

Electrochemistry

When an electrode is kept in contact with its own ions, a potential difference is developed between the electrode and the solution of the electrolyte. This potential difference is called standard electrode potential when the concentrations of the ionic and gaseous species are taken as 1 M and 1 bar respectively at 298 K.

Galvanic cell is an electrochemical cell that converts the chemical energy of the spontaneous redox reaction into electrical energy. The half cell in which oxidation takes place is called **anode** and it has negative potential with respect to the solution. The other half-cell in which reduction takes place is called **cathode** and it has positive potential w.r.t. the solution. When the two half-cells are joined, the electrons start flowing from anode having negative polarity to cathode with positive polarity.

The potential difference between the two electrodes is called cell potential. To maintain the flow of current in the external circuit, the two half-cells are joined by a salt bridge. The salt bridge maintains the electroneutrality in both the half-cells.

$$E_{\text{Cell}} = E_{\text{Cathode}} - E_{\text{Anode}}$$

If the concentrations of the oxidised and reduced forms of the species are unity then cell potential is called standard cell potential (E°_{cell})

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

The potential of individual half-cell is determined with the help of a reference electrode, e.g., standard hydrogen electrode (SHE) represented by $P_{\text{H}_2(\text{g})} / H_2(\text{g}, 1\text{bar}) / H^+(\text{aq}, 1\text{M})$, which is assigned a zero potential at all temperatures corresponding to the reaction : $2H^+(\text{aq}) + e^- \rightarrow H_2(\text{g})$

Significance of sign with standard electrode potential

$$E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V} \quad \text{and} \quad E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$$

– Ve sign with $E^{\circ}_{\text{Zn}^{2+}/\text{Zn}}$ means that reduction of Zn^{2+} to Zn is non-spontaneous but oxidation of Zn to Zn^{2+} occur spontaneously.

+ Ve sign with $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}}$ means that reduction of Cu^{2+} is spontaneous but oxidation of Cu to Cu^{2+} is non-spontaneous.

Nernst Equation for an electrode reaction : $M^{n+} + ne^- \rightarrow M_{(s)}$

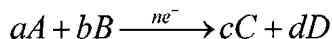
$$\text{Reaction quotient } (Q_c) = \frac{1}{[M^{n+}]}$$

The Nernst equation for this electrode reaction is :

$$E_{M^{n+}/M} = E_{M^{n+}/M}^{\theta} - \frac{2.303RT}{nf} \log \theta_c$$

$$= E_{M^{n+}/M}^{\theta} - \frac{0.059}{n} V \log \theta_c$$

Similarly Nernst equation for a cell reaction :



$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

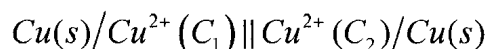
$$E_{cell} = E_{cell}^{\theta} - \frac{0.059}{n} V \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

At equilibrium, $E_{cell} = 0$ and $Q_c = K_c$

$$0 = E_{cell}^{\theta} - \frac{0.059}{n} V \log K$$

NOTE :- Concentration of pure solids and liquids does not change during the course of cell-reaction and therefore their concentration terms are not taken into account. Concentration of gaseous species are expressed in terms of partial pressure.

Concentration cells have the same electrodes but the concentrations of the solutions of the same electrolyte is different in the two half-cells. For example,



Cell reaction : $Cu_{RHC}^{2+} \rightarrow Cu_{LHC}^{2+}$

$$E_{cell} = - \frac{0.059}{2} V \log \frac{[Cu^{2+}]_{LHC}}{[Cu^{2+}]_{RHC}}$$

Here RHC means right half-cell and LHC, left half-cell.

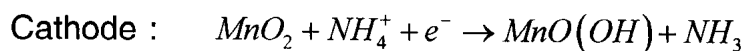
$$E_{cell} = - \frac{0.059}{2} V \log \frac{C_1}{C_2}$$

Electrochemical cell potential and Gibbs energy of reaction ($\Delta_r G$) are related as given below :

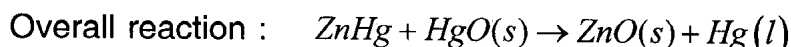
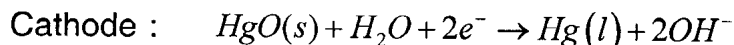
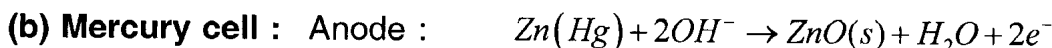
$$\Delta_r G = -n E_{cell} F$$

Here $\Delta_r G$ is an extensive thermodynamic property and E_{cell} is an intensive parameter. 'n' is the number of electrons involved in redox reaction. If the concentration of all the reacting species are taken as unity then we have $\Delta_r G^{\theta} = -n E_{cell}^{\theta} F$

1. Primary batteries

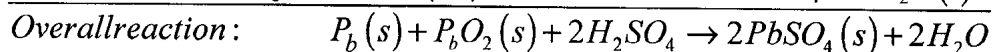
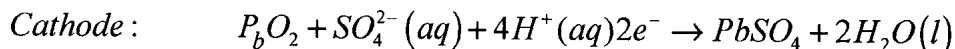
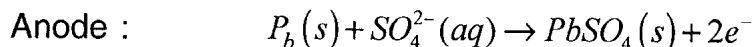


Mn is reduced from +4 oxidation state to +3 state. Ammonia produced forms a stable complex, $[Zn(NH_3)_4]^{2+}$. This cell is not rechargeable because the products formed during discharging cannot be converted into the reactants. The cell potential of nearly +1.5 V decreases with time since the concn. of ions involved in the cell reaction changes during discharging.



Cell potential of nearly 1.35 V remains constant during its life as the overall reaction does not involve any ion whose concn. can change during its life.

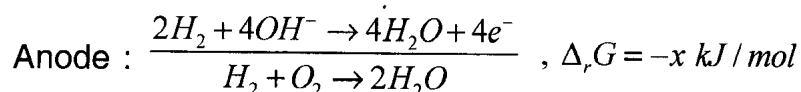
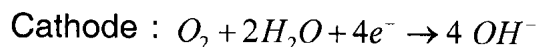
2. Lead storage battery is a secondary battery and is rechargeable. It consists of a lead anode and a grid of lead packed with PbO_2 as cathode. A 38% solution of H_2SO_4 is used as an electrolyte. During discharge following reaction occurs at electrodes.



On charging the battery, the reaction is reversed.

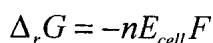
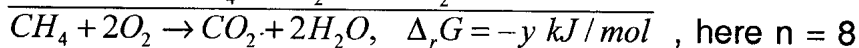
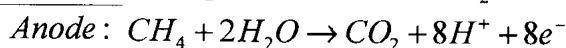
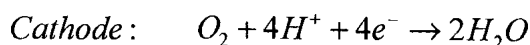
Fuel cell is a galvanic cell which converts the energy of combustion of fuels like H_2 , CH_4 , C_2H_6 , C_3H_8 , CH_3OH etc. directly into electrical energy.

In a fuel cell using H_2 as a fuel, the following reactions are occurring at electrodes.

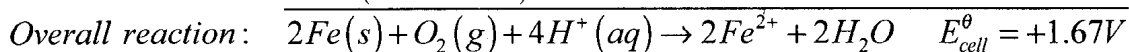
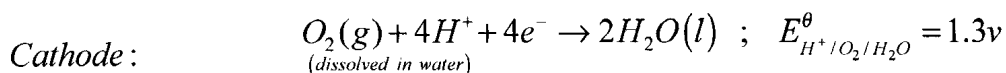
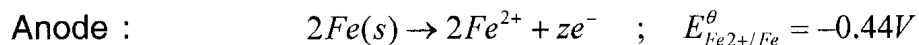


$\Delta_r G = -n E_{cell} F$. Here $n = 4$

In a fuel cell using CH_4 as a fuel, the reactions are :



Corrosion. Corrosion is an electrochemical phenomenon.



H^{+} ions are furnished by H_2CO_3 formed by the dissolution of CO_2 in water. More the concn. of H^{+} , faster is the reaction at cathode. Corrosion occurs at faster rate in saline water because the salts present in water perform the functions of salt bridge.

Atmospheric O_2 , further oxidises Fe^{2+} to Fe^{3+} to form hydrated Fe_2O_3 with further production of H^{+} ions which facilitate corrosion.

We can prevent the corrosion by preventing the surface of the metal to come in contact with atmosphere by covering the metallic surface with paint or by the layer of other metals (*Sn, Zn, etc.*).

The **conductivity** (k) of an electrolytic solution depends on :

(i) Concentration of electrolyte : k increases with the increase in concn.

(ii) Nature of solvent and its viscosity.

(iii) Size of solvated ions : solvation depends upon the charge/radius ratio. More this ratio, the more extensive the solvation of ions and lesser the mobility of ions and hence k decreases.

(iv) Temperature : ' k ' increase with the increase in temperature due to increase in the thermal energy of the ions resulting in the increase in ionic mobility.

Conductivity (k) is related to resistance as given below :

$$k = \frac{\text{Cell constant}}{\text{Resistance}} = \frac{l/A}{R}$$

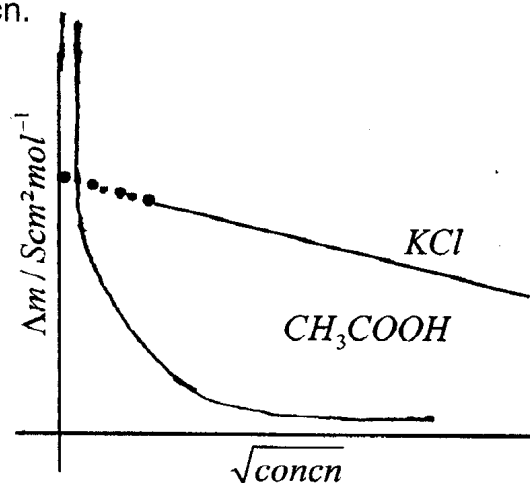
unit : $ohm^{-1}cm^{-1}$ or $S cm^{-1}$

Molar conductivity (Λ_m) is given by

$$\Lambda_m = \frac{k}{c} \text{ where } C = \text{molar concn.}$$

unit of $\Lambda_m = S cm^2 mol^{-1}$

Conductivity (k) decreases but molar conductivity (Λ_m) increases with the decrease in concentrations. It slowly increases with the decrease in concn. for strong electrolytes while the increase is very steep for weak electrolytes in very dilute solutions.



Molar conductivity at infinite dilution or zero concentration is called limiting molar conductivity denoted by Λ°_m or Λ^{∞}_m . Limiting molar conductivity (Λ°_m) of strong electrolyte is obtained by the extrapolation of curve at $\sqrt{conc} = 0$ but Λ°_m for weak electrolyte is determined by the use of Kohlrausch law of independent migration of ions which states that :

Limiting molar conductivity for an electrolyte is the sum of the contribution of molar conductivity of the ions in which it dissociates.

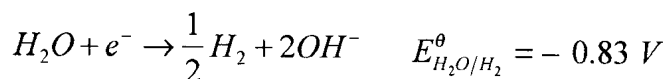
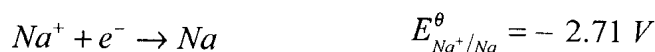
$\Lambda^{\circ}_m = \nu^+ \lambda^{\circ}_+ + \nu^- \lambda^{\circ}_-$ where ν^+ and ν^- are number of cations and anions furnished by an electrolyte.

(For Faraday's laws of electrolysis please refer the NCERT Text book for class XII Part I page 83.)

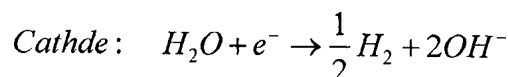
Products of Electrolysis depends on the nature of material being electrolysed and type of the electrodes being used. Inert electrodes (e.g., Pt or Au) do not take part in the chemical reactions and if the electrode is reactive, it participates in the electrode reaction. The products of electrolysis depend on the different oxidising and reducing species present in the electrolytic cell and their electrode potentials. Moreover some electrochemical process although feasible but do not seem to take place because extra potential (overvoltage) has to be applied.

Electrolysis of aqueous NaCl

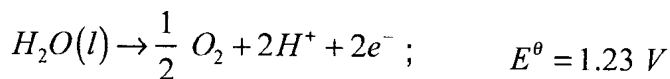
At cathode there is the competition between the following reduction reactions



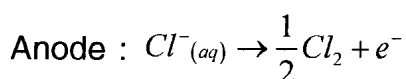
The reduction reaction with higher E^{θ} is preferred at cathode and therefore,



At the anode there is the competition between the following oxidation reactions :



At anode the reaction with lower E^{θ} is preferred and therefore water should get oxidised in preference to Cl^- . However, on account of overpotential of O_2 , the oxidation of Cl_2 ion is preferred.

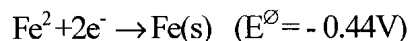
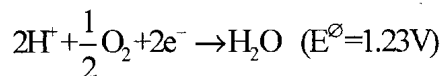


NOTE :- (i) During the electrolysis of aqueous solution of nitrates and sulphates, the oxidation of water occurs at anode in preference to the oxidation of NO_3^- or SO_4^{2-} . For example, during the electrolysis of aq. Na_2SO_4 , Na^+ is not reduced at cathode and SO_4^{2-} is not oxidised at anode. In this case water is oxidised at anode and water is also reduced at cathode.

UNIT- 8
(MOCK TEST)
ELECTROCHEMISTRY

- (1) Kohlrausch law states that at
- (a) Infinite dilution, each ion makes definite contribution to the limiting molar conductivity of an electrolyte whatever be the nature of other ion of the electrolyte.
 - (b) Finite dilution, each ion makes definite contribution to the limiting molar conductivity of an electrolyte whatever be the nature of other ion of the electrolyte.
 - (c) Infinite dilution, each ion makes definite contribution to the limiting molar conductivity of an electrolyte depending upon the nature of other ion of the electrolyte.
 - (d) Infinite dilution, each ion makes definite contribution to electrolytic conductance of an electrolyte whatever be the nature of the other ion of the electrolyte
- (2) Electrolysis of dilute aqueous NaCl solution was carried out by passing 10mA current. The time required to liberate 0.01 mole of H₂ gas at cathode is (1F=96500 C/mol)
- (a) 9.6×10^4 s
 - (b) 19.3×10^4 s
 - (c) 28.95×10^4 s
 - (d) 38.6×10^4 s
- (3) A dilute solution of NaBr is electrolysed using platinum electrodes. The products at anode and cathode are.
- (a) O₂, H₂
 - (b) Br₂, H₂
 - (c) Br₂, Na
 - (d) O₂, Na
- (4) The standard emf of cell: Zn (s)/ Zn²⁺ (aq, 0.01 M) || Fe²⁺ (aq, 0.001 M)/ Fe (s) at 298K is 0.3200V, then the value of equilibrium constant for the cell reaction is :-
- (a) $e^{\frac{0.32}{0.0295}}$
 - (b) $e^{\frac{0.32}{0.0591}}$
 - (c) $10^{\frac{0.32}{0.0295}}$
 - (d) $10^{\frac{0.32}{0.0591}}$

(5) The half-cell reaction for corrosion:



Find the ΔG^\ominus (in kJ) for the overall reaction:

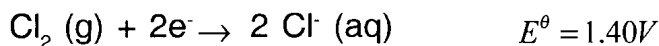
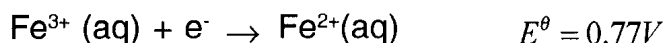
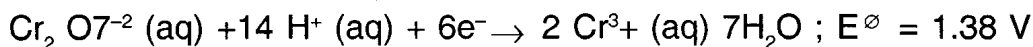
(a)-76

(b)-161

(c)-152

(d)-322

(6) Standard electrode potential data are useful for understanding the suitability of oxidant in a redox titration. Some half-cell reactions and their standard potentials are given below:-



Identify **incorrect** statement regarding the quantitative estimation of $\text{Fe}(\text{NO}_3)_2 (\text{aq})$

(a) MnO_4^- can be used in aqueous HCl

(b) $\text{Cr}_2\text{O}_7^{2-}$ can be used in aqueous HCl

(c) MnO_4^- can be used in aqueous H_2SO_4

(d) $\text{Cr}_2\text{O}_7^{2-}$ can be used in aqueous H_2SO_4

(7) The emf of concentration cell:

$\text{Zn (s)} / \text{Zn}^{2+} (0.01\text{M}) \parallel \text{Zn}^{2+} (0.1) / \text{Zn}$ is given by

(a) $E_{\text{cell}} = E_{\text{cell}}^\ominus - 2.303 \frac{RT}{F} \log \frac{0.10}{0.01}$

(b) $E_{\text{cell}} = E_{\text{cell}}^\ominus - 2.303 \frac{RT}{2F} \log \frac{0.01}{0.10}$

(c) $E_{\text{cell}} = E_{\text{cell}}^\ominus - 2.303 \frac{RT}{F} \log \frac{0.01}{0.10}$

(d) $E_{\text{cell}} = 2.303 \frac{RT}{2F} \log \frac{0.10}{0.01}$

- (8) Standard Gibbs energy of formation $\Delta_f G^\ominus$ in kJmol^{-1} at 298K for water is -237.2, The value of E^\ominus cell for the hydrogen-oxygen fuel cell is:
- (a) 1.458 V (b) 1.0229 V
(c) 1.229 V (d) 2.229 V
- (9) The standard reduction potentials of the three mettalic cations X,Y and Z are 0.52,-3.03 and -1.18V respectively. The order of reducing powers of the corresponding metal is
- (a) $y > z > x$ (b) $x > y > z$
(c) $z > y > x$ (d) $z > x > y$
- (10) The standard reduction potential for Fe^{2+} / Fe and Sn^{2+} / Sn are -0.44 and $-0.14V$ respectively. For the cell reduction $Fe^{2+} + Sn \rightarrow Fe + Sn^{2+}$, the E_{cell}^\ominus is :
- (a) + 0.30 V (b) - 0.58 V
(c) + 0.58 V (d) - 0.300 V
- (11) The correct order of molar conductivity at infinite dilution of LiCl, NaCl, and KCl is
- (a) $LiCl > NaCl > KCl$ (b) $KCl > NaCl > LiCl$
(c) $NaCl > KCl > LiCl$ (d) $LiCl > KCl > NaCl$
- (12) Standard electrode potentials for Fe^{2+} / Fe and Fe^{3+} / Fe^{2+} are -0.44 and $+0.77V$ respectively. Fe^{3+} , Fe^{2+} and Fe blocks are kept together, then
- (a) Fe^{3+} increases (b) Fe^{3+} decreases
(c) Fe^{2+} / Fe^{3+} remains unchanged (d) Fe^{2+} decreases
- (13) On the basis of information available from reaction : $\frac{4}{3}Al + O_2 \rightarrow \frac{2}{3}Al_2O_3$,
 $\Delta_r G = -827\text{kJ/mol}$ of O_2 , the minimum emf required to carry out the electrolysis of Al_2O_3 is
- (a) 2.14 V (b) 4.28 V
(c) 6.42 V (d) 8.56 V

Unit – 9

Chemical Kinetics

Consider the reaction : $2N_2O_5 \rightarrow 4NO_2 + O_2$

When a reaction proceeds, the concentration of a reactant decreases while that of a product increases with time. The rate of change of concentration of a reactant is called rate of consumption or disappearance of the reactant.

$$\text{Average rate of consumption of } N_2O_5 = -\frac{\Delta[N_2O_5]}{\Delta t}$$

Since $\Delta[N_2O_5]$ is a negative quantity, it is multiplied by -1 to make the rate of consumption a positive quantity.

Similarly, rates of formation of NO_2 and O_2 are given by

$$\text{Average rate of formation of } NO_2 = +\frac{\Delta[NO_2]}{\Delta t}$$

$$\text{Average rate of formation of } O_2 = +\frac{\Delta[O_2]}{\Delta t}$$

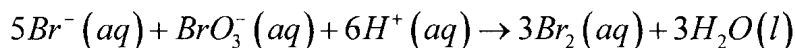
These rates can be equated if we divide the rate of change of concentration of a reactant or a product by its stoichiometric coefficient appearing in balanced chemical equation, that is,

$$\text{Average rate (r}_{av}\text{)/or Rate} = -\frac{1}{2} \frac{\Delta[N_2O_5]}{\Delta t} = +\frac{1}{4} \frac{\Delta[NO_2]}{\Delta t} = +\frac{\Delta[O_2]}{\Delta t}$$

Rate of a reaction at time ' t ' is the rate of reaction when Δt approaches zero.

$$\text{As } \Delta t \rightarrow 0, r_{inst} \text{ or rate} = -\frac{1}{2} \frac{d[N_2O_5]}{dt} = +\frac{1}{4} \frac{d[NO_2]}{dt} = +\frac{d[O_2]}{dt}$$

For the reaction :



We do not use the concentration of water for expressing the rate of reaction since change in the concentration of water is negligibly small. Hence, the rate of reaction is given as below :

$$\text{Rate} = -\frac{1}{5} \frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6} \frac{\Delta[H^+]}{\Delta t} = +\frac{1}{3} \frac{\Delta[Br_2]}{\Delta t}$$

Rate law : Consider a general reaction : $aA + bB \rightarrow cC + dD$

The rate law for this reaction is

$Rate = k[A]^x[B]^y$ where x and y may or may not be equal to the stoichiometric coefficients a and b of the reactants.

Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation. It is determined experimentally.

x = order of reaction w.r.t. the reactant A

y = order of reaction w.r.t. the reactant B

and $m+n$ = overall order of the reaction.

Units of rate constant depend upon the order of reaction.

$$Rate = k[A]^x[B]^y$$

$$k = \frac{Rate}{[A]^x[B]^y}$$

If $x+y=n$ = order of reaction, then we have

$$\text{unit of } k = \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concentration})^n} = \frac{(\text{Concn.})^{1-n}}{\text{time}} = \frac{M^{1-n}}{s}$$

For zero order reaction ($n=0$), unit of k is $mol L^{-1}s^{-1}$ or Ms^{-1}

For first order reaction ($n=1$), unit of k is s^{-1}

For second order reaction ($n=2$), unit of k is $L mol^{-1}s^{-1}$ or $M^{-1}s^{-1}$

ORDER AND MOLECULARITY

Molecularity is the number of reacting species taking part in an elementary reaction, i.e., the no. of species that collide simultaneously in order to bring about a chemical reaction.

For a bimolecular or termolecular elementary reactions, the order of reaction is the same as its molecularity and order w.r.t. each reactant is equal to its stoichiometric coefficient.

For unimolecular elementary reactions, the order of reaction is one at high concentration or pressure. At low pressure the reaction becomes second order but then the reaction is no longer an elementary reaction. Order of reaction can be zero, 1, 2, 3 or even a fraction but molecularity can never be zero or a non-integer. Order is applicable to elementary as well as complex reactions. For complex reaction, molecularity has no meaning. For complex reaction order is given by slowest step and generally molecularity of the slowest step is the same as the order of the overall reaction.

Zero order reaction : The rate of zero order reaction is independent of the concentration change.

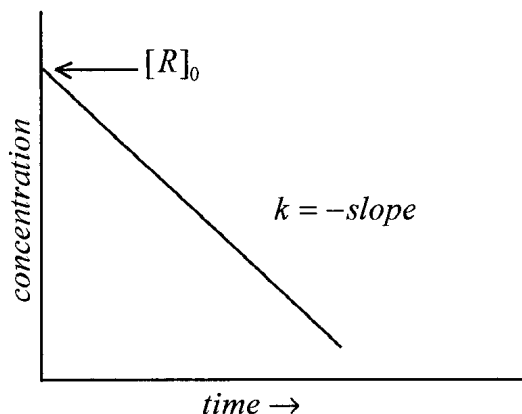
$$Rate = -\frac{d[R]}{dt} = k[R]^0 = k$$

$$k = \frac{[R]_0 - [R]}{t} \text{ where } [R]_0 = \text{Initial concentration}$$

$$[R] = \text{Concentration at time } t$$

Half-life of a reaction is the time in which one half of the initial concentration is consumed.

$$t_{1/2} = \frac{[R]_0}{2k} \text{ or } t_{1/2} \propto [R]_0$$



The decomposition of gaseous ammonia on hot platinum surface is a zero order reaction at high pressure.

$$\therefore \text{Rate} = k[NH_3]^0 = k$$

First order Reaction : $2N_2O_5 \rightarrow 4NO_2 + O_2$ is an example of first order reaction.

$$-\frac{d[R]}{dt} = k[R] \quad \dots\dots\dots (i)$$

$$t = \frac{1}{k} \ln \frac{[R]_0}{[R]} \text{ or } t_2 - t_1 = \frac{1}{k} \ln \frac{[R]_1}{[R]_2} \quad \dots\dots\dots (ii)$$

These relationships can be expressed in exponential form as given below

$$[R] = [R]_0 e^{-kt}$$

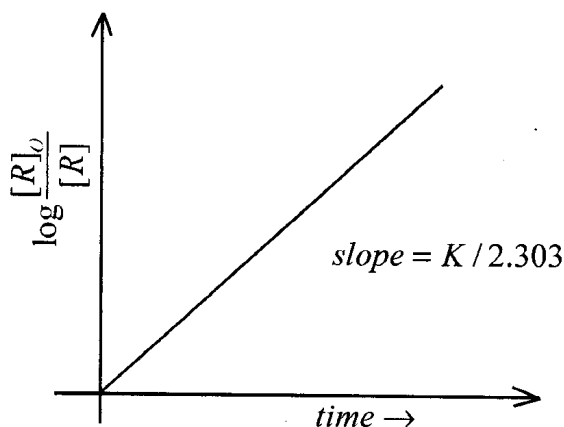
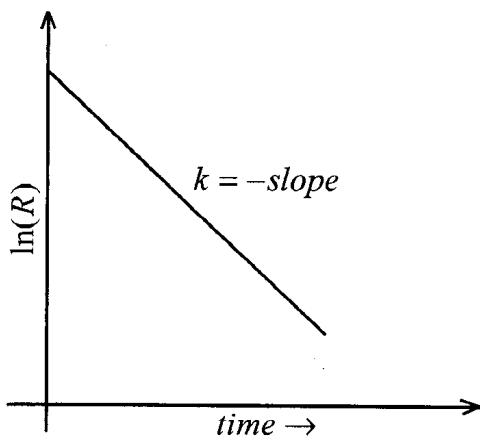
Equation (ii) can be rewritten as :

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]} \text{ or } t_2 - t_1 = \frac{2.303}{k} \log \frac{[R]_1}{[R]_2}$$

Expression for half-life for first order reaction :

$$t_{1/2} = \frac{0.693}{k}$$

Half-life period of first order reaction is independent of initial concentration of the reactant.



Pseudo First Order Reaction : A reaction which first order w.r.t. each of the two reactants but becomes first order reaction under certain experimental conditions, i.e., if one of the reactants is taken in excess.

NOTE :- Half-life period of n^{th} order reaction is inversely proportional to initial concentration raised to power $(n-1)$

$$t_{1/2} \propto \frac{1}{[R]_0^{n-1}}$$

Dependence of rate of reaction on temperature is described by Arrhenius equation

$$: k = Ae^{-Ea/RT} .$$

Ea = Activation energy and is given by energy difference between the activated complex and the reactant molecules.

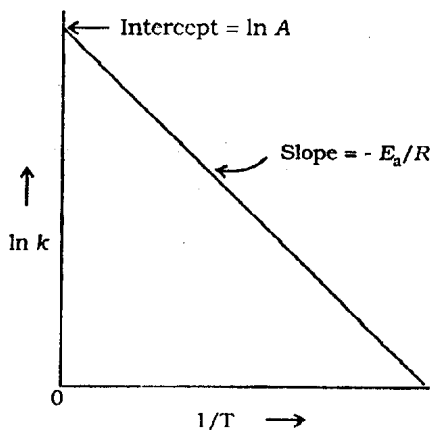
A = Arrhenius factor or pre exponential factor or frequency factor that has the units of rate constant. Natural logarithm of both sides of a Arrhenius equation gives :

$$\ln k = -\frac{Ea}{RT} + \ln A$$

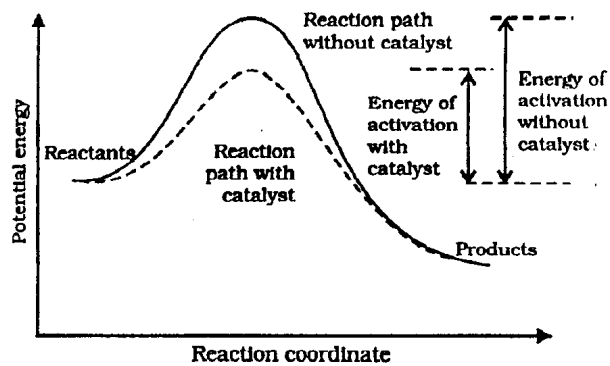
The plot of $\ln k$ and $\frac{1}{T}$ gives a straight line of slope = $-\frac{Ea}{R}$.

If k_1 and k_2 are rate constants at temperatures T_1K and T_2K then we have

$$\log \frac{k_2}{k_1} = -\frac{Ea}{2.303R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$



(Plot between $\ln k$ and $1/T$)



Effect of catalyst on activation energy

(Solid line denotes the reaction path without catalyst and dotted line, with catalyst)

Effect of Catalyst : A catalyst provides an alternative reaction path or reaction mechanism by reducing the activation energy between reactants and products by lowering the potential energy barrier. A catalyst can catalyse those reactions for which $\Delta_r G < 0$. It does not affect the equilibrium state, increases the rate of forward as well as reverse reaction in the same proportion without affecting the $\Delta_r H$ and the equilibrium is attained sooner.

Collision theory of Chemical reactions : The molecules are assumed to be hard spheres and the reaction is postulated to occur when molecules collide with each other. The rate of reaction for the following bimolecular elementary reaction : $A + B \rightarrow$ Products, is given by

$$\text{Rate} = Z_{AB} e^{-E_a/RT} \text{ where}$$

Z_{AB} = Collision frequency of the reactants, A and B.

$e^{-E_a/RT}$ = Fraction of molecules with energy equal to or greater than E_a .

The collisions in which molecules collide with sufficient kinetic energy (or threshold energy) and proper orientation are called effective collisions.

To account for effective collisions, another factor P, called the probability factor or steric factor is introduced, i.e.,

$$\text{Rate} = P Z_{AB} e^{-E_a/RT}$$

UNIT-9
CHEMICAL KINETICS
(MOCK TEST)

- (1) The specific rate constant of a first order reaction depends on
- (a) Initial concentration of the reactant(s) (b) Time of the reaction
(c) Temperature (d) Extent of the reaction
- (2) The rate of the reaction : $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ can be expressed in terms of time derivative of concentration of N_2 , H_2 , or NH_3 . Identify the correct relationship amongst the rate expressions.
- (a) $\text{Rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$ (b) $\text{Rate} = -\frac{d[\text{N}_2]}{dt} = -3 \frac{d[\text{H}_2]}{dt} = 2 \frac{d[\text{NH}_3]}{dt}$
(c) $\text{Rate} = \frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$ (d) $\text{Rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = 2 \frac{d[\text{NH}_3]}{dt}$
- (3) In a first order reaction the concentration of the reactant decreases from 400 mol dm^{-3} to 25 mol dm^{-3} in $2 \times 10^4 \text{ s}$. The rate constant in s^{-1} for this reaction is:
- (a) 4×10^{-4} (b) 1.386×10^{-4}
(c) 4×10^{-4} (d) 3.45×10^{-5}
- (4) The rate constant for the reaction : $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ is $3.0 \times 10^{-5} \text{ s}^{-1}$. If the rate of reaction is $2.40 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$, then $[\text{N}_2\text{O}_5]$ in mol L^{-1} is:
- (a) 1.4 (b) 1.2
(c) 0.04 (d) 0.8
- (5) Which one of the following statement for the order of reaction is not correct?
- (a) order can be determined experimentally.
(b) Order of reaction is equal to the sum of the powers of the concentration terms in the differential rate law.
(c) Powers of the concentration terms may may not be equal to the stoichiometric coefficients.
(d) order cannot be fractional.

(6) The reaction $R \rightarrow P$ follow first order kinetics. In 40 minutes the concentration of P changes from 0.1 to 0.025 M. The rate of reaction, when the concentration of P is 0.01 M is:

- (a) $3.47 \times 10^{-4} \text{ M min}^{-1}$ (b) $3.47 \times 10^{-5} \text{ M min}^{-1}$
 (c) $1.73 \times 10^{-4} \text{ M min}^{-1}$ (d) $1.73 \times 10^{-5} \text{ M min}^{-1}$

(7) The rate constants k_1 , and k_2 for two different reactions are $10^{16} e^{-\frac{2000}{T}}$ and $10^{15} e^{-\frac{1000}{T}}$ respectively. The temperature at which $k_1 = k_2$ is:

- (a) $\frac{2000}{2.303} \text{ k}$ (b) $\frac{1000}{2.303} \text{ k}$
 (c) -2000 k (d) -1000 k

(8) For the reaction: $R \rightarrow$ products, it is found that the rate of reaction increases by a factor of 6.25, when the concentration of "R" is increased by a factor of 2.5. The order of reaction with respect to "R" is

- (a) 2.5 (b) 2
 (c) 1 (d) 0.5

(9) The following data pertains to the reaction between A and B

S.No	[A]/mol L ⁻¹	[B]/mol L ⁻¹	Rate/mol L ⁻¹ s ⁻¹
(i)	1×10^{-2}	2×10^{-2}	2×10^{-4}
(ii)	2×10^{-2}	2×10^{-2}	16×10^{-4}
(iii)	2×10^{-2}	4×10^{-2}	16×10^{-4}

The rate law for the reaction is:

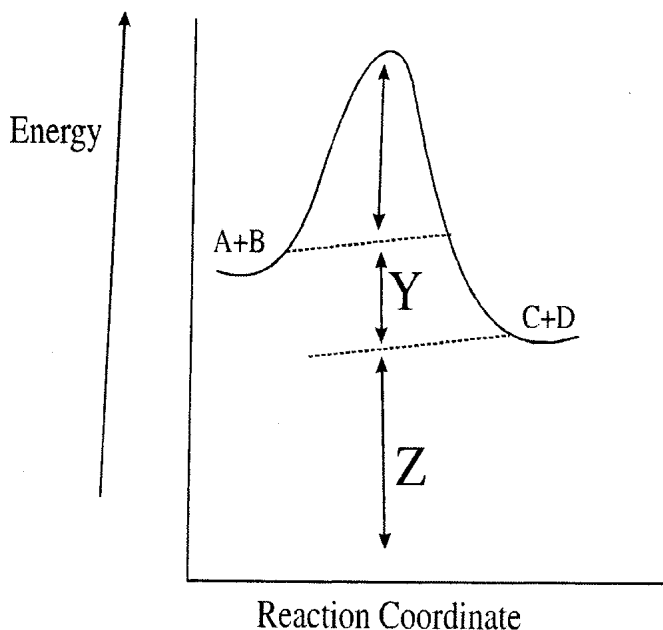
- (a) $\text{Rate} = k [A]^2 [B]$ (b) $\text{Rate} = k [A] [B]^2$
 (c) $\text{Rate} = k [A]^3 [B]^0$ (d) $\text{Rate} = k [A]^{1/2} [B]^{2.5}$

(10) The activation energy of a reaction is zero. The rate constant (k) of reaction of 280K is $1.6 \times 10^{-6} \text{ s}^{-1}$. The value of k for this at 300K is:

- (a) zero (b) $3.2 \times 10^{-5} \text{ s}^{-1}$
 (c) $1.6 \times 10^{-5} \text{ s}^{-1}$ (d) $1.6 \times 10^{-6} \text{ s}^{-1}$

- (11) If a reaction $A+B \rightarrow C$ is exothermic to the extent of 30kJ/mol and forward reaction has an activation energy of 70kJ/mol , the activation energy for the reverse reaction is:
- (a) 30 kJ/mol (b) 40 kJ/mol
(c) 70 kJ/mol (d) 100 kJ/mol

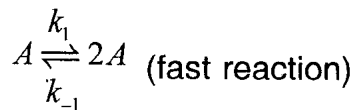
(12) Given the following diagram for the reaction $A + B \rightarrow C + D$



The enthalpy change and activation energy for the reverse reaction : $C+D \rightarrow A+B$ are respectively

- (A) x,y (B) $x,x+y$
(C) $-y,x+y$ (D) $y,y+z$

(13) A reaction proceeds by a two step mechanism



The rate law for the overall reaction is:

- (a) $\text{Rate} = k [A_2][B]$ (b) $\text{Rate} = k[A_2]^2 [B]$
(c) $\text{Rate} = k [A_2]^{1/2} [B]$ (d) $\text{Rate} = k[A_2]^{1/2}$

Surface Chemistry

Adsorption is essentially a surface phenomenon. The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption. For example, silica gel adsorbs moisture.

Adsorbate is the substance whose concentration accumulates at the surface of a the solid or a liquid called **adsorbent**.

Desorption is the process of removing the adsorbate from the surface of the adsorbent.

If a substance is uniformly distributed throughout the bulk of the solid, the phenomenon is known as **absorption**. In adsorption, the substance is concentrated on the surface and does not penetrate through the surface to the bulk of adsorbent. For example, anhydrous calcium chloride absorbs moisture.

Both the adsorption and absorption can take place simultaneously also. Then we use the term **sorption** to describe both the processes. When a chalk stick is dipped in ink, coloured molecules are adsorbed while solvent is absorbed. Adsorption is accompanied by the decrease in enthalpy as well as decrease in the entropy of the system. Since adsorption is a spontaneous process, therefore there is always decrease in the Gibbs energy. As the adsorption proceeds, ΔH becomes less and less negative, ultimately $|\Delta H| = |T\Delta S|$ and $\Delta G = 0$. At this state, equilibrium is attained.

NOTE :- In exceptional cases, chemisorption may be endothermic. For example, H_2 adsorbs endothermically on glass. The ΔS in the process $H_2(g) \rightarrow 2H(glass)$ is sufficiently positive making $\Delta G = \Delta H - T\Delta S$ negative. Similarly, highly hydrated solutes, when adsorbed on solids have positive ΔH but there is large positive ΔS due to release of water molecules during adsorption.

[For comparison between physisorption (Van der Waals adsorption) and chemisorption, refer the NCERT text book part I pages 124-125.]

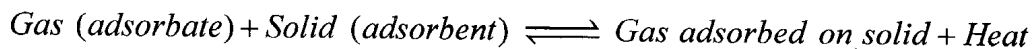
Adsorption of nitrogen on iron : At 83 K nitrogen is physisorbed on iron surface at N_2 molecules. At room temperature, practically there is no adsorption of nitrogen on iron. At 773 K and above, nitrogen is chemisorbed on iron surface as nitrogen atoms.

Factors affecting adsorption of gases :-

(a) Nature of adsorbate : Higher the critical temperature of gas, the more easily it will be physisorbed on the solid. A gas can be chemisorbed on the solid if it is capable of forming chemical bonds with the solid.

(b) Surface area of the adsorbent : Greater the surface area, the more the extent of adsorption.

(c) Temperature. Adsorption is an exothermic process involving the equilibrium :

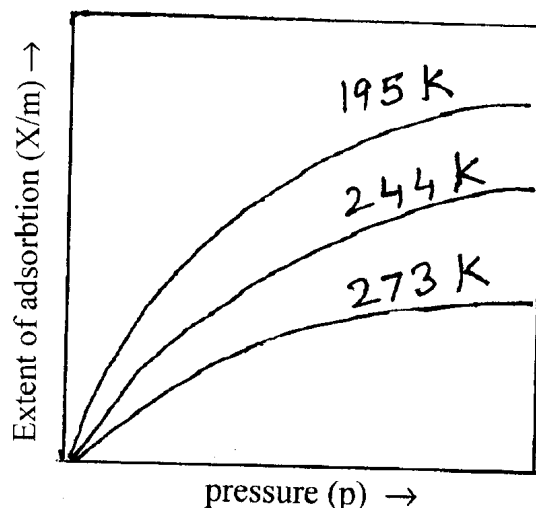


Applying Le Chatelier principle, increase of temperature decreases the adsorption and vice versa.

(d) Pressure. Adsorption increases with pressure at constant temperature. The effect is large if temperature is kept constant at low value.

(e) Activation of the solid adsorbent. This means increasing the adsorbing power of the solid adsorbent. This can be done by subdividing the solid adsorbent or by removing the gases already adsorbed by passing superheated steam.

Freundlich adsorption isotherm :



These curves show that at a fixed pressure, there is the decrease in the extent of physical adsorption with the increase in temperature. The relationship between the quantity of gas adsorbed by unit mass of adsorbent and pressure of the gas at constant temperature

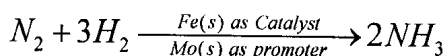
is expressed by the following relation : $X/m = KP^{1/n}$; $(n > 1)$

For adsorption from solution, the concentration of solution is taken into account

$$X/m = KC^{1/n} ; (n > 1)$$

Homogeneous and heterogeneous catalysis : When the reactants and the catalyst are in the same phase, the process is called homogeneous catalysis and if they are in different phases then the processes are the examples of heterogeneous catalysis. A catalyst enhances the rate of reaction without itself getting used up in the reaction.

Promoters are the substances that enhance the activity of a catalyst while poisons decrease the activity of the catalyst.



In heterogeneous catalysis, the reactants in gaseous state or in solution are adsorbed on the surface of solid catalyst. This results in the increase in concentration of reactants on the surface of solid Catalyst and hence in the rate of reaction. Adsorption being an exothermic process, the enthalpy of adsorption is utilised in increasing the rate of reaction.

[For shape selective catalysis and enzyme catalysis please refer to the NCERT

In Colloid or Colloidal dispersion, diameters of particles of the dispersed phase range from 1nm to 1000 nm.

(1) **Classification based on the physical state of dispersed phase and dispersion medium :**

Types of colloidal systems

Dispersed phase	Dispersion medium	Name	Examples
Solid	Solid	Solid sol	Some coloured glasses
Solid	Liquid	Sol	Paints, muddy water
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud
Gas	Solid	Solid foam	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream

(2) **Classification based on nature of interaction between dispersed phase and dispersion medium :** The colloidal sols are divided in two categories as lyophilic (solvent attracting) and lyophobic (solvent repelling).

Lyophilic colloids/sols

- (i) These are the organic substances like gum, starch, gelatin etc. which when mixed with the liquid directly form the colloidal sol.
- (ii) They are reversible.
- (iii) Their viscosity is higher and surface tension is lower than that of the dispersion medium.
- (iv) They are quite stable and are not easily precipitated or coagulated.

Lyophobic colloids/sols

- (i) These are inorganic substances like metals, their sulphides etc. which do not form the colloidal sol directly. These solutions are prepared indirectly.
- (ii) They are irreversible.
- (iii) Their viscosity and surface tension are nearly same as that of the dispersion medium.
- (iv) They are easily precipitated by adding a small amount of a suitable electrolyte.

(3) **Classification based type of particles of the dispersed phase :**

(a) **Multimolecular colloids :** A large number of atoms (as in case of gold sol) and smaller molecules (as in case of sulphur sol) having diameter less than 1nm aggregate via weak van der waals forces to form particles in the colloidal range.

(b) **Macromolecular colloids :** Macromolecules having colloidal dimensions form dispersion in a suitable solvent. Examples of macromolecules are starch, cellulose, proteins, enzymes and synthetic polymers like polythene, nylon 66, polystyrene, synthetic

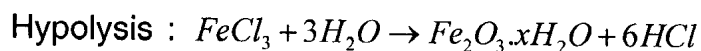
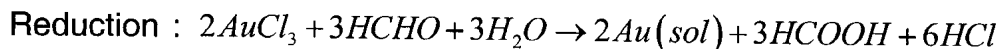
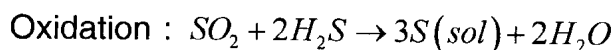
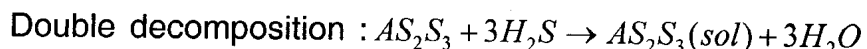
rubber, etc.

(c) **Associated colloids (Micelles)** : Surface active agents such as soaps and synthetic detergents behave as strong electrolytes at low concentration, but at higher concentrations exhibit colloidal properties due to the formation of aggregates called micelles or associated colloids.

Formation of micelles takes place only above a particular temperature called **Kraft temperature** (T_k) and above a particular concentration called **critical micelle concentration (CMC)**. For soaps the CMC is 10^{-4} to 10^{-3} mol/L. These colloids have both lyophobic and lyophilic parts.

Formation of colloids :

(a) Chemical methods like double decomposition, oxidation, reduction and hydrolyses are used to form the molecules which then aggregate forming the colloids.



(b) Bredig's Arc method : Colloidal sols of metals such as Au, Ag, Pt, etc. are prepared by this method.

(c) Peptisation : It is the process converting a precipitate into colloidal sols by shaking it with a dispersion medium in presence of a small amount of electrolyte. The precipitate adsorbs on its surface the ions of the electrolyte common to the lattice of the precipitate and then the precipitate breaks into charged colloidal particles.

Purification of Colloidal solutions : While the traces of electrolyte is essential for the stability of the colloidal solution, larger quantities coagulate it. Hence to reduce the concentration to a requisite minimum, dialysis, electro dialysis and ultrafiltration are used.

Properties exhibited by colloidal solutions :

(a) **Colligative properties.** The values of colligative properties are of small order as compared to values shown by true solutions of the same concentration.

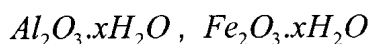
(b) **Tyndall effect.** The Tyndall effect observed in colloidal solution is due to scattering of light by colloidal particles in all directions provided (i) the diameters of dispersed particles is not much smaller than the wavelength of light used and (ii) refractive indices of dispersed phase and dispersion medium differ greatly in magnitude.

(c) **Brownian movement.** The zig-zag motion of colloidal particles is due to the unbalanced bombardment of the colloidal particles by the molecules of dispersion medium. This movement is responsible for the stability of sols.

(d) **Charge on colloidal particles** : Colloidal particles always carry an electric charge.

Positively charged sols

Hydrated metal oxides, e.g.,



Haemoglobin (blood)

Oxides sols, e.g., TiO_2

Basic dyes, e.g., methylene blue sol

Negatively charged solsMetal sols, e.g., , Ag, Au Metallic sulphides, e.g., As_2S_3, Sb_2S_3, CdS

Sols of starch, gum, gelatin, clay, charcoal, etc.

Acid dyes, e.g., eosin, congo red sols

The charge on sol particles is due to one or more reasons, viz, due to (i) electron capture by sol during electrodispersion of metals (ii) preferential adsorption of ions from the solution and / or formulation of electrical double layer.

Having acquired a positive or negative charge by selective adsorption on the surface of a colloidal particle, the fixed layer of ions attract the counter ions from the medium forming a mobile or diffused layer. The potential difference between the fixed layer of ions and diffused layer of counter ions is called **electrokinetic or zeta potential**.

(e) **Electrophoresis** : The movement of charged sol particles towards the oppositely charged electrode under the effect of electric field applied across the colloidal solution, is called electrophoresis.

If the movement colloidal particles is prevented by some means, it is observed that dispersion medium begins to move in an electric field. This phenomenon is called electroosmosis.

(f) **Coagulation or precipitation of sols** : It is the process of changing the colloidal particles in a sol into the insoluble precipitate by addition of some suitable electrolytes.

The coagulation of lyophobic sols can be carried out in the following ways :-

(i) By electrophoresis (ii) by boiling (iii) by prolonged dialysis (iv) by the addition of electrolytes.

Coagulation of lyophilic sols : This is done by adding (i) an electrolyte and (ii) a suitable solvent which can dehydrate the dispersed phase.

Hardy-Schulze rule : A negative ion causes the precipitation of positively charged sol and vice versa. The greater the valence of the coagulating ion added, the greater its power to cause the precipitation. In the coagulation of a negative sol, the flocculating power is in the order $Al^{3+} > Ba^{2+} > Na^+$. Similarly, in the coagulation of a positive sol, the

flocculating power is in the order $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$

Coagulating value : The minimum concentration of an electrolyte in mmol per litre required to cause the precipitation of a sol in two hours, is called coagulating value. The

smaller the amount required, the higher will be the coagulating power of an ion.

Lyophilic colloids are used to protect the lyophobic colloids. When a lyophilic sol is added, its particles form a layer around the lyophobic particles. This layer of lyophilic particles is extensively solvated

To compare the protective action of different lyophilic colloids, Zsigmondy (1901) introduced a term called gold number. Gold number of a protective colloid is the minimum weight of it in milligrams which must be added to 10 ml of a standard red gold sol so that no coagulation of the gold sol (i.e. the change of colour from red to blue) takes place when 1 ml of 10% sodium chloride solution is rapidly added to it.

Evidently, smaller the gold number of a protective colloid, the greater is its protective action. The gold numbers of a few protective colloids are given below :

Sol	Gold number	Reciprocal
Gelatin	0.005 – 0.01	200–100
Casein	0.01 – 0.02	100 – 50
Haemoglobin	0.03 – 0.07	33 –14

Emulsion : Colloidal systems in which both dispersed phase and dispersion medium are liquids. These can be of :

(i) Water in oil type (W/O type) : Examples are milk and vanishing cream.

(ii) oil in water type (O/W type) : Examples are butter, cream and cold cream, soaps and detergents are most frequently used as emulsifiers for the stabilisation of the emulsion of O/W type and long chain alcohols, heavy metal salts of fatty acids for the emulsion of W/O type.

UNIT-10
MOCK TEST
SURFACE CHEMISTRY

- (1) Rate of physisorption increases with the
(a) decrease in temperature (b) increase in temperature
(c) decrease in pressure (d) decrease in surface area
- (2) Adsorption of gases on solid surface is generally exothermic because
(a) entropy of gas decreases during adsorption
(b) entropy of gas increases during adsorption
(c) enthalpy of adsorption is positive
(d) Gibbs energy increases
- (3) Lyophilic sols are
(a) irreversible
(b) prepared from inorganic compounds like metal oxides and sulphides
(c) coagulated by adding electrolytes
(d) self stabilizing
- (4) In a chemical reaction, a catalyst
(a) alters the amounts of products.
(b) lowers the activation energy.
(c) decreases $\Delta_r H$ for forward reaction.
(d) increases $\Delta_r H$ for the reverse section.
- (5) Which one of the following statements is correct?
(a) Lyophobic colloids do not easily coagulate on adding electrolytes.
(b) Lyophobic colloids are reversible in character.
(c) Lyophilic colloids are reversible in character.
(d) Lyophilic colloids are easily coagulated by electrolytes.

- (6) According to langmuir adsorption isotherm, when the pressure of a gas is very large, the extent adsorption is
- directly proportional to pressure.
 - Inversely proportional to pressure.
 - directly proportional to the square of pressure.
 - Independent of pressure.
- (7) In the coagulation of arsenic sulphide solution , the flocculating powers of given ions are such that
- $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$ (b) $\text{Na}^+ > \text{Ba}^{2+} > \text{Al}^{3+}$
 - $\text{Cl}^- > \text{SO}_4^{2-} > \text{PO}_4^{3-}$ (d) $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+$
- (8) Of the following which is not correct?
- As the adsorption proceeds , ΔH becomes less and negative, ultimately ΔH becomes equal to $T\Delta S$ and ΔG becomes zero.
 - The formation of micelles taken place above Kraft temperature T_k and above critical micelle concentration (CMC).
 - The potential difference between the fixed layer and the diffused layer of opposite charges around the collidal particle is called electrokinetic potential or zeta potential.
 - Hydrated aluminium oxide, $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ sol consists of positively charged particles, when electric field is applied across the sol, charged sol particles move towards the oppositely charged electrode. This phenomenon is called electroosmosis.
- (9) Gold numbers of protective colloids a,b,c and d are 0.50, 0.01, 0.10 and 0.005 respectively. The correct order of their protective powers is
- $d < a < c < b$ (b) $c < b < d < a$
 - $a < c < b < d$ (d) $b < d < a < c$
- (10) Which one of the following statements is correct?
Peptisation is a process of
- precipitation of colloidal particles
 - purification of colloids
 - dispersing precipitate into colloidal solution
 - protection of colloidal solution

UNIT-11

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

Mosley, the English physicist showed that atomic number is more fundamental property of an element than its atomic mass. Therefore, the position of an element in the periodic table depends on its atomic number.

Modern periodic laws: The physical and chemical properties of elements are the periodic functions of their atomic numbers.

Types of Elements: s-, p-, d- and f- blocks :

s-block elements : Group 1 (alkali metals) and group 2 elements (alkaline earth metals) which respectively have $n s^1$ and ns^2 outer most electronic configuration.

p-block elements belong to groups 13 to 18. The outermost electronic configuration is $ns^2 np^{1-6}$. He ($1s^2$) is a s-block element but is positioned with the group 18 elements ($ns^2 np^6$) because it has completely filled valence shell and as a result, exhibits properties characteristic of other noble gases.

d-block elements (Transition elements) are the elements of group 3 to 12 having outer electronic configuration $(n-1) d^{1-10} ns^{1-2}$. Four transition series are 3d, 4d, 5d and 6d which is incomplete. Atomic radius generally decreases across a period and increases as we descend the group.

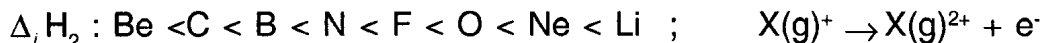
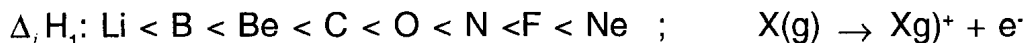
A cation is smaller but the anion is larger than the parent atom. In case of isoelectronic species, the cation with greater positive charge has smaller radius but anion with greater negative charge has the larger radius.

Ionization enthalpy ($\Delta_i H$) is the enthalpy change for the reaction: $X_{(g)} \rightarrow X_{(g)}^+ + e^-$

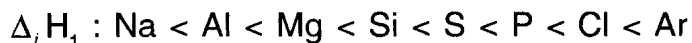
Second ionization enthalpy ($\Delta_i H_2$) is more than the first ionization enthalpy ($\Delta_i H_1$)

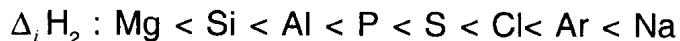
$$\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3 < \dots$$

For the elements of second period, the correct order of increasing ionization enthalpy ($\Delta_i H$) is:



For the elements of third period, the correct increasing order of ionization enthalpy is





For the group 1 elements, the ionization enthalpy decreases in the order:



Electrons gain enthalpy (Δ_{egH}) is the enthalpy change for the reaction : $\text{X}(\text{g}) + \text{e}^- \rightarrow \text{X}_{(\text{g})}^-$.

f-block elements (Inner-transition series)

Lanthanoides characterised by the filling of 4f orbitals, are the elements following lanthanum from $_{52}\text{Ce}$ to $_{71}\text{Lu}$. Actinoides characterised by the filling of 5f orbitals, are the elements following actinium $_{90}\text{Th}$ to $_{103}\text{Lr}$. Characteristic outer electronic configuration is $(n-2)f^{1-14} (n-1)d^{0-1} ns^2$.

Cause of periodicity in the properties of elements is the periodic repetition of similar electronic configuration of elements as the atomic number increases. Regular variation in physical and chemical properties are observed as we descend the group and move across a period from left to right in the periodic table.

Metals, Non-metals and Metalloids: Metals are usually solid at room temperature [Hg is an exceptions Ga and Cs also have low melting points(303k and 302 k respectively)]

Metallic character increases down the group and decreases along a period as we move from left to right. Si, Ge, As, Sb and Te are present on boarder time between metals are non-metals and therefore, are known as metalloids or semimetals.

Trends in physical properties:

Atomic radius refers to both covalent or metallic radius whether the element is a non-metal or metal. Noble gas being monoatomic have large non-bonded radii which can be compared not with the covalent radii but the van der waals radii of the elements. The atomic size generally decreases across a period while increases regularly down the group.

Depending on the element, Δ_{egH} can be either exothermic or endothermic. For example ,group 17 elements have large negative values of Δ_{egH} because they attain noble gas electronic configuration by picking up an electron .Noble gases have large positive electron gain enthalpies beause electron has to enter next higher principal quantum level resulting in very unstable electronic configuration. The Δ_{egH} for N is approximately zero.

Relationship between Δ_{egH} and electron affinity :

$$\Delta_{\text{eg}} H (\text{electron gain enthalpy}) = -A_e (\text{electron affinity}) - 5/2RT$$

Trend in Δ_{egH} : Electron gain enthalpy generally becomes more negative across a period as we move right to left and within a group becomes less negative down the group.

Exceptions: P,S,Cl have more negative Δ_{egH} than N,O, F respectively.

Second electron gain enthalpy of an atom is always positive.

Electronegativity(EN): It is the qualitative measure of an atom in a chemical compound to attract the shared electrons to itself.

Pauling scale, Mulliken-Jaffe scale and Allred and Rochow scale have been developed to measure the electronegativity (X). The most widely used scale is Pauling scale which is based on bond energy data. The difference in electronegativity of two atoms A and B is given by the relationship:

$$X_B - X_A = 0.18 \sqrt{\Delta}$$
, Δ value is expressed in Kcal/mol Where $\Delta = E_{A-B} - \sqrt{E_{A-A} \cdot E_{B-B}}$ and is called resonance energy. Here E_{A-B} , E_{A-A} and E_{B-B} represent bond dissociation energies of bonds A-B, A-A and B-B respectively. By giving a reference value of 2.1 to H, the maximum electronegativity value of 4 is assigned to F.

Anomalous properties of second period elements

Each element of second period, i.e., first element of each of group I and II and groups 13-17 shows many properties which are not shown by its congeners. Their anomalous behaviour is attributed to their small size, large charge/radius ratio, high electronegativity, non-availability of d-orbitals in their valence shell. Thus the first member of each group has only four valence orbitals (one 2s and three 2p orbitals) for bonding, whereas the second member of the group has nine valence orbitals (one 3s, three 3p and five 3d orbitals). As a consequence of this, maximum covalency of first member of each group is limited to "4", whereas the other members of the group can expand their valence shell to accommodate more than four pairs of electrons. For example, B from $[BF_4]^-$ and Al, $[AlF_6]^-$. In addition to this, the first member of p-block elements displays greater ability to form $P_\pi - P_\pi$ multiple bonds to itself. (e.g. C=C, C \equiv C, N=N, N \equiv N, O=O) and to other second period elements (e.g., C=O, C=N, C \equiv N, N=O) compared to subsequent members of the group.

MOCK TEST

UNIT - 11

PERIODICITY IN PROPERTIES

1. Write the IUPAC names of the elements having atomic numbers: 104, 110 and 117.
2. An element has the outer electronic configurations. $5f^{14} 6d^{10} 7s^2 7p^5$. In which group would you place this element?
3. Write neutral species which are isoelectronic with (a) CN^- (b) ClO^- .
4. Write the elements B, Al, Mg and K in the decreasing order of their metallic character.
5. Write the correct order of chemical reactivity in terms of oxidizing property of elements: F, Cl, O and N.
6. The first ionization enthalpy in eV of Be and B respectively are:
(a) 8.29, 9.32 (b) 9.32, 8.29 (c) 9.32, 9.32 (d) 8.29, 8.29
7. The electron gain enthalpies of halogens are:
F = -332, Cl = -349, Br = -324, I = -295 kJ mol^{-1}
The more negative value for Cl compared to that of F is due to
(a) higher atomic radius of F
(b) smaller electronegativity of F
(c) weaker electron-electron repulsion in Cl
(d) more vacant p-subshell in Cl
8. The formation of the oxide ion, $O^{2-}_{(g)}$ requires first an exothermic and then endothermic step as shown below: $O(g) + e^- \rightarrow O^-(g)$ $\Delta_r H^\ominus = -142 \text{ kJ mol}^{-1}$
 $O^-(g) + e^- \rightarrow O^{2-}(g)$ $\Delta_r H^\ominus = + 844 \text{ kJ mol}^{-1}$
This is because
(a) oxygen is more electronegative
(b) oxygen has large negative electron gain enthalpy
(c) O^- will tend to resist the addition of another electron.

(d) O^- ion has comparatively larger size than oxygen atom.

9. The increasing order (lowest first) of first ionisation enthalpy of elements B,P,S and F is

(a) $B < P < S < F$

(b) $B < S < P < F$

(c) $F < S < P < B$

(d) $P < S < B < F$

Hint: P has exactly half-filled 2p – sub-shell and hence, it has higher $\Delta_i H$ than that of S.

10. Following statements regarding periodic trends of chemical reactivity of alkali metals and halogens are given. Which of these statements gives the correct picture?

(a) In both the alkali metals and halogens, chemical reactivity increases with the increase in atomic number down the group.

(b) In alkali metals, chemical reactivity increases but in halogens it decreases down the group.

(c) The reactivity decreases in alkali metals but increases in halogens down the group.

(d) In both the alkali metals and the halogens, the chemical reactivity decreases down the group.

11. The correct order of electronegativity of hybrid orbitals is

(a) $sp < sp^2 < sp^3$ (b) $sp < sp^2 > sp^3$ (c) $sp > sp^2 > sp^3$ (d) $sp > sp^2 < sp^3$

Hint: Electronegativity depends upon the s-character in the hybrid orbital

12. Identify the least stable ion from the following:

(a) Li

(b) Be^-

(c) B^-

(d) C^-

13. The correct order of second ionization enthalpy ($\Delta_i H_2$) in the following:

(a) $F > O > N > C$

(b) $O > F > N > C$

(c) $O > N > F > C$

(d) $C > N > O > F$

Hint : $O^+ : 2p_x^1, 2p_y^1, 2p_z^1$ and $F^+ : 2p_x^2, 2p_y^1, 2p_z^1$ Hence, $\Delta_i H_2$ of O is more than that of F

14. The correct order of ionic radii of the ions: Li^+ , Mg^{2+} , K^+ and Al^{3+} is

(a) $Li^+ < Mg^{2+} < Al^{3+} < K^+$

(b) $K^+ < Mg^{2+} < Al^{3+} < Li^+$

(c) $Al^{3+} < Mg^{2+} < Li^+ < K^+$

(d) $Al^{3+} < Li^+ < Mg^{2+} < K^+$

Hint: $r(Li^+)$ is more than that of $r(Al^{3+})$

Principles and Processes of Isolation of Elements

Minerals are naturally occurring chemical substances in earth's crust obtainable by mining. Ores of a metal are minerals which are used as source of that metal profitably.

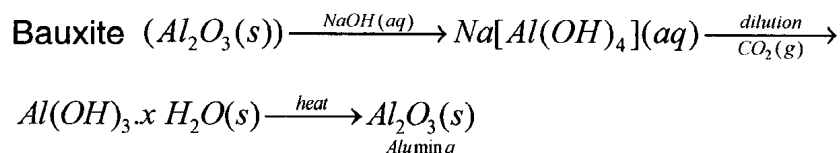
Aluminium is the most abundant metal and the oxygen is most abundant element in the earth's crust. Iron is the second most abundant metal in the earth's crust. Silver, gold, Platinum, sulphur, oxygen and nitrogen are the elements that occur in native or free state.

Many gem-stones are impure form of Al_2O_3 , the impurities range from Cr (in ruby) to Co (in sapphire) [For principal ores of Al, Fe, Cu and Zn, please refer Table 6.1 in the NCERT Text Book, Part I, Class XII, Page 148]. Concentration of ores depends upon the difference in physical properties of the compound of metal present and that of the gangue.

Froth floatation process is used for the concentration of sulphide ores. A suspension of powdered ore is made with water. To it collectors (e.g pine oils, fatty acids, xanthates etc.) and froth stabilisers (e.g., cresols, aniline which enhance the non-wettability of the mineral particles and froth stabilisers (e.g., cresol and aniline) which stabilise the froth are added. Sometimes the depressants are added to separate the sulphide ores. enhance non-wettability of mineral particles stabilise the froths) are added. Sometimes depressants are added to separate the sulphide ores.

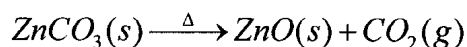
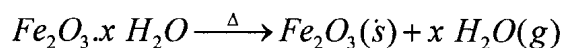
For example NaCN is used as a depressant to selectively prevent Zns from coming to froth but only allows PbS to come with froth. NaCN forms a layer of $Na_2[Zn(CN)_4]$ on the surface of Zns that prevent it from coming to froth.

Leaching, is useful in case the ore is soluble in a suitable solvent.

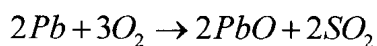
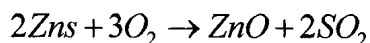


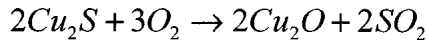
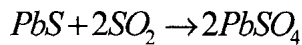
Conversion of concentrated ore to an oxide

- (a) The hydrated or carbonate ores are heated when the volatile matter escapes leaving behind the metal oxide

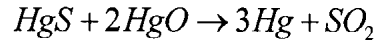
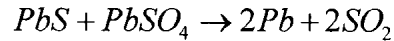
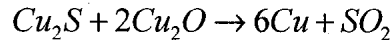


- (b) **Roasting** : The sulphide ore is heated in a regular supply of air below the melting point of metal to convert the metal into its oxide or sulphate. Sometimes a part of the sulphide may act as reducing agent in the subsequent step.





Note :- In auto reduction : For example, the partly converted Cu_2O reduces Cu_2S



Reduction of oxide to metal : Reduction means electron gain or electronation. For the reduction of metal oxides heating is required. To understand the variation in temperature requirement for thermal reduction (pyrometallurgy) and to predict which element will suit as reducing agent for a metal oxide ($MxOy$), Gibbs energy interpretations are made at any specified temperature

$$\Delta G = \Delta H - T\Delta S$$

For any reaction :-

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

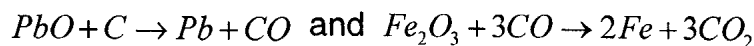
when a reaction proceeds towards products, K will be positive which implies that ΔG will be negative.

When the value of ΔG is negative, only then the reaction proceed. If ΔS is positive, on increasing the temperature (T), the value of $T\Delta S$ would increase (i.e.; $(\Delta H < T\Delta S)$) and then, ΔG will be -ive.

If the reactants and products of two reactions are put together in a system and the net ΔG of the two reactions is -ve, the overall reaction will occur spontaneously.

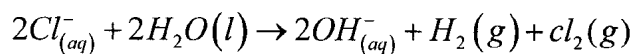
Ellingham diagram :- Gibbs energy (ΔG^θ) for formation of oxides (per mol of O_2) are plotted against temperature T. It is evident that elements, for which Gibbs energy of formation of oxides (per mol of oxygen) is more negative, can reduce the oxides of elements for which Gibbs energy of formation (per mol of O_2) is less negative, that is, the reduction of oxide represented by upper line is feasible by the element represented by lower line.

Reduction by Carbon :- (Smelting) : It is the process of extraction of metal from its roasted or calcined ore by heating with powdered coke in presence of a flux. In smelting oxides are reduced to molten metal by carbon or carbon monoxide.



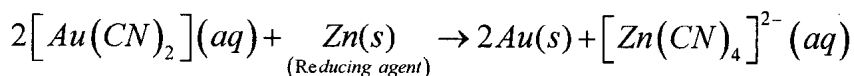
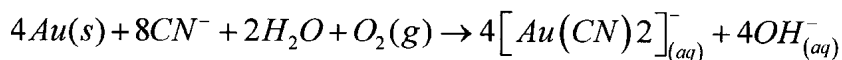
Electrochemical Principles of metallurgy : In simple electrolysis of molten salt, M^{n+} are discharged at negative electrodes. Sometimes a flux is added for making molten mass more conducting as in the electrolysis of molten alumina, CaF_2 or $Na_3[AlF_6]$ is added to lower the melting point of mix and bring the conductivity.

Some extractions are based on oxidation for non-metals. For example, extraction of Cl_2 from brine is the oxidation of Cl^- in aqueous medium.



$$\Delta G^\theta = +422KJ$$

Leaching of Ag or Au with CN^- involves the oxidation of $Ag \rightarrow Ag^+$ or $Au \rightarrow Au^+$



Refining of Metals

Distillation : Useful for low boiling metals like zinc and mercury.

Liquation : Useful for low boiling metals like zinc.

Electrolytic refining : Anode : Impure metal; cathode : strip of pure metal.

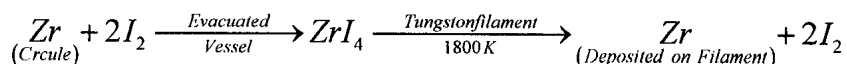
Soluble metal salt solution is used as an electrolyte.

Zone refining is based on the principle that impurities are more soluble in the melt than in the solid state of metal. Pure metals are crystallised out of the melt and impurities move into molten zone. This is used for metals of very high purity, e.g., Ge, Si, B, Ga and In.

Vapour phase refining : Impure Metal is converted into volatile compound which is then decomposed to get pure metal.



Van Arkel method for refining Zr or Ti : This method is used to remove all oxygen and nitrogen present in the form of impurity in certain metals like Zr or Ti.

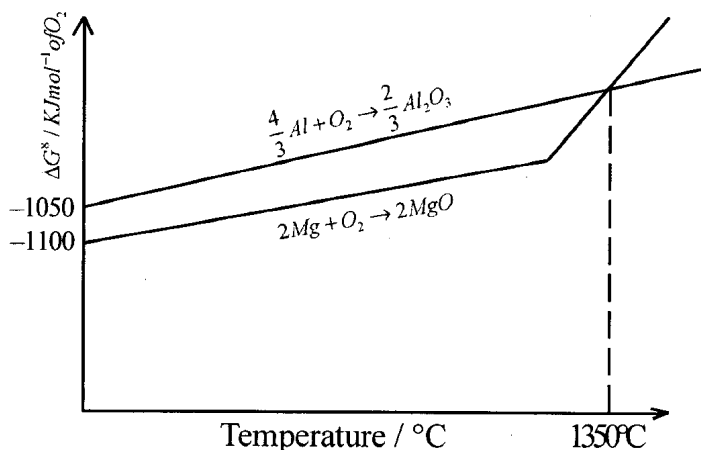


Chromatographic methods : This method is based on the principle that different components of a mixture are differently adsorbed on a adsorbent. The adsorbed components are removed (eluted) by using suitable solvent (elutant).

MOCK TEST

UNIT – 12

- (i) How is cast iron different from pig iron?
- (ii) Why is the reduction of metal oxide easier if metal formed is in the liquid state at the temperature of reduction?
- (iii) Does the pH of the solution of brine decrease/increase when the solution is subjected to electrolysis. Explain.
- (iv) In the metallurgy of iron CO acts a reducing agent at lower temperature range but carbon reduces iron oxide at higher temperature range. Explain why?
- (v)



Is it true that under certain conditions, Mg can reduce Al_2O_3 and Al can reduce MgO ? What are those conditions? [Hint :- (Take the help of Ellingham diagram)]

- (1) Froth floatation process may be used to increase concentration of the mineral in
 - (a) Bauxite
 - (b) Calamine
 - (c) Haemetite
 - (d) Chlcopyrites
- (2) The slag obtained during the extraction of copper from copper pyrites is mainly of :-
 - (a) $CuSiO_3$
 - (b) $FeSiO_3$
 - (c) Cu_2O
 - (d) Cu_2S
- (3) Heating the ore with carbon with the simultaneous removal of slag is called :-
 - (a) roasting
 - (b) calcination
 - (c) smelting
 - (d) leaching
- (4) Cryolite is used in electrolysis of alumina :-
 - (a) to increase the conductivity and decrease the melting point of mix.
 - (b) to decrease the conductivity and increase the melting point of mix.

- (c) to increase the conductivity and melting point of mix.
- (d) to decrease the conductivity and melting point of mix.

(5) In the extraction of copper from sulphide ore, the metal is formed by reduction of Cu_2O with :-

- (a) FeS (b) CO
- (c) Cu_2S (d) SO_2

(6) The method of zone refining of metals is based on the principle of :-

- (a) greater mobility of pure metal than that of impurity
- (b) higher melting point of impurity than that of pure metal
- (c) higher noble character of solid metal than that of impurity
- (d) greater solubility of impurity in molten state than in the solid.

(7) Pyrolusite is an :-

- (a) sulphide ore (b) oxide ore
- (c) carbonate ore (d) phosphate ore

(8) Pick out the incorrect statement :-

- (a) Calamine and siderite are carbonates.
- (b) Argentite and cuprite are oxides.
- (c) Zinc blende and iron pyrites are sulphides.
- (d) Malachite and azurite are the ores of copper.

(9) 'German silver' does not have :-

- (a) Cu (b) Zn
- (c) Ni (d) Ag

(10) The metal which purified by fractional distillation is :-

- (a) Zn (b) Cu
- (c) Al (d) Si

(11) Identify the reaction that does not take place in Blast furnace :-

- (a) $2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$
- (b) $CO_2 + C \rightarrow 2CO$
- (c) $CaCO_3 \rightarrow CaO + CO_2$
- (d) $FeO + SiO_2 \rightarrow FeSiO_3$

(12) Native silver forms a water soluble complex with dilute solution of NaCN in presence of :-

- (a) nitrogen
- (b) oxygen
- (c) Carbon dioxide
- (d) argon

(13) Extraction of Zinc from zinc blende is achieved by :-

- (a) electrolytic reduction.
- (b) roasting followed by reduction with carbon.
- (c) roasting followed by reduction with other metal.
- (d) roasting followed by self-reduction.

(14) Blister copper is :-

- (a) impure copper
- (b) Copper alloy
- (c) pure copper
- (d) copper having $\sim 1\%$ impurity

(15) Which metal has greater tendency to form oxide

- (a) Al
- (b) Mg
- (c) Cr
- (d) Fe

Hydrogen

Hydrogen ($1s^1$) can gain one electron to form H^- ion like halogens. It can also lose its electron to form H^+ ion like alkali metals.

It also differs from them. H^+ does not exist freely and is always associated with other atoms or molecules. It is unique in behaviour and is, therefore, placed separately in periodic table.

It is the most abundant element in the universe. Earth does not possess enough gravitational pull to retain the light H_2 molecules, so it is not found in the atmosphere.

Isotopes of Hydrogen :-

(i) Protium, 1_1H (ii) Deuterium 2_1H or D (iii) Tritium, 3_1H or T

Tritium is radioactive and shows β^- -activity ($t_{1/2} = 12.33 \text{ years}$)

Harold C. Urey was awarded Nobel Prize for separating deuterium.

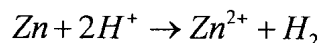
They almost show similar chemical properties but they show different rates of reactions mainly due to their different bond dissociation enthalpies.

$$\left[\Delta H_{(D-D)} = 443.35 \text{ and } \Delta H_{(H-H)} = 435.88 \text{ kJ mol}^{-1} \right]$$

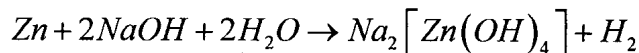
Hydrogen forms more chemical compounds than any other element of the periodic table.

Preparation of dehydrogen (H_2) :-

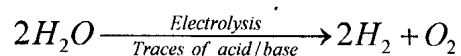
(i) By the action of dilute acids on zinc



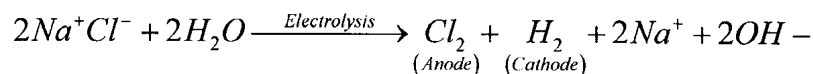
(ii) By the action of aqueous alkali on zinc



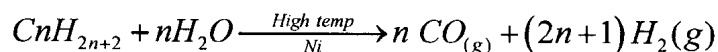
(iii) By the electrolysis of acidified water

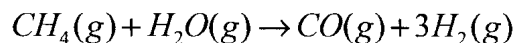


(iv) By the electrolysis of aq. solution of NaCl



(v) By the reaction of steam on hydrocarbons or coke

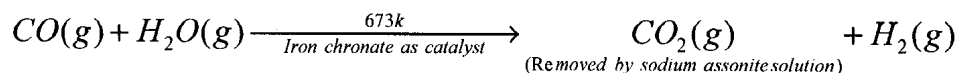




Mixture of CO and H_2 is called water gas or synthesis gas or syngas. The process of producing syngas from coal is called coal gasification.



Water gas – shift reaction is used to increase the production of dihydrogen by reacting CO of syngas with steam .



Dihydrogen has two nuclear spin isomers called ortho and para-dihydrogen. Their nuclei have parallel and anti parallel nuclear spins respectively.

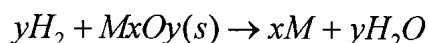
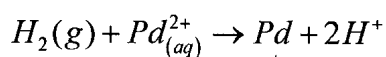
Chemical Properties : It is relatively unreactive at room temperature due to high bond dissociation enthalpy of H–H bond. It shows reactions by (i) loss of electron to form H^+ (ii) the gain an electron to form H^- ion (iii) sharing of electrons to form single covalent bond.

Reaction with : $H_2 + X_2 \rightarrow 2HX$ ($\times = F, Cl, Br, I$) and reactivity increases in the order $I_2 < Br_2 < Cl_2 < F_2$.

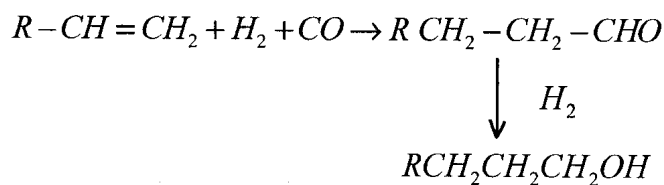
Reaction with Oxygen : $2H_2 + O_2 \rightarrow 2H_2O$; $\Delta H^\theta < 0$.

Reaction with Metals : $H_2 + 2M(g) \rightarrow 2M^+H^-$; M = an alkali metal

Reaction with metal ions and metal oxide :



Hydroformylation of alkene :



Hydrides :-

(1) **Ionic hydrides** are formed with most of s-block elements. Significant covalent character is found in LiH , BeH_2 and MgH_2 . Infact BeH_2 and MgH_2 are

polymeric in nature.

(2) **Covalent or molecular hydrides** are formed with most of p-block elements.

They are further classified as :-

(a) **Electron deficient hydrides** are formed by group 13 elements e.g., B_2H_6 .
They act as Lewis acids.

(b) **Electron precise hydrides** are formed by group 14 elements, e.g., CH_4 .

(c) **Electron rich hydrides** have lone pair(s) of electrons on the central atoms of the molecules. Elements of group 15-17 form this type of hydrides.

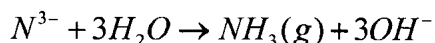
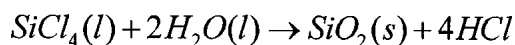
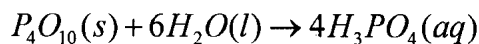
Examples are NH_3 , HF etc. Presence of lone pair(s) on highly electronegative atoms like N, O and F in hydrides results in intermolecular hydrogen bond formation leading to the association of molecules resulting in exceptionally high m.p and b.p.

(3) **Metallic or non-stoichiometric or interstitial hydrides** are formed by d- and f-block elements. For example, $LaH_{2.87}$, $TiH_{1.5-1.8}$, $Zr, H_{1.3-1.75}$ etc.

Water : Water shows unusual properties in condensed phase due to presence of extensive hydrogen bonding. Polar Covalent compounds are also soluble in water due to the formation of hydrogen bonds with water molecules.

Ice : Each O-atom is tetrahedrally surrounded by four other oxygen atoms, i.e. a water molecule can form a maximum of four hydrogen bonds with the four other molecules of water.

Chemical properties of Water : Water is amphoteric in nature. It has the ability of undergoing oxidation as well as reduction. Due to high dielectric constant it has strong hydrating tendency. Covalent and some ionic substances are hydrolysed by water.



Many salts are crystallised in water as hydrated salts :-



Hydrogen bonded water : $[Cu(H_2O)_4]SO_4 \cdot H_2O$: Here fifth water molecule, outside the coordination sphere, is hydrogen bonded to SO_4^{2-} ion.

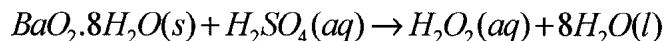
Hard and Soft Water : For cause and removal of temporary and permanent hardness please refer the NCERT Text book XI Class Part II pages 283-284.

Heavy Water (D_2O): It is manufactured by electrolytic enrichment of normal water and used as moderator in nuclear reactors.

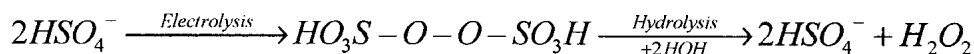
Hydrogen peroxide (H_2O_2) :

Preparation :-

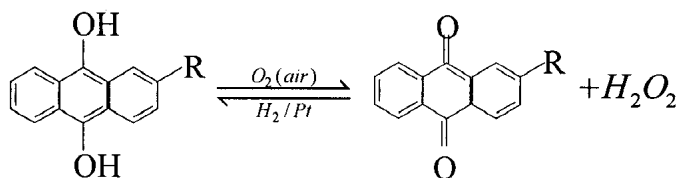
(a) by acidifying the barium peroxide



(b) Peroxodisulphate obtained by the electrolytic oxidation of acidified sulphate solution, on hydrolysis gives H_2O_2

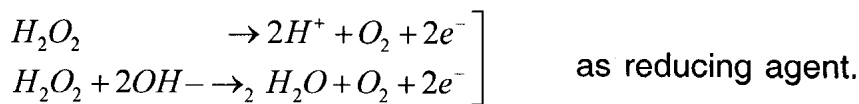
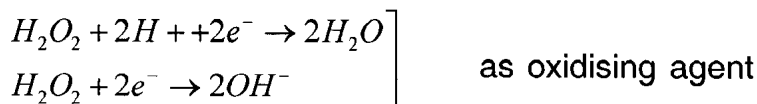


(c) **Industrial preparation :**



H_2O_2 is not stored in glass bottles because of traces of alkali present in glass catalyse the decomposition reaction : $H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$. It is also decomposed by exposure of light. Therefore, it is stored in wax-lined glass or plastic vessels.

It acts both as oxidising and reducing agent in acidic as well as alkaline medium.



It acts as a bleaching agent and its bleaching action is due to the oxidation of colouring matter.

The strength of H_2O_2 solution is expressed as percentage strength or as volume strength as given below :

$$\text{Molality} \times 11.2 = \text{volume strength}$$

$$\text{Normality} \times 5.6 = \text{volume strength}$$

MOCK TEST

UNIT – 13

- (i) Consider the reactions of H_2 with (a) Na and (b) Cu_2O . Which species are oxidised/ reduced
- (ii) Compare the structure of H_2O and H_2O_2 .
- (iii) How does H_2O_2 act as a bleaching agent?
- (iv) What is the molarity of 30 vol H_2O_2 solution?
- (v) The process $\frac{1}{2}H_2(g) + e^- \rightarrow H^-(g)$, $\Delta H = +151 \text{ kJ mol}^{-1}$, yet salt-like hydrides are known. How do you account for this formation of salt-like hydrides.
- (1) The oxidation states of most electronegative element in the products of the reaction of BaO_2 with dil H_2SO_4 are :
- (a) 0 and -1 (b) -1 and -2
(c) -2 and 0 (d) -2 and +1
- (2) The O–O–H bond angle in H_2O_2 is :-
- (a) $109^\circ.28'$ (b) $106^\circ.28'$
(c) 120° (d) 94.8°
- (3) The volume strength of 1.5 N. H_2O_2 solution is :-
- (a) 4.8 (b) 5.2
(c) 8.8 (d) 8.4
- (4) Ortho and para-hydrogen differ in :-
- (a) atomic number (b) atomic mass
(c) spins of protons (d) number of neutrons
- (5) Polyphosphates are used as water softening agents because they :-
- (a) form soluble complexes with anionic species
(b) precipitate anionic species
(c) form soluble complexes with cationic species
(d) precipitates anionic species.

(6) Which of the following pairs of substances on reaction will not evolve H_2 gas?

- (a) Fe and H_2SO_4 (b) Cu and HCl (aq)
(c) sodium and ethanol (d) Iron and steam

(7) Heavy water (D_2O) is obtained by :-

- (a) boiling water (b) fractional distillation of water
(c) prolonged electrolysis of water (d) heating H_2O_2

(8) The correct order, in which O–O bond length increases in the following, is :-

- (a) $O_3 < H_2O_2 < O_2$ (b) $H_2O_2 < O_2 < O_3$
(c) $O_2 < H_2O_2 < O_3$ (d) $O_2 < O_3 < H_2O_2$

Hint - Compare the bond order of O_2 and O_2^{2-} , O_3 has partial double bond character due to resonance. Bond order is inversely proportional to bond length.

(9) 11.2 volume H_2O_2 solution has a molarity of :-

- (a) 1.0 (b) 0.5 (c) 11.2 (d) 1.12

(10) Hydrolysis of one mol of peroxodisulphuric acid produces :-

- (a) two mol of H_2SO_4
(b) two mol of peroxomonosulphuric acid
(c) one mol sulphuric acid and one mol of peroxomonosulphuric acid and one mol of hydrogen peroxide.
(d) one mol of sulphuric acid, one mol of peroxomonosulphuric acid and one mol of hydrogen peroxide.

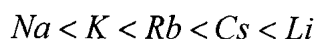
s-block Elements

I. Trends in atomic and physical properties

Flame colouration: All the alkali metals impart characteristic colours to the flame. Due to the low ionization enthalpy, the electrons of alkali metals can be easily excited to the higher energy levels by the small energy provided by the Bunsen flame. When these excited electrons return to the ground state, the absorbed energy is emitted in the visible region of the electromagnetic spectrum and hence the flame appears coloured.

Photoelectric effect: Due to low ionization enthalpies, alkali metals especially K and Cs show photoelectric effect (i.e. eject electrons when exposed to light) and hence are used in photoelectric cells.

Reducing character: All the alkali metals are good reducing agents due to their low ionization enthalpies. Their reducing character, however, follows the order :

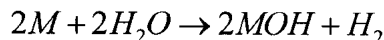


The reducing character of any metal is measured in terms of its electrode potential which among other things depends upon its (i) heat of vaporization (ii) ionization energy and (iii) heat of hydration. Since Li^+ ion has the smallest size, its heat of hydration has the highest value. Therefore, among the alkali metals Li has the highest negative electrode potential ($E^\circ = -3.05\text{volts}$) and hence is the strongest reducing agents.

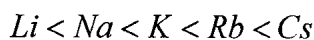
Mobility of ions in aqueous solution: The alkali metal ions exist as hydrated ions $M^+(H_2O)_x$ in the aqueous solution. The degree of hydration, however, decreases with the ionic size as we move from Li^+ to Cs^+ . In other words, Li^+ ion is most highly hydrated e.g. $[Li(H_2O)_6]^+$. Since the mobility of ions is inversely proportional to the size of their hydrated ions, therefore, amongst the alkali metal ions, lithium has the lowest ionic mobility.

II. Chemical properties

Reaction with water: All the alkali metals readily react with water evolving hydrogen.



The reactivity, however, increase down the group as the electropositive character of the metal increases :-



Reaction with oxygen: All the alkali metals when heated with oxygen form different types of oxides. For example, lithium forms lithium oxide (Li_2O), sodium forms sodium peroxide (Na_2O_2), while K, Rb and Cs form their respective superoxides

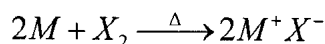
(MO_2 where M = K, Rb or Cs). Super oxides are coloured and paramagnetic as these possess three electron bond ($:O\cdot\cdot O:$)⁻ where one unpaired electron is present. All oxides, peroxides and superoxides are basic in nature. To protect the alkali metals from air and moisture, they are usually kept in hydrocarbon solvents such hexane, benzene, toluene and kerosene oil.

Reaction with hydrogen: All the alkali metals when heated with hydrogen form ionic crystalline hydrides of the general formula M^+H^-

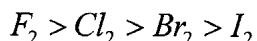


The reactivity of alkali metals towards hydrogen decreases as we move down the group i.e. $Li > Na > K > Rb > Cs$. This is mainly due to the reason that the lattice energy of these hydrides decrease progressively as the size of the metal cation increases. Thus, the stability of hydrides decreases from LiH to CsH.

Reaction with halogens: All the alkali metals react vigorously with halogens to form their respective ionic crystalline halides of the general formula, M^+X^- where M = Li, Na, K, Rb or Cs and X = F, Cl, Br or I.

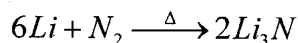


The reactivity of alkali metals towards a particular halogen increases in the order : $Li < Na < K < Rb < Cs$ while that of halogen towards a particular alkali metal decreases in the order :

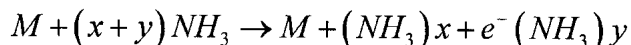


With the exception of LiF, all other lithium halides are covalent. Being covalent, LiCl, LiBr and LiI are insoluble in water but are soluble in organic solvents like pyridine, benzene, alcohols and ethers.

Reaction with nitrogen: Only lithium reacts with nitrogen to form lithium nitride (Li_3N).

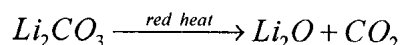


Solubility in liquid ammonia: All the alkali metals dissolve in liquid ammonia giving deep blue solutions when dilute, due to the presence of ammoniated (solvated) electrons in the solution :



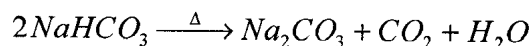
These electrons are excited to higher energy levels and the absorption of photons occurs in the red region of the spectrum. Thus the solution appears blue.

Nature of carbonates and bicarbonates: Li_2CO_3 is much less stable and decomposes on heating to red heat to give Li_2O and CO_2



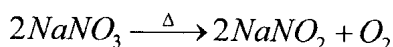
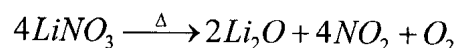
The stability of the other carbonates increases from Na_2CO_3 to Cs_2CO_3 as the basic strength of the corresponding metal hydroxide increases from $LiOH$ to $CsOH$.

Similarly, the bicarbonates of all the alkali metals are known. $LiHCO_3$ does not exist as a solid but exists in solution while all other bicarbonates exist as solids. All bicarbonates on heating form carbonates with the evolution of CO_2



The solubility of the carbonates and bicarbonates increases as we move down the group probably due to lower lattice energies.

Nature of Nitrates. $LiNO_3$ on heating decomposes to give NO_2 and O_2 while the nitrates of the other alkali metals decompose on heating to form nitrites and O_2 .



All nitrates are very soluble in water.

III. Diagonal relationship

Lithium shows diagonal relationship with magnesium since they have almost the same ionic radii. $r(Li^+) = r(Mg^{2+})$

Lithium resembles magnesium in the following respects :-

(vii) both combine with oxygen to form monoxides, e.g., Li_2O and MgO

(viii) both $LiOH$ and $Mg(OH)_2$ are weak bases

(ix) both $LiCl$ and $MgCl_2$ are predominantly covalent and hence are soluble in organic solvents, such as alcohol and pyridine.

(x) both Li and Mg combine with nitrogen to form their respective nitrides, Li_3N and Mg_3N_2 .

IV. Anomalous behaviour of lithium.

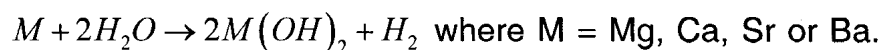
Flame colouration: Like alkali metal salts, alkaline earth metal salts also impart characteristic flame colouration. As we move down the group from Ca to Ba , the ionization energy decreases, hence the energy or the frequency of the emitted light increases. Consequently, the colour imparted to the flame shows a gradual shift from red to violet. Thus :

Ca : Brick red **Sr** : Crimson red **Ba** : Apple green **Ra** : Crimson

Be and Mg because of their high ionization energies, however, do not impart any characteristic colour to the Bunsen flame.

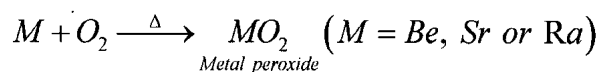
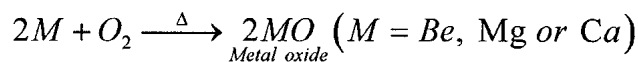
II. Chemical properties

1. **Reaction with water.** They react with H_2O evolving H_2 gas.



The chemical reactivity of the metal with H_2O , however, increases as we move from Mg to Ba. For example, Be does not react even with boiling water, Mg reacts with boiling water while Ca, Sr and Ba react vigorously even with cold water.

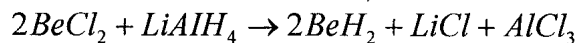
3. **Reaction with oxygen.** The affinity for oxygen increases down the group. Thus, Be, Mg and Ca when heated with oxygen form monoxides while Sr, Ba and Ra form peroxides.



4. **Reaction with hydrogen.** All the alkaline earth metals except Be, combine with H_2 directly on heating to form metal hydrides of the general formula, MH_2 .



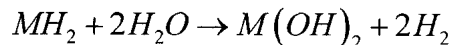
BeH_2 can, however, be prepared by reducing $BeCl_2$ with $LiAlH_4$.



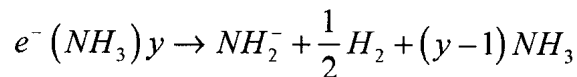
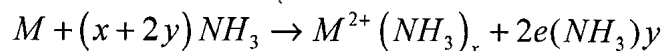
BeH_2 is covalent, MgH_2 are polymeric while others are monomeric.

CaH_2 is also called hydrolith.

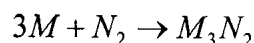
All the hydrides react with water to evolve H_2 and thus behave as strong reducing agents.



5. **Solubility in liquid ammonia.** Like alkali metals, all alkaline earth metals dissolve in liquid ammonia giving bright blue solutions (when dilute) due to solvated electrons but concentrated solutions are bronze coloured due to the formation of metal clusters. These solutions decompose very slowly forming amides and evolving H_2 .

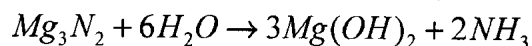


6. **Reaction with nitrogen:** When heated with N_2 , alkaline earth metals form their respective nitrides.



The ease of formation of nitrides increases from Be to Ba.

These nitrides react with water to evolve NH_3 , e.g.,

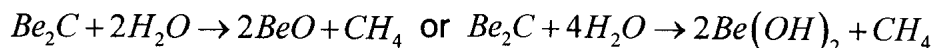
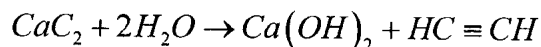


7. **Reaction with carbon:** When heated with carbon, alkaline earth metals form their respective carbides of the general formula MC_2 (except beryllium) and are called acetylides containing the discrete C_2^{2-} anion.

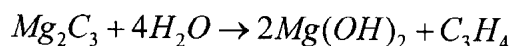


Under the conditions beryllium, however, forms Be_2C called methanide containing the discrete C^{4-} anion.

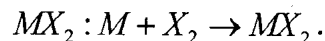
All these carbides are ionic in nature and react with water to form acetylene. Be_2C , however gives methane.



On heating MgC_2 gives Mg_2C_3 called allylide which contains the discrete C_3^{4-} anion and gives allylene (methyl acetylene) on hydrolysis.



Reaction with halogens: When heated with halogens (F_2 , Cl_2 , Br_2 , or I_2), all the alkaline earth metals form halides of the general formula,

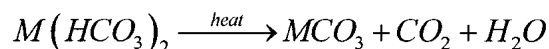


Solubilities of sulphates: The solubilities of sulphates of alkaline earth metals decrease as we move down the group from Be to Ba. This is mainly due to the reason that as the size of the cation increases, the heat of hydration decreases while the lattice energy remains about the same (because the sulphate anion is so big that increase in size of the cations down the group does not make any difference). Thus, the solubilities decrease in the order :

$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$. The negligible solubility of $BaSO_4$ in water is used in both qualitative and quantitative analysis.

Solubilities of bicarbonates and carbonates: The bicarbonates of the

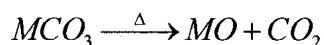
alkaline earth metals do not exist in the solid state but are known only in solution. On heating, these bicarbonates decompose forming carbonates with the evolution of CO_2 .



The solubilities of the carbonates decrease as we move down the group from Be to Ba i.e., $BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$. This is mainly due to the reason that as the size of the cation increases, the lattice energies of their carbonates remain almost unchanged as in case of sulphates whereas the heats of hydration of the cations decrease.

The extremely low solubility of alkaline earth metal carbonates in water is used in the precipitation of Ba^{2+} , Sr^{2+} and Ca^{2+} as their carbonates in the V group of qualitative analysis of basic radicals.

Thermal stabilities of carbonates: The carbonates of alkaline earth metals decompose on heating forming metal oxide and carbon dioxide.



Thermal stabilities of sulphates: Like carbonates, thermal stabilities of sulphates also increase as the basic character of the metal hydroxide increases. This is shown by the temperature at which decompositions occur:

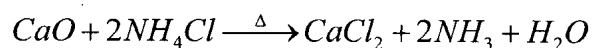
$BeSO_4$	$MgSO_4$	$CaSO_4$	$SrSO_4$
773 K	1168 K	1422 K	1647 K

INDUSTRIALLY IMPORTANT COMPOUND

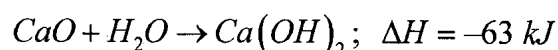
- (i) **Calcium oxide, Quick lime, Burnt lime, lime, CaO.** It is obtained by thermal decomposition of calcium carbonate at 1070 –1270 K.



It is a basic oxide and hence reacts with acids, SO_2 etc. On heating with ammonium salts, it gives ammonia :



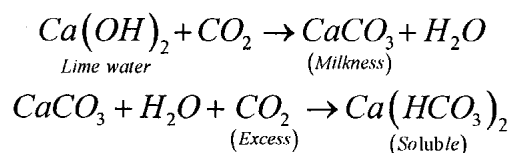
- (ii) **Calcium hydroxide, Slaked lime, $Ca(OH)_2$.** It is also called lime water and is obtained by dissolving quick lime in water.



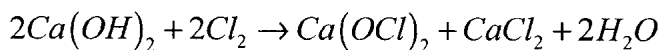
The reaction is highly exothermic and produces a hissing sound. Its suspension in water is called milk of lime.

When CO_2 is passed through lime water, it first turns milky due to the

formation of insoluble $CaCO_3$ but if the passage of CO_2 is continued, the solution becomes clear due to the formation of soluble calcium bicarbonate.

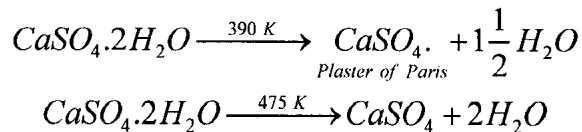


It reacts with Cl_2 to give bleaching powder



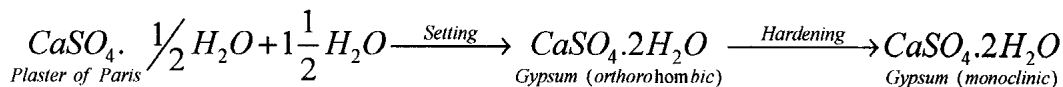
Active constituent of bleaching powder is $Ca(OCl)_2$

- (iii) **Gypsum, Calcium sulphate dihydrate, $CaSO_4 \cdot 2H_2O$.** When heated to 390 K, it gives Plaster of Paris and when heated to 475 K, it loses water of crystallization completely to form anhydrous $CaSO_4$. It is also called dead burnt plaster since it has no tendency to set.



Gypsum is added to cement to slow down its rate of setting.

- (iv) **Plaster of Paris, Calcium sulphate hemihydrate, $CaSO_4 \cdot \frac{1}{2}H_2O$.** When mixed with water, it forms first a plastic mass which sets into a solid mass (setting of Plaster of Paris) within 5-15 minutes. The setting of Plaster of Paris is believed to be due to rehydration and its reconversion into gypsum.



During setting, it undergoes slight expansion. It is used in surgical bandages, casting, moulding and dentistry.

- (v) **Calcium chloride, $CaCl_2 \cdot 6H_2O$.** It is a deliquescent solid, by product of Solvay's process. In fused state, it is a good desiccant (drying agent). It can not be used to dry alcohol or NH_3 as it forms addition products with them.

- (viii) Solubilities of carbonates decrease down the magnesium group due to decrease in :-
- (a) entropy of solution formation (b) lattice energies of solids
(c) hydration energy of cations (d) inter-ionic attraction
- (ix) In curing cement plasters, water is sprinkled from time to time. This helps in
- (a) converting sand into silicic acid
(b) keeping it cool
(c) developing interlocking needle like crystals of hydrated silicates
(d) hydrating sand and gravel mixed with cement.
- (x) Photoelectric effect is maximum in :-
- (a) Cs (b) Na (c) K (d) Li
- (xi) Which of the following metal has most stable carbonate?
- (a) Na (b) Mg (c) Al (d) Si
- (xii) A sodium salt of unknown anion when treated with $MgCl_2$ gives white precipitate only on boiling. The anion is :-
- (a) SO_4^{2-} (b) HCO_3^- (c) CO_3^{2-} (d) NO_3^-
- (xiii) A solid compound 'X' on heating gives CO_2 gas and a residue. The residue mixed with water forms 'Y'. On passing an excess of CO_2 through 'Y' in water, clear solution 'Z' is obtained. On boiling 'Z', compound 'X' is reformed. The compound 'X' is
- (a) $Ca(HCO_3)_2$ (b) $CaCO_3$ (c) Na_2CO_3 (d) K_2CO_3
- (xiv) One mole of magnesium nitride on reaction with an excess of water gives :-
- (a) one mole of ammonia (b) one mole of nitric acid
(c) two moles of ammonia (d) two moles of nitric acid
- (xv) The ionic mobility of alkali metal ions in aqueous solution is maximum for :-
- (a) K^+ (b) Rb^+ (c) Li^+ (d) Na^+
- (xvi) The correct order of mobility of the alkali metal ions in aqueous solution is:-
- (a) $Rb^+ > K^+ > Na^+ > Li^+$ (b) $Li^+ > Na^+ > K^+ > Rb^+$
(c) $Na^+ > K^+ > Rb^+ > Li^+$ (d) $K^+ > Rb^+ > Na^+ > Li^+$