advanced 2017)

## ELECTRICAL RESISTANCE AND CONDUCTANCE

- Ohm's law relates the current, potential difference (E) and the resistance (R) of the conductor as  $i = E/R$ .
- The SI unit of electric resistance is ohm ( $\Omega$ ). At a given temperature resistance is directly proportional to length (l) and inversely proportional to area of cross section (a) of the conductor, i.e.,  

$$R \propto \frac{l}{a} \text{ or } R = \frac{\rho \times l}{a}$$
 where  $\rho$  is specific resistance or resistivity, if l and a are unity then,  $R = \rho$
- Conductance (C) is the reciprocal of resistance.  

$$C = \frac{1}{R}$$
 Its unit is  $\text{ohm}^{-1}$  or mho. The SI unit is Siemens (S).

## Specific, Equivalent and Molar Conductivities

- Specific Conductance ( $\kappa$ )  
 Since,  $C = \frac{1}{R}$  and  $R = \frac{\rho \times l}{a}$   $\therefore C = \frac{1}{\rho} \times \frac{a}{l} = \kappa \frac{a}{l}$ .  
 $\kappa$  is called specific conductance. Specific conductance of an electrolyte is the conductance of  $1 \text{ cm}^3$  solution between electrodes placed 1 cm apart.  

$$\therefore \kappa = C \times \frac{l}{a}$$
 $l/a$  is called cell constant. Unit of  $\kappa$  is  $\text{ohm}^{-1} \text{ cm}^{-1}$  or  $\text{mho cm}^{-1}$ . The SI unit is  $\text{S m}^{-1}$ .

- Equivalent Conductance, ( $\Lambda$ ) is more useful in comparing the conducting power of different electrolyte solutions, having different concentrations of ions.

If  $1 \text{ cm}^3$  solution contains 1 gm equivalent weight of electrolyte then conductance of the solution = equivalent conductance.

If concentration, C is given in gram equivalents per litre, then,

$$V = \frac{1000}{C} \text{ or, } \Lambda = \kappa \times V = \kappa \times \frac{1000}{C}$$

C in g- eq/litre = normality

Unit of  $\Lambda$  is  $\text{ohm}^{-1} \text{ m}^2 \text{ g eq}^{-1}$ .

- Molar conductance ( $\Lambda_m$ ) or molar conductivity is defined as the conducting power of all the ions produced by one mole of electrolyte in the solution.  
 $\therefore \Lambda_m = \kappa \times V_m$ , where  $V_m$  = volume of solution containing 1 mole of electrolyte.

If  $C_m$  is concentration in moles litre $^{-1}$  then,

$$\Lambda_m = \kappa \times \frac{1000}{C_m}; C_m = \text{molarity}$$

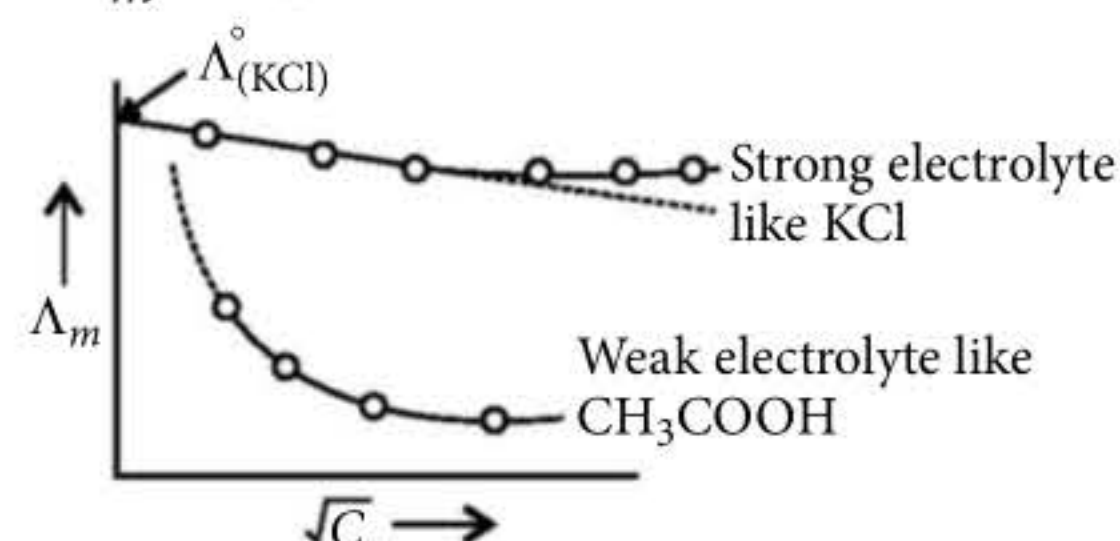
In SI system, concentration  $C_m$  is expressed as moles/ $\text{m}^3$  and volume  $V_m$  as  $\text{m}^3$  per mole.

$$V_m = \frac{1}{C_m}, \therefore \Lambda_m = \kappa \times V_m = \frac{\kappa}{C_m}$$

Unit of  $\Lambda_m$  is  $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , in SI system it is  $\text{ohm}^{-1} \text{ m}^2 \text{ mol}^{-1}$ .

- Variation of molar conductivity with concentration :** For a strong electrolyte, Debye-Huckel Onsager equation is as follows :

$$\Lambda_m = \Lambda_m^{\circ} - A\sqrt{C}$$



Here,  $\Lambda_m^{\circ}$  = Molar conductivity at infinite dilution (Limiting molar conductivity)

$\Lambda_m$  = Molar conductivity at V-dilution

A = Constant which depends upon nature of solvent and temperature

C = Concentration

Plot of  $\Lambda_m$  against  $C^{1/2}$  (for a strong electrolyte) is a straight line with intercept equal to  $\Lambda_m^{\circ}$  and slope equal to  $-A$ .

Thus,  $\Lambda_m^c$  decreases linearly with  $\sqrt{C}$ , when  $C = 0$ ,  $\Lambda_m^c = \Lambda_m^{\circ}$ .  $\Lambda_m^{\circ}$  can be determined experimentally.

## KOHLRAUSCH'S LAW

“At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion with which it is associated and that the molar conductance of any electrolyte at infinite dilution is given by the sum of the contributions of the two ions”. This is called Kohlrausch's law.

$$\Lambda_m^\infty = \lambda_+^\infty + \lambda_-^\infty$$

$\lambda_+^\infty$  and  $\lambda_-^\infty$  are molar ionic conductances at infinite dilution for cations and anions.

### Applications of Kohlrausch's Law

- It is useful in the calculation of  $\lambda_m^\infty$  for weak electrolytes, e.g.,

$$\Lambda_{m\text{CH}_3\text{COOH}}^\infty = \Lambda_{m\text{CH}_3\text{COONa}}^\infty + \Lambda_{m\text{HCl}}^\infty - \Lambda_{m\text{NaCl}}^\infty$$

- In the calculation of degree of dissociation, e.g.,

$$\alpha = \frac{\text{molar conductivity at conc. } C}{\text{molar conductivity at infinite dilution}} = \frac{\Lambda_m^C}{\Lambda_m^\infty}$$

- Useful in calculation of solubility of a sparingly soluble salt. The solution of a sparingly soluble salt becomes saturated at infinite dilution, then  $\Lambda_m = \Lambda_m^\infty$  and molarity = solubility, hence

$$\Lambda_m = \frac{\kappa \times 1000}{\text{molarity}}$$

$$\text{or solubility (moles L}^{-1}\text{)} = \frac{\kappa \times 1000}{\Lambda_m^\infty}$$

### PEEP INTO PREVIOUS YEARS

3. Following limiting molar conductivities are given as :

$$\lambda_{m(\text{H}_2\text{SO}_4)}^\circ = x \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_{m(\text{K}_2\text{SO}_4)}^\circ = y \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_{m(\text{CH}_3\text{COOK})}^\circ = z \text{ S cm}^2 \text{ mol}^{-1}$$

$\lambda_m^\circ$  (in  $\text{S cm}^2 \text{ mol}^{-1}$ ) for  $\text{CH}_3\text{COOH}$  will be

- (a)  $x - y + 2z$                       (b)  $x + y - z$   
(c)  $x - y + z$                         (d)  $(x - y)/2 + z$

(Odisha NEET 2019)

4. The molar conductivity of a  $0.5 \text{ mol/dm}^3$  solution of  $\text{AgNO}_3$  with electrolytic conductivity of  $5.76 \times 10^{-3} \text{ S cm}^{-1}$  at 298 K is

- (a)  $2.88 \text{ S cm}^2/\text{mol}$               (b)  $11.52 \text{ S cm}^2/\text{mol}$   
(c)  $0.086 \text{ S cm}^2/\text{mol}$         (d)  $28.8 \text{ S cm}^2/\text{mol}$

(NEET-II 2016)

### POINTS FOR EXTRA SCORING

➤ Thermodynamic efficiency ( $\eta$ ) of a fuel cell

$$= \frac{\Delta G}{\Delta H} = - \frac{nFE}{\Delta H}$$

- $\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$  (when different number of electrons are involved)

$$-n_3FE_3^\circ = -n_1FE_1^\circ - n_2FE_2^\circ$$

$$n_3E_3^\circ = n_1E_1^\circ + n_2E_2^\circ \text{ or } E_3^\circ = \frac{n_1E_1^\circ + n_2E_2^\circ}{n_3};$$

if  $n_1 = n_2 = n_3$ ,  $E_3^\circ = E_1^\circ + E_2^\circ$

➤  $E_{\text{H}^+/\text{H}_2} = E_{\text{H}^+/\text{H}_2}^\circ - 0.0591 \log \frac{1}{[\text{H}^+]}$

$$= 0 - 0.0591(-\log[\text{H}^+]) = -0.0591 \text{ pH}$$

$$\therefore \text{pH} = -\log[\text{H}^+]$$

As pH of the solution increases, electrode potential of hydrogen electrode decreases.

- For concentration cell,  $\text{Zn} \mid \text{Zn}^{2+}_{(C_1)} \parallel \text{Zn}^{2+}_{(C_2)} \mid \text{Zn}$ ;

$$E_{\text{cell}} = \frac{0.0591}{2} \log \left( \frac{C_2}{C_1} \right) (C_2 > C_1)$$

For gas concentration cell,

$$\text{Pt}, (\text{H}_2)_{P_1} \mid \text{HCl} \mid (\text{H}_2)_{P_2}, \text{Pt}$$

$$E_{\text{cell}} = 0.0591 \log \frac{P_2}{P_1} (P_2 > P_1)$$

- Determination of transport number :

$$t_{\pm}^\circ = \frac{\lambda_{\pm}^\circ}{\Lambda_m^\circ} = \frac{\lambda_{\pm}^\circ}{\lambda_+^\circ + \lambda_-^\circ}$$

where,  $t_+^\circ$  = Transport number of cation,

$t_-^\circ$  = Transport number of anion

## Chemical Kinetics

- Chemical kinetics is the branch of chemistry which deals with rate and mechanism of chemical reaction.
- The speed with which the reactants are converted into products is called rate of the reaction.
- The rate of reaction is defined as change in the concentration of any one of the reactants or products per unit time.

### RATE EXPRESSIONS

- For a general reaction :  $aA + bB \rightarrow cC + dD$

Rate of disappearance of A =  $-d[A]/dt$

Rate of disappearance of B =  $-d[B]/dt$

Rate of appearance of C =  $d[C]/dt$

Rate of appearance of D =  $d[D]/dt$

The positive sign shows that concentrations of C and D increases with time and the negative sign indicates that concentrations of A and B decrease with time.

Instantaneous rate of reaction :

$$-\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

Average rate of reaction :

$$-\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

- **Units of rate of reaction**

mol L<sup>-1</sup> s<sup>-1</sup> or mol L<sup>-1</sup> min<sup>-1</sup> (concentration time<sup>-1</sup>).  
For gaseous reactions; atm min<sup>-1</sup> or atm s<sup>-1</sup>

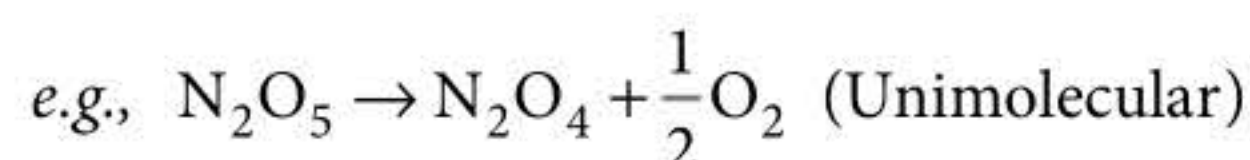
### Factors Influencing Rate of a Reaction

- **Concentration** : Greater the concentrations of the reactants, faster is the rate of reaction.
- **Physical state of reactants** : Reactions involving gaseous reactants are faster than reactions containing solid and liquid reactants.
- **Temperature** : The rate of reaction increases with increase of temperature. For most of the reactions, rate of reaction becomes almost double with 10° rise of temperature.
- **Presence of catalyst** : A catalyst generally increases the speed of a reaction.
- **Surface area of reactants** : For a reaction involving a solid reactant or catalyst, the greater is the surface area, the faster is the reaction.
- **Presence of light** : Photochemical reactions take place in the presence of light only.

### RATE LAW

- Rate law or rate equation are the mathematical expression which expresses the observed rate of a reaction in terms of the concentration of the reacting species with each term raised to some power, which may or may not be same as the stoichiometric coefficient of that reactant in a balanced chemical equation. e.g.,  $aA + bB \rightarrow \text{product}$   
Rate =  $k[A]^a[B]^b$ .

- Rate constant of a reaction is the rate of the reaction when the molar concentration of each of the reactant is unity i.e.,  $[A] = [B] = 1$ , Rate =  $k$
- Order of the reaction is the sum of exponents of the concentration terms in the rate law.
- Order of reaction can be zero, integer or fractional.
- Certain bimolecular reactions which follow the first order kinetics are called pseudounimolecular reactions.
- The units of rate constant depend upon the order of reaction.
- The units of the rate constant can be remembered by this formula ; liter<sup>*n*-1</sup> mole<sup>1-*n*</sup> sec<sup>-1</sup> where, *n* is the order of the reaction.
- Molecularity of a reaction is defined as the number of reacting molecules which collide simultaneously to bring about a chemical reaction.



- **Difference between Order and Molecularity**

	Order	Molecularity
1.	It is an experimental quantity.	It is a theoretical concept.
2.	It is the sum of the powers of the concentration terms in rate law.	It is the number of species which simultaneously collide.
3.	It may have fractional values.	It has only whole number values.
4.	It can be zero.	It cannot be zero.

- **Half-life of reaction** : The time in which the concentration of a reactant is reduced to one half of its initial concentration is called half-life of the reaction.  $t_{1/2} \propto \frac{1}{a^{n-1}}$  where, *n* is the order of the reaction.

### RATE LAW, INTEGRATED RATE EQUATIONS FOR THE REACTIONS OF DIFFERENT ORDERS

Order	Rate law	Integrated rate law	Half-life	Units of rate constant	Graph
0	Rate = $k[A]^0$	$[A]_t = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$	mol L <sup>-1</sup> s <sup>-1</sup>	$[A]$ vs $t$ ; slope = $-k$
1	Rate = $k[A]^1$	$\ln[A]_t = -kt + \ln [A]_0$	$t_{1/2} = 0.693/k$	s <sup>-1</sup>	$\ln[A]$ vs $t$ ; slope = $-k$
2	Rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$t_{1/2} = 1/k [A]_0$	L mol <sup>-1</sup> s <sup>-1</sup>	$1/[A]$ vs $t$ ; slope = $k$

2	Rate = $k[A][B]$	$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0[A]}{[A]_0[B]}$	-	$\text{L mol}^{-1} \text{s}^{-1}$	$1/[A]$ vs $t$ ; slope = $k$
$n$	Rate = $k[A]^n$	$(n-1)kt = \frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}}$	$t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}}$	$(\text{mol L}^{-1})^{1-n} \text{s}^{-1}$	$\frac{1}{[A]^{n-1}}$ vs $t$ ; slope = $(n-1)k$

### PEEP INTO PREVIOUS YEARS

5. If the rate constant for a first order reaction is  $k$ , the time ( $t$ ) required for the completion of 99% of the reaction is given by  
 (a)  $t = 2.303/k$  (b)  $t = 0.693/k$   
 (c)  $t = 6.909/k$  (d)  $t = 4.606/k$   
 (NEET 2019)
6. The reaction  $2X \rightarrow B$  is a zeroth order reaction. If the initial concentration of  $X$  is 0.2 M, the half-life is 6 h. When the initial concentration of  $X$  is 0.5 M the time required to reach its final concentration of 0.2 M will be  
 (a) 12.0 h (b) 9.0 h (c) 7.2 h (d) 18.0 h  
 (JEE Main 2019)

### ARRHENIUS EQUATION

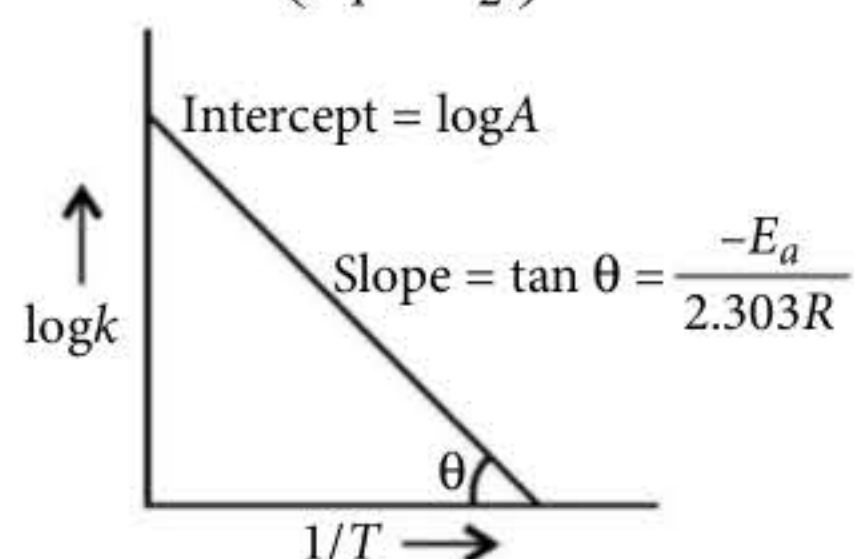
The effect of temperature on the rate of reaction and hence on the rate constant  $k$ , was proposed by Arrhenius, which is known as Arrhenius equation.

$$k = Ae^{-E_a/RT}$$

where,  $k$  = Rate constant,  $A$  = Pre-exponential factor,  $T$  = Temperature in kelvin,  $E_a$  = Activation Energy  
 The factor  $e^{-E_a/RT}$  represents fraction of molecules that have kinetic energy greater than  $E_a$ .

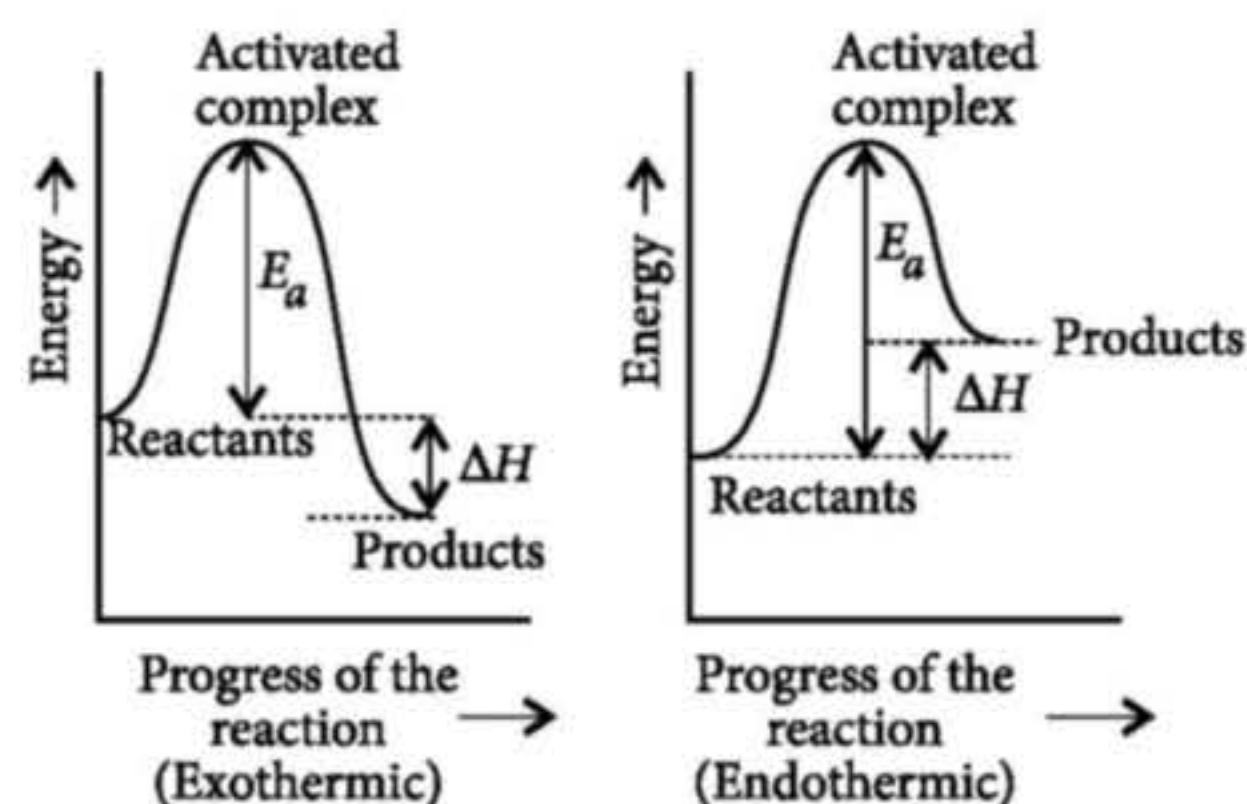
### Logarithmic Expression

$$\log_{10} \left( \frac{k_2}{k_1} \right) = \frac{E_a}{2.303 R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$



### ACTIVATION ENERGY

- The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy ( $E_a$ ).



- Activation energy = Threshold energy - Average kinetic energy of reacting molecules
- Activation energy ( $E_a$ )  
 $= E_{(\text{activated complex})} - E_{(\text{ground state})}$
- $\Delta H$  = Activation energy of forward reaction - Activation energy of backward reaction

### COLLISION THEORY

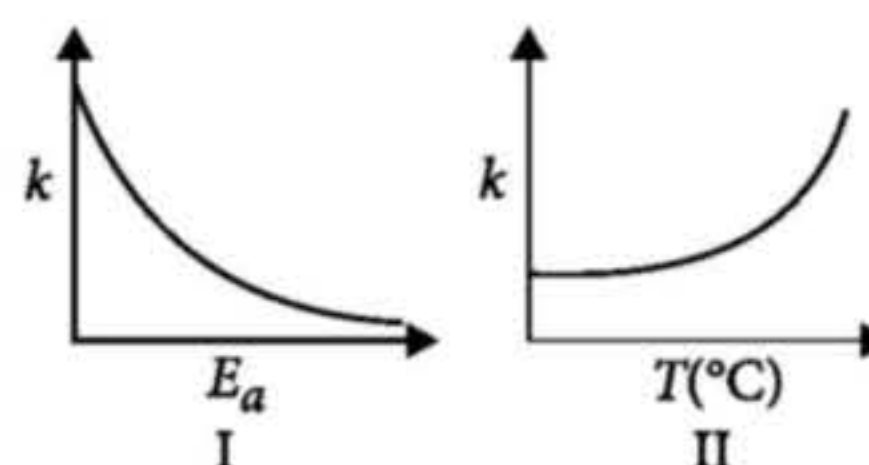
- According to this theory rate of reaction depends upon the number of effective collisions which in turn depends upon energy factor and orientation factor.

$$k = PZ_{AB} e^{-E_a/RT}$$

$P$  = Probability or orientation factor

### PEEP INTO PREVIOUS YEARS

7. Consider the given plots for a reaction obeying Arrhenius equation ( $0^\circ\text{C} < T < 300^\circ\text{C}$ ): ( $k$  and  $E_a$  are rate constant and activation energy, respectively)



Choose the correct option.

- (a) I is right but II is wrong.  
 (b) Both I and II are wrong.  
 (c) I is wrong but II is right.  
 (d) Both I and II are correct. (JEE Main 2019)

8. In a bimolecular reaction, the steric factor  $P$  was experimentally determined to be 4.5. The correct option(s) among the following is(are)
- experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation
  - the value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally
  - the activation energy of the reaction is unaffected by the value of the steric factor
  - since  $P = 4.5$ , the reaction will not proceed unless an effective catalyst is used.

(JEE Advanced 2017)

### POINTS FOR EXTRA SCORING

- For a reversible reaction at equilibrium,

$$\left(\frac{dx}{dt}\right)_{\text{forward}} = \left(\frac{dx}{dt}\right)_{\text{backward}}$$

The overall rate of reaction,

$$\frac{dx}{dt} = \left(\frac{dx}{dt}\right)_{\text{forward}} - \left(\frac{dx}{dt}\right)_{\text{backward}} = 0$$

- Some useful relationships between time periods for different fractions of reaction of first order to complete.
- $$t_{3/4} \text{ or } t_{75\%} = 2t_{1/2}, t_{87.5\%} = 3t_{1/2}, t_{93.75\%} = 4t_{1/2}, t_{96.87\%} = 5t_{1/2}, t_{99.9\%} = 10t_{1/2}$$
- General expression for time taken for  $n^{\text{th}}$  fraction of a reaction of 1st order to complete (by putting  $x = \frac{a}{n}$ ,  $t = t_{1/n}$ );  $t_{1/n} = \frac{2.303}{k} \log \frac{n}{n-1}$
- Average life ( $\tau$ ) is taken as the reciprocal of the disintegration constant ( $k$ ), i.e.,
- $$\tau = \frac{1}{k} = \frac{t_{1/2}}{0.693} = 1.44 \times t_{1/2}$$
- Amount of the substance left after ' $n$ ' half-lives
- $$= \frac{[A]_0}{2^n}$$

## Surface Chemistry

### ADSORPTION

- Adsorption is the phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or solid, resulting in a higher concentration of molecules on the surface.
- Adsorption is a surface phenomenon.
- The substance being adsorbed is called adsorbate and the substance on whose surface it is being adsorbed is called the adsorbent.
- Sorption is a term used when both absorption and adsorption occur simultaneously.
- Desorption is the reverse of adsorption, i.e., the removal of the adsorbed substance from the surface of the adsorbent.
- Occlusion is a term used for adsorption of gases on a metal surface.
- Adsorption is specific and selective in nature.

### Type of Adsorption

- **Based on Concentration :**
  - **Positive adsorption :** If the concentration of adsorbate is more at the surface as compared

to its concentration in the bulk phase then it is called positive adsorption.

- **Negative adsorption :** If concentration of adsorbate is less at the surface as compared to its concentration in the bulk phase then it is called negative adsorption.
- **Based on forces existing between adsorbate molecule and adsorbent :**
  - **Physical adsorption :** If the forces of attraction existing between adsorbate and adsorbent are van der Waals' forces, then adsorption is called physical adsorption.
  - **Chemical adsorption :** If the forces of attraction existing between adsorbate particles and adsorbent are almost of the same strength as chemical bonds then adsorption is called chemical adsorption.

## Quotable Quote

"An experiment is a question which science poses to Nature, and a measurement is the recording of Nature's answer."

MAX PLANCK

## Differences between Physisorption and Chemisorption :

Property	Physisorption	Chemisorption
Enthalpy	Low enthalpy, in the order of 20-40 kJ mol <sup>-1</sup> .	High enthalpy, in the order of 80-240 kJ mol <sup>-1</sup> .
Reversibility	Reversible process	Irreversible process
Effect of temperature	With the increase in temperature, extent of adsorption decreases because adsorption is an exothermic process and kinetic energy of gas molecules increases with temperature.	Chemisorption first increases with temperature upto a certain extent and then decreases. A gas adsorbed at low temperature by physical adsorption may change into chemisorption at high temperature.
Selectivity	Not selective in nature.	Highly selective in nature.
Nature and state of adsorbate	The extent of adsorption depends upon the ease of liquefaction of the gas.	The state of adsorbed molecules may be different from that in the bulk.
Activation energy	No appreciable energy needed.	High activation energy needed.
Pressure	Increase in pressure increases adsorption.	Increase in pressure decreases adsorption.
Layers	Multimolecular layer.	Mono-molecular layer.

## ADSORPTION ISOTHERM

Graph between extent of the adsorption  $\left(\frac{x}{m}\right)$  and pressure ( $P$ ) at a given temperature is called adsorption isotherm. There are two types of adsorption isotherms:

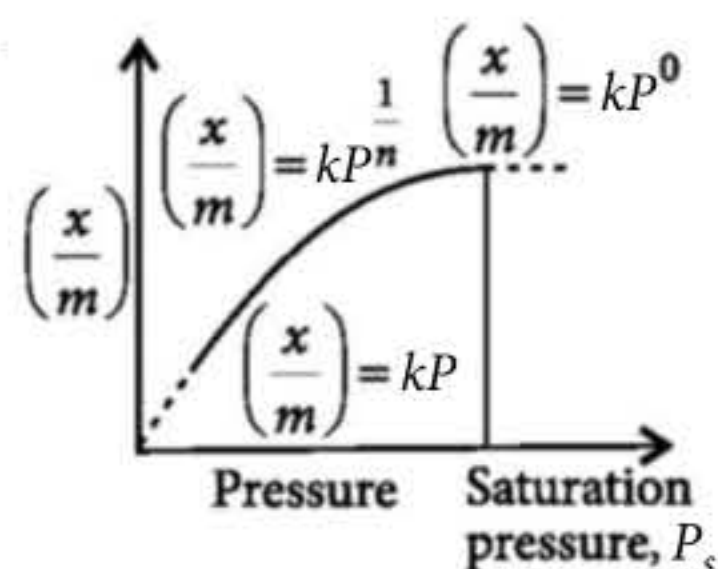
### • Freundlich Adsorption Isotherm :

Freundlich's Equation,

$$\frac{x}{m} = k \times P^{1/n}$$

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$$

where  $x$  = mass of adsorbate adsorbed,  
 $m$  = mass of adsorbent,  $P$  = pressure



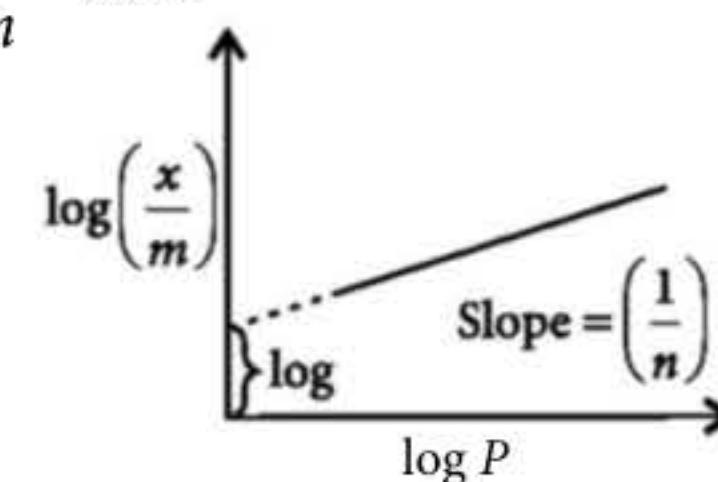
- At low pressure :  $\frac{x}{m} = k \times P$

- At intermediate pressure :

$$\frac{x}{m} = k \times P^{1/n},$$

Where,  $n \geq 1$

- At high pressure :  $x/m = \text{constant}$



- **Langmuir Adsorption Isotherm** : Assuming adsorption to be unimolecular, Langmuir deduced a relationship theoretically :

$$\frac{x}{m} = \frac{aP}{1 + bP}$$

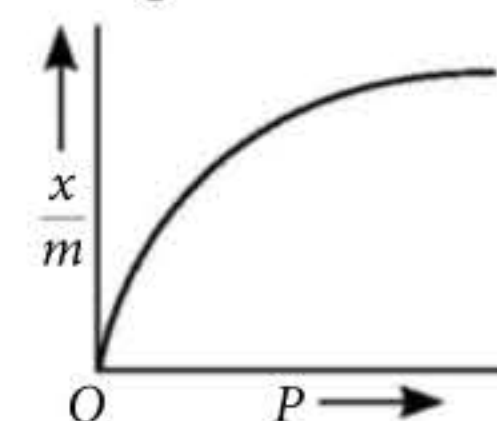
Where,  $a$  and  $b$  Langmuir parameters which depends upon the nature of the gas adsorbate, the nature of solid adsorbent and the temperature.

**Case-I** : At very high pressure  $bP \gg 1$ ,

$$\therefore \frac{x}{m} = \frac{aP}{bP} = \frac{a}{b} = \text{constant}$$

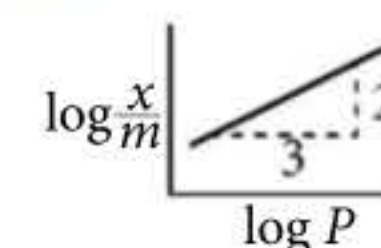
**Case-II** : At very low pressure  $bP \ll 1$

$$\therefore \frac{x}{m} = aP$$



## ✓ PEEP INTO PREVIOUS YEARS

9. Adsorption of a gas follows Freundlich adsorption isotherm.  $x$  is the mass of the gas adsorbed on mass  $m$  of the adsorbent.



The plot of  $\log \frac{x}{m}$  versus  $\log P$  is shown in the given

graph.  $\frac{x}{m}$  is proportional to

- (a)  $P^2$  (b)  $P^3$   
 (c)  $P^{2/3}$  (d)  $P^{3/2}$  (JEE Main 2019)
10. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C. For this process, the correct statement is
- (a) the adsorption requires activation at 25°C  
 (b) the adsorption is accompanied by a decrease in enthalpy  
 (c) the adsorption increases with increase of temperature  
 (d) the adsorption is irreversible.

(JEE Advanced 2013)



## CATALYST

**Catalysis** : Substances which accelerate the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction, are known as *catalysts*, and the phenomenon is known as *catalysis*.

### Homogeneous Catalysis

The process in which the reactants and the catalyst are in the same phase. *e.g.*, oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  by NO as catalyst (lead chamber process), hydrolysis of methyl acetate by HCl, hydrolysis of sugar by  $\text{H}_2\text{SO}_4$ .

### Shape-selective Catalysis

The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules. *e.g.*, Zeolites,  $M_{x/n}[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot m\text{H}_2\text{O}$ , having honey-comb like structures.

### Heterogeneous Catalysis

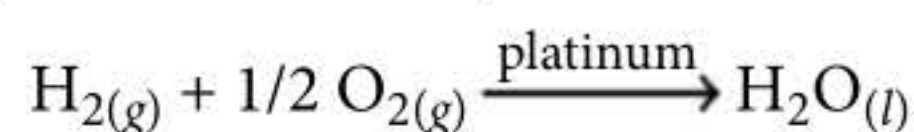
The process in which the reactants and the catalyst are in different phases. *e.g.*, oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  by Pt, manufacture of  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2$  by Fe (Haber's process), oxidation of  $\text{NH}_3$  to NO by Pt (Ostwald's process), hydrogenation of vegetable oils by Ni.

### Enzyme Catalysis

Many biochemical reactions are catalysed by complex nitrogenous organic compounds (proteins or enzymes) which are also called *biochemical catalysts* and the phenomenon is known as *biochemical catalysis*.

- Activity of a catalyst refers to the ability of a catalyst to accelerate chemical reaction.

*e.g.*, Pt acts as a catalyst in the reaction,



- Selectivity of a catalyst refers to the ability of a catalyst to direct a reaction to yield a particular product (excluding others), *e.g.*, *n*-heptane selectively gives toluene in presence of platinum as catalyst.

- Some enzymatic reactions :

	Enzyme	Source	Enzymatic reaction
1.	Invertase	Yeast	Sucrose $\rightarrow$ glucose and fructose
2.	Zymase	Yeast	Glucose $\rightarrow$ ethyl alcohol and carbon dioxide
3.	Diastase	Malt	Starch $\rightarrow$ maltose
4.	Maltase	Yeast	Maltose $\rightarrow$ glucose
5.	Urease	Soyabean	Urea $\rightarrow$ ammonia and carbon dioxide.

### PEEP INTO PREVIOUS YEARS

- Which of the following is not an example of heterogeneous catalytic reaction?
  - Haber's process
  - Hydrogenation of vegetable oils
  - Combustion of coal
  - Ostwald's process

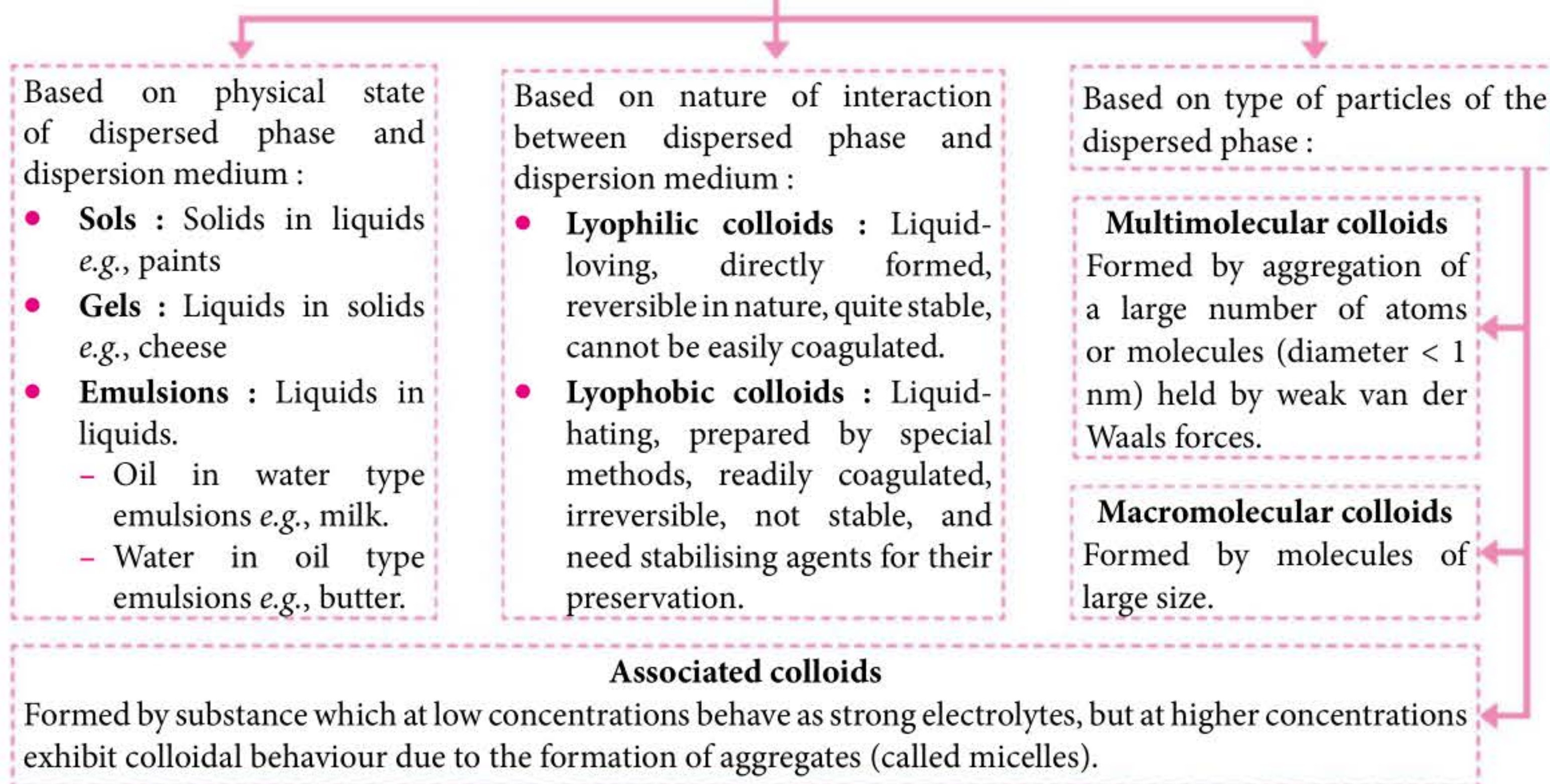
(JEE Main 2019)
- Which one of the following statements is not correct?
  - The value of equilibrium constant is changed in the presence of a catalyst in the reaction at equilibrium.
  - Enzymes catalyse mainly biochemical reactions.
  - Coenzymes increase the catalytic activity of enzyme.
  - Catalyst does not initiate any reaction.

(NEET 2017)

## COLLOIDAL STATE

- Colloidal state of matter is a state in which the size of the particles (1 to 1000 nm) is such that they can pass through filter paper but not through animal or vegetable membrane.

## Classification of Colloids



### Preparation of Colloids

Lyophobic sols are prepared indirectly by any of the following methods :

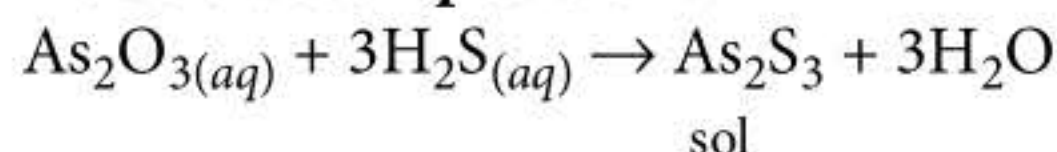
#### Dispersion or Disintegration Methods

- Electro-dispersion by Bredig's arc method is used to prepare sols of metals like Ag, Cu, Au, Pt etc. A direct current is passed through electrodes of the metal, the electric arc vapourizes the metal and vapours condense in the medium to form a sol.
- Peptization involves the conversion of a freshly prepared precipitate into colloidal size particles by shaking with a suitable electrolyte, e.g., freshly prepared  $\text{Fe}(\text{OH})_3$  is treated with  $\text{FeCl}_3$  or  $\text{AgI}$  with  $\text{AgNO}_3$  etc. The electrolyte used is called a peptizing agent.

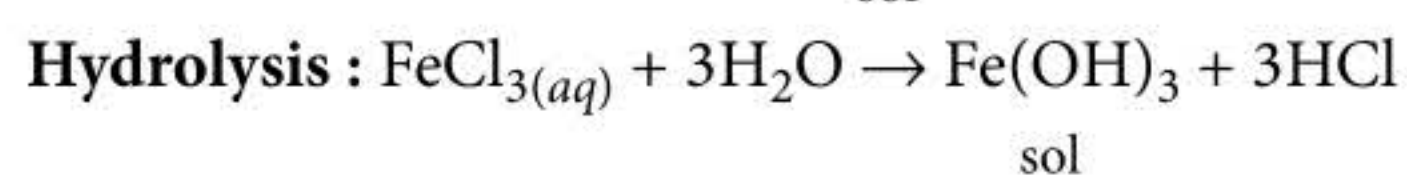
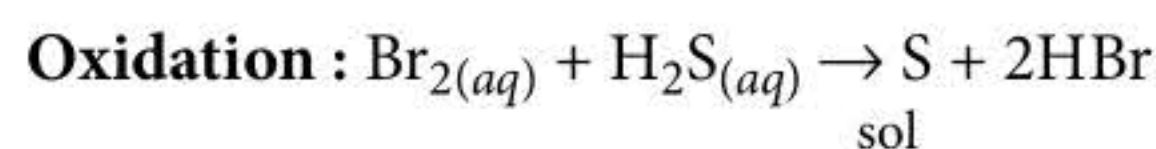
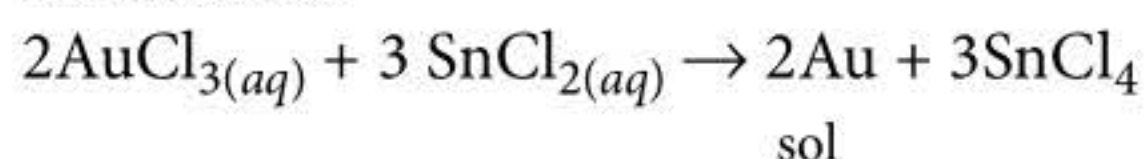
#### Condensation or Aggregation Methods

- These methods involve the joining together smaller particles to form colloidal size particles.
- Chemical methods involve different chemical reactions yielding a sol, e.g.,

##### Double decomposition :



##### Reduction :



- Exchange of solvent is the method used to prepare sols of substances less soluble in water, e.g., water is added to a solution of sulphur or phosphorus in alcohol to yield a sol.

### Properties of Colloidal Solutions

- **Colligative properties :** Colloids show colligative properties like relative lowering of vapour pressure, elevation of boiling point, etc. and magnitude of colligative properties of colloids is much less than true solutions due to larger size of colloidal particles.

### Monthly Test Drive CLASS XI ANSWER KEY

- |           |             |             |         |           |
|-----------|-------------|-------------|---------|-----------|
| 1. (a)    | 2. (a)      | 3. (b)      | 4. (b)  | 5. (d)    |
| 6. (b)    | 7. (d)      | 8. (c)      | 9. (c)  | 10. (a)   |
| 11. (d)   | 12. (a)     | 13. (a)     | 14. (d) | 15. (b)   |
| 16. (b)   | 17. (d)     | 18. (c)     | 19. (a) | 20. (b,d) |
| 21. (b,c) | 22. (a,b,c) | 23. (b,c,d) | 24. (6) | 25. (4)   |
| 26. (5)   | 27. (d)     | 28. (a)     | 29. (c) | 30. (b)   |

- **Tyndall effect (Optical property)** : Scattering of light by colloidal particles due to which the path of light beam becomes visible.
- **Brownian movement (Mechanical property)** : Zig-zag movement of colloidal particles due to the unbalanced bombardment by the molecules of dispersion medium.
- **Charge on colloidal particles** : Colloidal particles always carry an electric charge and nature of charge (+ve or -ve) is same on all the particles in a given colloidal solution. The charge is due to preferential adsorption of ions from solution.
- **Electrophoresis (Electrical property)** : Movement of colloidal particles towards one of the electrodes on passage of electricity through colloidal solution. The direction depends on the type of charge on colloidal particles.

### Coagulation

The stability of the colloidal system is due to the existence of charged particles. If the charges are neutralised or destroyed, then the colloidal solution gets precipitated. This is called Coagulation or Flocculation. It can be done by

- adding electrolyte
- mutual action of sols
- persistent dialysis
- by cooling
- by electrophoresis.
- **Coagulation value** : The minimum concentration of the electrolyte required in millimoles per litre of solution to cause coagulation or flocculation is called coagulation value.
- **Hardy—Schulze rule** : According to this rule the coagulating power of the active ion increases with the valency of the active ion.
- **Gold number** : It is defined as the minimum amount of the protective colloid in milligrams which must be added to 10 mL solution of standard gold sol, which prevents coagulation on adding one mL of 10% NaCl solution.

### PEEP INTO PREVIOUS YEARS

13. The correct option among the following is
- colloidal particles in lyophobic sols can be precipitated by electrophoresis
  - colloidal medicines are more effective because they have small surface area
  - addition of alum to water makes it unfit for drinking
  - Brownian motion in colloidal solution is faster if the viscosity of the solution is very high.

(JEE Main 2019)

14. On which of the following properties does the coagulating power of an ion depend?
- The magnitude of the charge on the ion alone.
  - Size of the ion alone.
  - Both magnitude and sign of the charge on the ion.
  - The sign of charge on the ion alone.

(NEET 2018)

### POINTS FOR EXTRA SCORING

- Colloidal antimony is used in curing Kala-azar.
- Argyrol is a silver sol used as eye lotion.
- Colloidal solution of gold in water is called 'Purple of cassius'.
- Catalyst lowers the activation energy and does not change the value of equilibrium constant but helps in attaining the equilibrium faster.
- The graphs plotted  $T$  vs  $P$  for given amount of adsorption are known as adsorption isostere.
- The flocculation of an emulsion, viz. the formation of aggregates, may be followed by coalescence. If coalescence is extensive it leads to the formation of a macrophase and the emulsion is said to break.
- The deltas at the mouths of great rivers are formed by the precipitation of the charged clay particles carried in suspension in the river water, by the action of salts present in sea-water.
- Blood is a colloidal system of an albuminoid substance.

### Answer Key For Peep Into Previous Years

1.	(b)	2.	(a)	3.	(d)	4.	(b)	5.	(d)	6.	(d)
7.	(d)	8.	(a,c)	9.	(c)	10.	(b)	11.	(c)	12.	(a)
13.	(a)	14.	(c)								