Civinnovate

Discover, Learn, and Innovate in Civil Engineering

Ionic Equilibria & Electro Chemistry

- Acid - having H^+ ion

1) weak acid (organic acid)
e.g. $HCOOH$
CH_3COOH
$H_2C_2O_4$

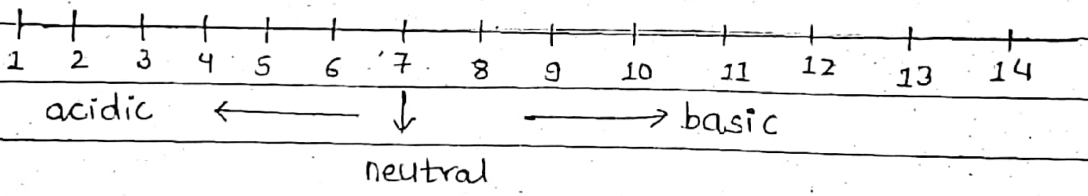
2) strong acid (mineral a
e.g. HCl, HNO_3
H_2SO_4.
H_3PO_4.

- Base - having OH^- ion

1) weak base
e.g. NH_4OH
$Fe(OH)_3$

2) strong base
e.g. $NaOH$, KOH
$Mg(OH)_2$, $Ca(OH)_2$

Acid has pH less than 7
Base has pH more than 7



Buffer solution

Those solution which can resist the change in pH even on addition of strong acid or base is known as buffer solution. It consists of reserve acid as well as base. Reserve acid controls the added base & reserve base controls the added acid. As a result, pH remains unchanged.

Types of Buffer solution

On the basis of composition, there are 2 types of buffer solution:

1) Acidic buffer solution
2) Basic buffer solution

1. Acidic Buffer Solution

Such type of buffer solution which is prepared by mixing weak acid and its salt with strong base is known as acidic buffer solution. Its working pH value is below 7.

e.g. $CH_3COOH + CH_3COONa$
$HCOOH + HCOONa$, etc.

2. Basic Buffer Solution

Such type of buffer solution which is prepared by mixing weak base and its salt with strong acid is known as basic buffer solution. Its pH value is above 7.

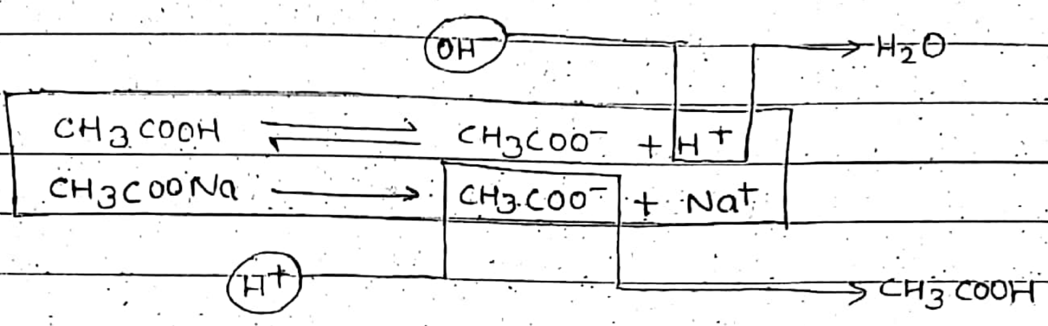
e.g. $NH_4OH + NH_4Cl$
$NH_4OH + (NH_4)_2SO_4$
$NH_4OH + NH_4NO_3$
blood
sea water

Q.) What is buffer solution? Mention its types. How mixture of formic acid & sodium formate acts as buffer solution?
7 marks

Mechanism of Buffer solution

Mechanism of buffer solution to resist change in pH even addition of small amount of strong acid & strong base is known as buffer action. This buffer action mainl works by two principles:
1) Le chateiron's principle
2) Common ion effect

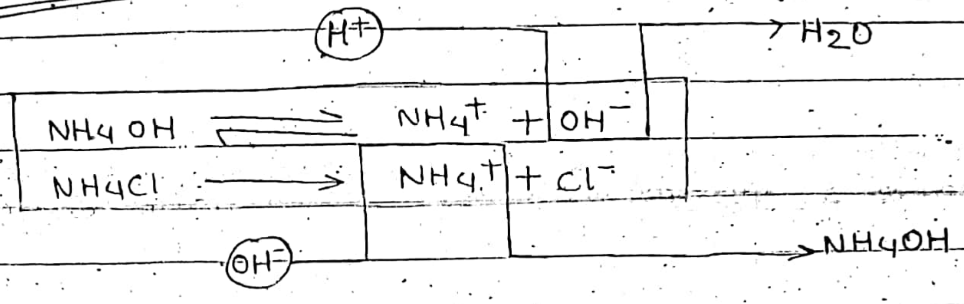
Mechanism of acidic buffer solution



Suppose an acidic buffer solution is prepared by mixin weak acid (CH_3COOH), which is partially ionized, in its salt with strong base (CH_3COONa), which is completely ionized. When small amount of strong acid is added, then added acid (H^+) reacts with acetate ion (CH_3COO^-) produce CH_3COOH which is weak acid as well as composition of itself buffer. So, there is no considerabl change in pH value.

On addition of small amount of strong base, added ba (OH^-) reacts with H^+ ion to form water (H_2O) which cannot change the pH value of solution.

Mechanism of basic buffer solution



Suppose a basic buffer solution is prepared by mixing weak base (NH4OH), which ionizes partially and its salt with strong acid (NH4Cl), which is completely ionizes. When small amount of acid (H^+) is added, the added acid (H^+) reacts with OH^- ion and forms water H_2O, which cannot change the pH of the solution.

Similarly, when a small amount of base (OH^-) is added, added base reacts with ammonium ion (NH_4^+) to form NH_4OH (ammonium hydroxide) which is weak base and composition of buffer solution. So, there is no considerable change in pH value.

pH : The potential of Hydrogen ion concentration is k/a pH value. Mathematically, it is negative logarithm of hydrogen ion concentration.

i.e. $pH = -\log[H^+]$ where, $[H^+]$ is concentration of H^+
$pOH = -\log[OH^-]$ $[OH^-]$ is " " OH^-

$pH + pOH = 14$

Calculate the pH value of following ~~acid~~ :

i) 0.0001 M HCl

ii) 0.00001 M H_2SO_4

iii) 10^{-3} M HNO_3

iv) 10^{-2} M H_3PO_4

v) 10^{-2} M NaOH

vi) 10^{-6} M $Ca(OH)_2$

vii) 10^{-7} M HCl

viii) 10^{-8} M H_2SO_4.

ix) 10^{-9} M NaOH

x) 10^{-10} M $Mg(OH)_2$

i) $HCl \rightleftharpoons H^+ + Cl^-$

0.0001 0.0001 0.0001

$pH = -\log[H^+] = -\log(0.0001) = 4$

ii) $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}$

0.00001 2×0.00001 0.00001

$= 2 \times 10^{-5}$

$pH = -\log[H^+] = -\log(2 \times 10^{-5}) = 4.69$

iii) $HNO_3 \rightleftharpoons H^+ + NO_3^-$

10^{-3} 10^{-3} 10^{-3}

$pH = -\log[H^+] = -\log[10^{-3}] = 3$

iv) $H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{---}$

10^{-2} 3×10^{-2} 10^{-2}

$pH = -\log[H^+] = -\log[3 \times 10^{-2}] = 1.52$

v) $NaOH \rightleftharpoons Na^+ + OH^-$

10^{-2} 10^{-2} 10^{-2}

$pOH = -\log[OH^-] = -\log[10^{-2}] = 2$

$pH = 14 - pOH$

$= 14 - 2$

$= 12$ //

vi) $Ca(OH)_2 \rightleftharpoons Ca^{++} + 2OH$

10^{-6} 10^{-6} 2×10

$pOH = -\log[OH^-] = -\log[2$

$= 5.69$

$pH = 14 - pOH$

$= 14 - 5.69$

$= 8.30$ //

pH of buffer solution

The pH of buffer sol^n can be determined by using eq^n which is called Henderson equation.

1) For acidic buffer sol^n, Henderson eq^n is given as:

$$pH = p^{Ka} + \log \frac{[salt]}{[acid]}$$ # conc. must be in molarity

where,

$p^{Ka} = -\log K_a$, K_a is ionization constant of acid

[salt] = molar concentration of salt

[acid] = " " " acid

2) For basic buffer sol^n, Henderson eq^n is given as:

$$pH = 14 - p^{K_b} - \log \frac{[salt]}{[base]}$$

where,

$p^{K_b} = -\log K_b$, K_b is ionization constant of base

[salt] = molar concentration of salt

[base] = " " " base

Derivation of Henderson's eq^n.

For Acidic Buffer solution

Suppose acidic buffer sol^n is prepared by mixing weak ac HA and its salt BA, which are ionizes as follows:

$$HA \overset{K_a}{\rightleftharpoons} H^+ + A^- \text{ (weakly ionized)}$$

$$BA \longrightarrow B^+ + A^- \text{ (completely ionized)}$$

K_a be the ionization constant of weak acid. According to law of mass action, ka is given as

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

Since BA is completely ionized to give A^-, $[A^-] \approx [BA]$.

So,

$$K_a = \frac{[H^+][BA]}{[HA]} = \frac{[H^+]\,[salt]}{[acid]}$$

$$\text{or, } \frac{K_a\,[acid]}{[salt]} = [H^+]$$

Taking log on both sides,

$$\log[H^+] = \log\left(\frac{K_a.[acid]}{[salt]}\right)$$

$$\log[H^+] = \log K_a + \log\frac{[acid]}{[salt]}$$

Taking -ve on both sides,

$$-\log[H^+] = -\log K_a + \log\frac{[salt]}{[acid]}$$

$$\therefore \boxed{pH = pK_a + \log\frac{[salt]}{[acid]}}$$

This is the Henderson's eqn. for acidic buffer solution.

For Basic Buffer solution

Suppose basic buffer soln. is prepared by mixing weak base BOH and its salt BA, which are ionizes as follows:

$$BOH \overset{K_b}{\rightleftharpoons} B^+ + OH^- \quad \text{(weakly ionized)}$$

$$BA \longrightarrow B^+ + A^- \quad \text{(completely ionized)}$$

K_b be the ionization constant of weak base. According t
law of mass action, K_b is given as

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

Since BA is completely ionized to give B^+, $[B^+] \approx [BA$

$$K_b = \frac{[BA][OH^-]}{[BOH]}$$

$$\text{or, } K_b = \frac{[salt][OH^-]}{[base]}$$

$$\text{or, } \frac{K_b[base]}{[salt]} = [OH^-]$$

Taking log on both sides,

$$\log[OH^-] = \log\left(\frac{K_b.[base]}{[salt]}\right)$$

$$\log[OH^-] = \log K_b + \log\frac{[base]}{[salt]}$$

Taking -ve on both sides,

$$-\log[OH^-] = -\log K_b + \log\frac{[salt]}{[base]}$$

$$\text{or, } pOH = pK_b + \log\frac{[salt]}{[base]}$$

$$\text{or, } 14 - pH = pK_b + \log\frac{[salt]}{[base]}$$

$$\therefore \boxed{pH = 14 - pK_b - \log\frac{[salt]}{[base]}}$$

This is the Henderson's eqn. for basic buffer solution

1. It is applicable for determining pH ~~of~~ value of unknown buffer solution.
2. It is used to calculate the concentration of salt used in buffer solution.
3. It is used to calculate the concentration of acid or base used in buffer soln.
4. It can be used to determine ionization constant value.

Uses of buffer solution

1. It is used to calibrate pH meter.
2. It is used to maintain water quality.
3. It is used in wine making.
4. It is used to minimize ~~acid rain~~ effect of acid rain in soil.
5. It is used to control pH of some reaction in industry.

Buffer capacity

Buffer capacity is defined as the no. of moles of acid or base added per litre of the buffer required to cause unit change in pH.

Mathematically,

$$\text{buffer capacity} = \frac{\text{no. of moles of acid / base added per litre}}{\text{pH change}}$$

Some numericals related to buffer solⁿ.

1. 300 ml of 0.2 M formic acid is mixed with 400 ml of 0.1 M sodium formate. Calculate the pH of resulting solution. Given: [pKa for formic acid = 3.74]

Solⁿ.

For acid

$V_1 = 300$ ml

$M_1 = 0.2$ M

In ~~For~~ mixture

$V_2 = 300+400 = 700$ ml

$M_2 = [HCOOH]$

$M_1 V_1 = M_2 V_2$

or, $300 \times 0.2 = [HCOOH] \times 700$

∴ $[HCOOH] = 3/35$ M

For ~~a~~ salt

$V_1 = 400$

$M_1 = 0.1$ M

In mixture

$V_2 = 700$ ml

$M_2 = [HCOONa]$

$M_1 V_1 = M_2 V_2$

or, $0.1 \times 400 = [HCOONa] \times 700$

∴ $[HCOONa] = 2/35$ M

Now, we have,

$$pH = pKa + \log\frac{[salt]}{[acid]} = pKa + \log\frac{[HCOONa]}{[HCOOH]}$$

$$= 3.74 + \log\left(\frac{2/35}{3/35}\right)$$

$$= 3.56$$

∴ The pH of resulting solⁿ. is 3.56 //

Type 1

2. 200 ml of 0.1 M acetic acid is mixed with 400 ml of 0.2 M sodium acetate solution. Calculate the pH of resulting mixture. Given $K_a = 1.8 \times 10^{-5}$.

Soln.

For acid

$V_1 = 200$ ml

$M_1 = 0.1$ M

In mixture

$V_2 =$ ~~400 ml~~ $200 + 400 = 600$ ml

$M_2 = [CH_3COOH]$

$M_1V_1 = M_2V_2$

$0.1 \times 200 = [CH_3COOH] \times 600$

$\therefore [CH_3COOH] = 1/30$ M

For salt

$V_1 = 400$ ml

$M_1 = 0.2$ M

In mixture

$V_2 = 600$ ml

$M_2 = [CH_3COONa]$

$M_1V_1 = M_2V_2$

$0.2 \times 400 = [CH_3COONa] \times 600$

or, $\therefore [CH_3COONa] =$ ~~4/35 M~~ $2/15$ M

We have,

$$pH = p^{Ka} + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

$$= -\log K_a + \log \left(\cancel{\frac{4/35}{1/35}}\right) \left(\frac{2/15}{1/30}\right)$$

$$= -\log(1.8 \times 10^{-5}) + \log(4)$$

$$= 5.34$$ //

Type 2

3. A buffer contains ~~0.1 M of~~ 0.1 mole/litre of both NH_4Cl NH_3. Calculate the pH of solution when 0.001 mole of HC is added to it. [$pK_b = 4.74$ for ammoni

Soln.

Initial concn. of $NH_3 = 0.1$ mole/l

" " " $NH_4Cl = 0.1$ mole/l

After addition of HCl ;

concn of NH_3 will decrease

concn of NH_4Cl will increase

$$\underset{0.001M}{NH_3} + \underset{0.001M}{HCl} \longrightarrow \underset{0.001M}{NH_4Cl}$$

So, $[NH_3] = 0.1 - 0.001 = 0.099$ M

$[NH_4Cl] = 0.1 + 0.001 = 0.101$ M

∴ We have, for basic buffer soln.,

$$pOH = pK_b + \log\frac{[NH_4Cl]}{[NH_3]}$$

$$= 4.74 + \log\left(\frac{0.101}{0.099}\right)$$

$$= 4.75$$

∴ $pH = 14 - pOH = 14 - 4.75 = 9.25$ //

4. A buffer soln. contains 0.1 mole/litre acetic acid & sodi acetate. What will be its pH ? Also calculate change in pH when 0.001 mole NaOH is added to it.

Soln. For case I :

Initial concn. of acetic acid $= 0.1$ mole/l $[CH_3COOH]$

" " " sodium acetate $= 0.1$ mole/l $[CH_3COONa]$

∴ For acidic buffer solⁿ,

$$pH = pKa + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

$$= 4.74 + \log \left(\frac{0.1}{0.1}\right)$$

$$= 4.74$$

For case II :

When 0.001 mole NaOH is added,

concⁿ of CH_3COOH decreases

concⁿ of CH_3COONa increases

So, $[CH_3COOH] = 0.1 - 0.001 = 0.099$

$[CH_3COONa] = 0.1 + 0.001 = 0.101$

Now,

$$pH' = pKa + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

$$= 4.74 + \log \left(\cancel{0.099}\ \frac{0.101}{0.099}\right)$$

$$= \cancel{4.753}\ 4.748$$

∴ change in pH = pH' − pH

$= 4.748 - 4.74$

$= 0.008$ //

5. A buffer solⁿ contains 0.1 mole/litre NH_4OH & NH_4 ~~Calculate the pH of solution when 0.001 mole of HCl is added to it~~ What will be its pH ? Also calculate change in when 0.001 M HCl is added to it.

Solⁿ:

For case I :

Initial conc. of $[NH_4OH] = 0.1$ $[NH_4OH]$

" " " $NH_4Cl = 0.1$ $[NH_4Cl]$

For basic buffer solⁿ,

$$pH = \cancel{pK_b}\ 14 - pK_b - \log\frac{[NH_4Cl]}{[NH_4OH]}$$

$$= 14 - 4.74 - \log\left(\frac{\cancel{0.1}}{\cancel{0.1}}\right)$$

$$= 9.26$$

For case II :

When 0.001 M HCl is added,

conc. of NH_4OH decreases

conc. of NH_4Cl increases.

So, $[NH_4OH] = 0.1 - 0.001 = 0.099$

$[NH_4Cl] = 0.1 + 0.001 = 0.101$

Now,

$$pH' = 14 - pK_b - \log\frac{[NH_4Cl]}{[NH_4OH]}$$

$$= 14 - 4.74 - \log\left(\frac{0.101}{0.099}\right)$$

$$= 9.25$$

∴ change in pH = 9.26 − 9.25

= 0.0086 //

Electrochemistry

Electrolytic cell

A branch of chemistry which deals with conversion of electrical energy into chemical energy is known as electrolchemistry.

Electrochemical cell

The device which is used to convert electrical energy into chemical energy or vice versa is known as electrochemical cell.

There are 2 types of electrochemical cell. They are:

i) Electrolytic cell

ii) Galvanic cell or voltaic cell

1. Electrolytic cell

In this cell, anode & cathode are dipped in same electrolytic solution, in single voltameter. Here, chemical rxn occurs in electrolytic solution by passage of electricity.

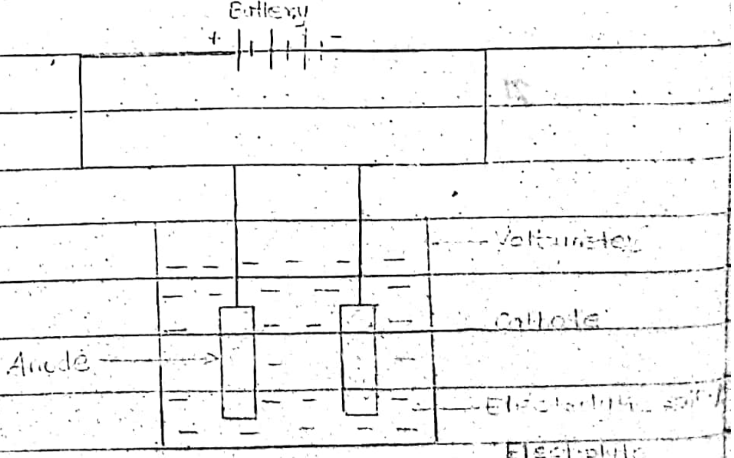


fig. Electrolytic cell

Anode: Oxidation Cathode (Reduction)

$Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$ $2Na^+ + 2e^- \rightarrow 2Na$

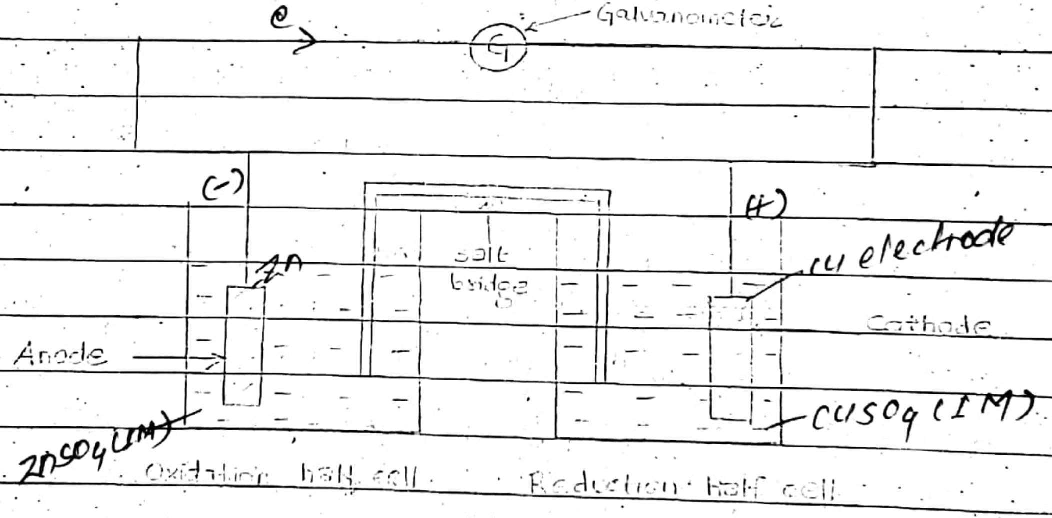
or, $2Cl^- \rightarrow Cl_2 + 2e.$ Net Rx^n: $2NaCl \rightarrow Cl_2 + 2Na$

Electrolytic solⁿ. gets decomposed into cation & anion b passing electricity. Cations get deposited at cathode wher anions get deposited at anode. For e.g. cell used in electroplating, cell used in electrorefining, cell used i electrolysis of water, etc.

2. Galvanic cell or voltaic cell

Such type of electrochemical cell in which chemica energy gets converted into electrical energy, It is known as galvanic cell. It is also called voltaic ce

In this cell, electricity is generated due to spontaneous redox chemical reaction occurance at electrolytic solution.



In this cell, anode & cathode are dipped in respective differen electrolytic solution, in different voltameter. At anode, oxidation rxn occurs so anode containing compartment is called oxidation half cell whereas reduction rxn occurs at cathode so cathode containing compartment is known as reduction half cell. These two cells are connecte

Reaction:

$Zn - 2e \rightarrow Zn^{++}$ (anode)

$Cu^{++} + 2e \rightarrow Cu$ (cathode)

by salt bridge to complete electric circuit. Galvanometer is used to indicate flow of current.

Differences betn Galvanic cell & electrolytic cell

	Electrolytic cell	Galvanic cell
1.	In electrolytic cell, anode & cathode are dipped in same electrolytic ~~cell~~ soln.	In galvanic cell, anode & cathode are dipped in different electrolytic soln.
2.	Anode & cathode are connected to the +ve & -ve terminals of battery resp.	Anode & cathode are connected to the galvanometer.
3.	Salt bridge is not used.	Salt bridge is used to complete electric circuit.
4.	Anode is positive part of the cell & cathode is negative part of the cell.	Anode is negative part of the cell & cathode is positive part of the cell.
5.	In electrolytic cell, chemical rxn is carried out by passing electric current.	In galvanic cell, electric current is produced due to chemical reaction.
6.	The redox reactions occuring at the electrodes are non-spontaneous and takes place only when electrical energy is supplied.	The redox reactions occuring at the electrodes are spontaneous.

7.	Electrolytic cell cannot be represented by cell notation.	Galvanic cell can be represented by cell notation.
8.	e.g. cell used in electroplating, electrorefining, etc.	e.g. cell used in vehicle.

Cell notation & cell reaction of Galvanic cell

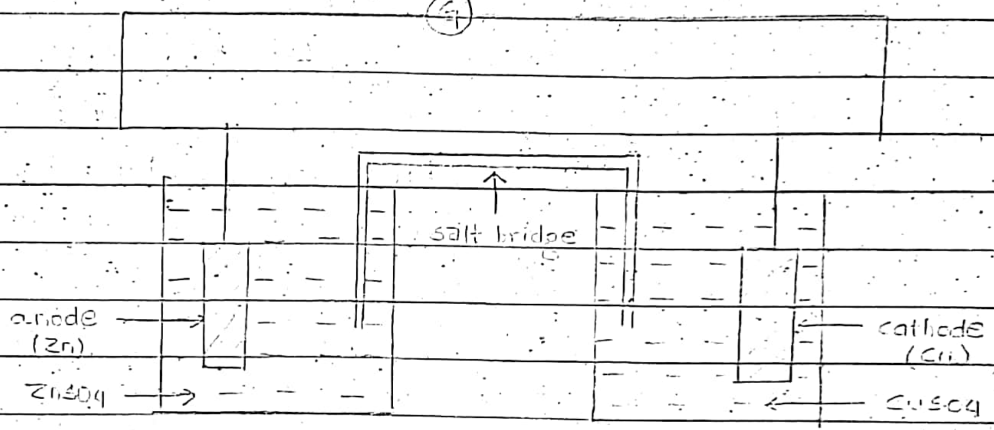


fig. Galvanic cell

Cell notation is:

$$Zn(s) / ZnSO_4(M) // CuSO_4(M) / Cu(s)$$

OR

$$Zn(s) / Zn^{++}(M) // Cu^{++}(M) / Cu(s)$$

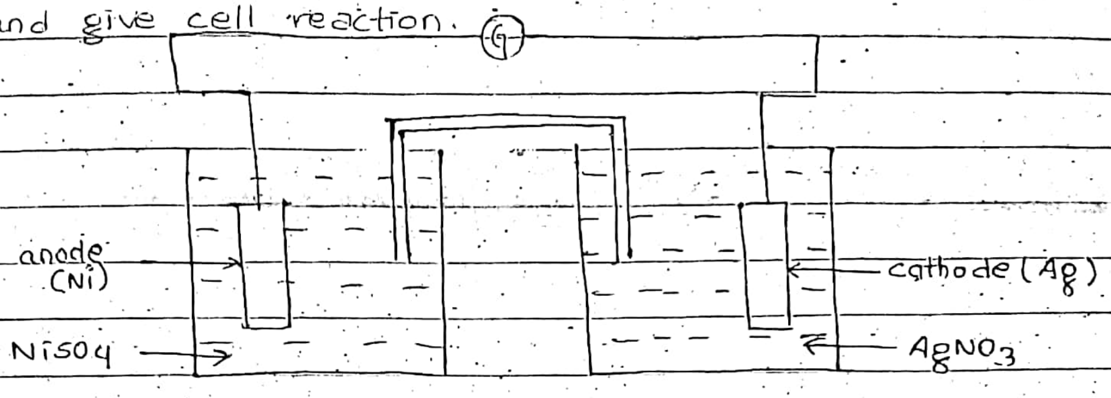
Cell reaction: At anode,

$$Zn - 2e^- \longrightarrow Zn^{++}$$

At cathode, $Cu^{++} + 2e^- \longrightarrow Cu$

Net cell reaction: $Zn + Cu^{++} \longrightarrow Cu + Zn^{++}$

8. Construct following galvanic cell, $Ni(s)/NiSO_4(M)//AgNO_3(M)/Ag(s)$ and give cell reaction.



Cell reaction : At anode : $Ni - 2e^- \longrightarrow Ni^{++}$

At cathode : $[Ag^+ + e^- \longrightarrow Ag] \times 2$

$Ni + 2Ag^+ \longrightarrow Ni^{++} + 2Ag$

Net cell r^{xn} : $Ni + 2Ag^+ \longrightarrow 2Ag + Ni^{++}$

Salt bridge

It is inverted U-shaped glass tube containing concentrated solution of ~~strong~~ inert electrolyte like KCl, KNO_3, NH_4Cl, NH_4NO_3, etc. fused by agar-agar gel. It has following functions:

1. It is used to complete electric circuit.
2. It is used to separate electrolytic solution externally.
3. It is used to connect electrolytic solution internally.
4. It is used to minimize junction potential.
5. It is used to maintain neutrality of the solⁿ in two half cells.

Single electrode potential :-

When any metal rod is dipped in its salt solution, then there occur oxidation, reduction reaction as follows:

$M - ne^- \longrightarrow M^{n+}$ oxidation r^{xn}

$M^{n+} + ne^- \longrightarrow M$ reduction r^{xn}

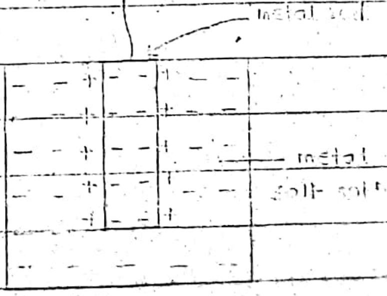


fig. single electrode potential

Due to these reactions, there may occur electric double la
of charge. Due to which certain potential is developed a
is called single electrode potential.

The magnitude of single electrode potential depends on
i) Nature of metal / electrode
ii.) Concentration of sol^n
iii) Temperature
iv) Pressure.

There are 2 types of single electrode potential:
1) Oxidation potential 2) Reduction potential

1. Oxidation potential
The electrode potential generated due to oxidation r^{xn} is K
oxidation potential. It can be denoted by $E_{M/M^{n+}}$. e.g.
For Zn, it is denoted as

$E_{Zn/Zn^{++}}$ (oxidation potential of Zn)

For Cu, it is denoted as

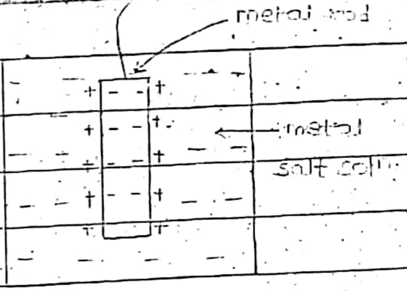
$E_{Cu/Cu^{++}}$ (oxidation potential of Cu)

2. Reduction potential
The electrode potential generated due to reduction r^{xn} i
K/a reduction potential. It can be denoted by $E_{M^{n+}/M}$. e
For Zn, it is denoted as

$E_{Zn^{++}/Zn}$ (reduction potential of Zn)

Standard electrode potential (E°)

The single electrode potential generated when any metal rod is dipped in its solution of 1 M concentration at 25°C and 1 atmospheric pressure is K/a standard electrode potential.



There are 2 types of standard electrode potential:

1) Standard oxidation potential $[E^\circ_{Zn/Zn^{++}}]$
2) Standard reduction potential [~~$E^\circ_{Zn/Cu}$~~ $[E^\circ_{Zn^{++}/Zn}, E^\circ_{Cu^{++}/Cu}]$

Emf of cell

The sum of standard oxidation potential & standard reduction potential is K/a emf of cell. It is denoted by E°_{cell}. Mathematically,

$$
\begin{aligned}
E^\circ_{cell} &= E^\circ_{oxidation} + E^\circ_{reduction} \\
&= E^\circ_{oxidation}(\text{Anode}) + E^\circ_{reduction}(\text{cathode}) \\
&= -E^\circ_{reduction}(\text{Anode}) + E^\circ_{reduction}(\text{cathode}) \\
&= E^\circ_{reduction(\text{cathode})} - E^\circ_{reduction(\text{anode})}
\end{aligned}
$$

$$\therefore E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

Q. Write cell rxn, cell notation and E°_{cell} of Zn-Cu cell, also construct this cell.

Cell notation : $Zn(s)/Zn^{++}(M) // Cu^{++}(M)/Cu(s)$

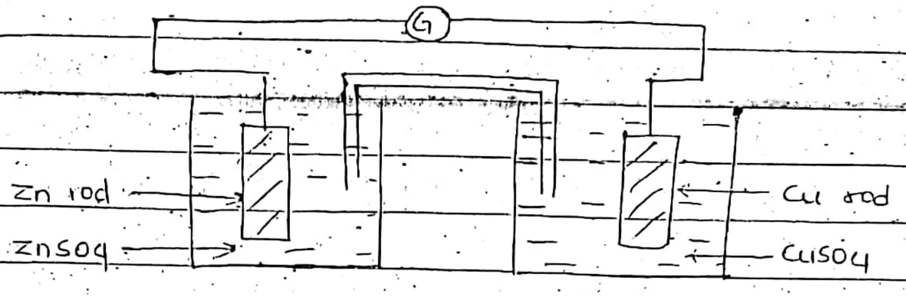
Cell rxn : At anode, $Zn - \cancel{2e^-} \longrightarrow Zn^{++}$

$Cu^{++} \cancel{+ 2e^-} \longrightarrow Cu$

Net cell rxn : $Zn + Cu^{++} \longrightarrow Cu + Zn^{++}$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= E^\circ_{Cu^{++}/Cu} - E^\circ_{\cancel{Zn/}Zn^{++}/Zn}$



Q. Write cell rxn, cell notation and E°_{cell} of ~~Zn-Cu~~ Ni-Ag cell & construct this cell.

Cell notation : $Ni(s) / Ni^{++}(M) // Ag^{+}(M) / Ag(s)$

Cell rxn :

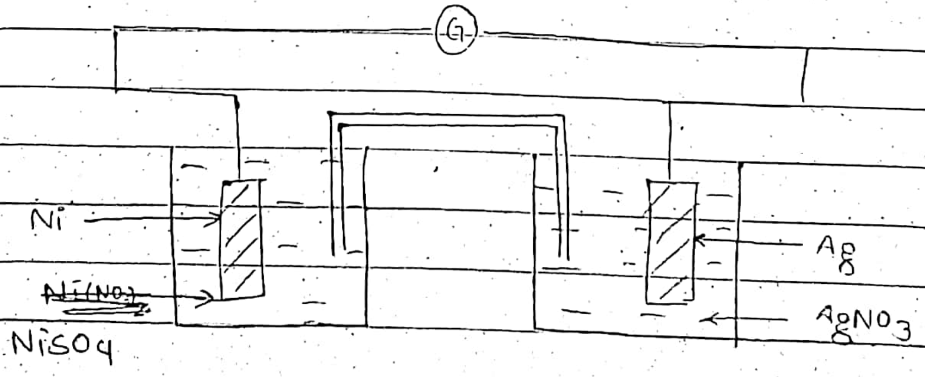
At anode, $Ni - \cancel{2e} \longrightarrow Ni^{++}$

At cathode, $[Ag^{+} + \cancel{e^-} \longrightarrow Ag] \times 2$

$Ni + 2Ag^{+} \longrightarrow 2Ag + Ni^{++}$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

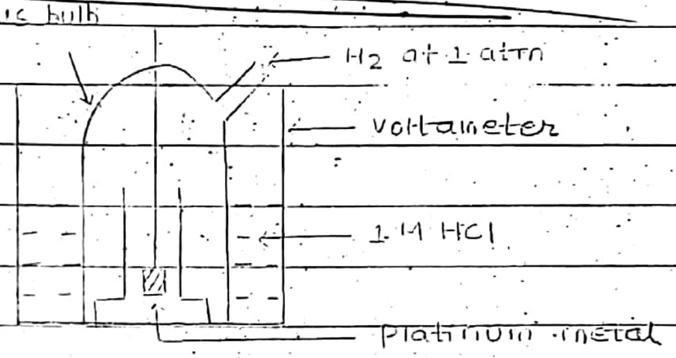
$= E^\circ_{Ag^{+}/Ag} - E^\circ_{Ni^{++}/Ni}$



Measurement of emf of single electrode potential.

It is not possible to measure emf of single electrode without coupling with reference electrode. So, it is necessary to couple single electrode with reference electrode for the measurement of emf. For this purpose, SHE (Standard Hydrogen Electrode) is used. It is also called NHE (Normal Hydrogen Electrode).

SHE (Standard Hydrogen Electrode) /NHE



Standard hydrogen electrode is a reference electrode in which platinized Platinum is taken in a glass bulb which is placed in voltameter containing 1 Molar HCl. Hydrogen gas is bubbled through glass bulb at 1atm pressure. The electrode potential of SHE is supposed to be 0 volt at 25°C.

To measure standard electrode potential of metals which is more electropositive than hydrogen like Zn, Fe, etc., SHE is used connected as cathode.

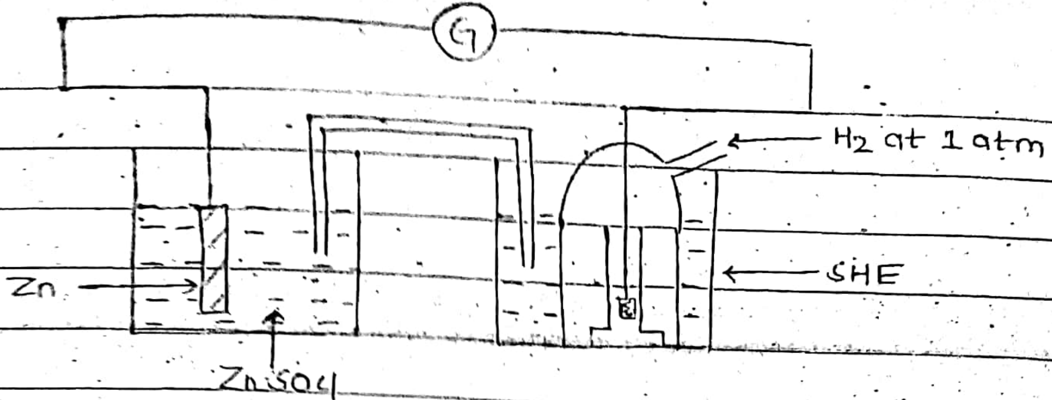


fig. Measurement of st. electrode potential of Zn.

Cell notation

Zn/ZnSO4 // HCl (1M) / H_2 (1atm), pt

Cell rxn

At anode, $Zn - 2e^- \longrightarrow Zn^{++}$

At cathode, $2H^+ + 2e^- \longrightarrow H_2$

$Zn + 2H^+ \longrightarrow Zn^{++} + H_2$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$= E^\circ_{2H^+/H_2} - E^\circ_{Zn^{++}/Zn}$$
$$= 0.0 - (-0.76)$$
$$= 0.76\ V$$

So, standard electrode potential of zinc is 0.76 V //

To measure standard electrode potential of metal which is less electropositive than hydrogen, SHE is connected as anode.

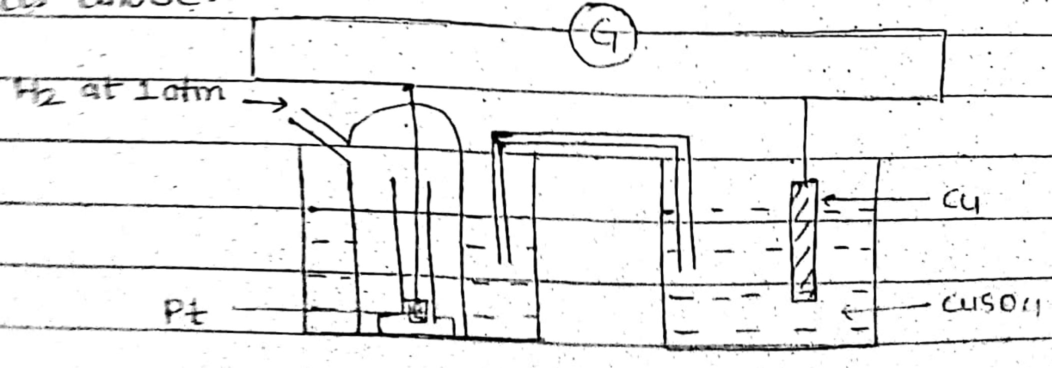


fig. Measurement of st. electrode potential of Cu

Cell notation

$H_2(1atm), Pt / H^+(1M) // CuSO_4 / Cu$

Cell rxn

At anode, $H_2 - \cancel{2e^-} \longrightarrow 2H^+$

At cathode, $Cu^{++} + \cancel{2e^-} \longrightarrow Cu$

$$H_2 + Cu^{++} \longrightarrow 2H^+ + Cu$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$= E^\circ_{Cu^{++}/Cu} - E^\circ_{2H^+/H_2}$$

$$= 0.34 - 0.0$$

$$= 0.34\ V$$

So, standard electrode potential of Cu is 0.34 V//

Q. What is SHE? Explain its structure along with its half cell notation.

- Half cell notation of SHE

1) As anode,

$H_2(1atm), Pt / H^+(1M)$

2) As cathode,

$HCl(1M) / H_2(1atm), Pt$

Electrochemical series (ECS)

The arrangement of different electrodes on the basis of their increasing order of standard reduction potential is known as electrochemical series (ECS).

Electrode	Reaction	Standard Red^n Potential (in volt)
Li	$Li^+ + e^- \longrightarrow Li$	-3.05
K	$K^+ + e^- \longrightarrow K$	-2.93
Ca	$Ca^{++} + 2e \longrightarrow Ca$	-2.87
Na	$Na^+ + e \longrightarrow Na$	-2.71
Mg	$Mg^{++} + 2e \longrightarrow Mg$	-2.37
Al	$Al^{+++} + 3e \longrightarrow Al$	-1.66
Zn	$Zn^{++} + 2e \longrightarrow Zn$	-0.76
Cr	$Cr^{+++} + 3e \longrightarrow Cr$	-0.79
Fe	$Fe^{++} + 2e \longrightarrow Fe$	-0.44
Cd	$Cd^{++} + 2e \longrightarrow Cd$	-0.40
Ni	$Ni^{++} + 2e \longrightarrow Ni$	-0.25
Sn	$Sn^{++} + 2e \longrightarrow Sn$	-0.14
Pb	$Pb^{+++} + 2e \longrightarrow Pb$	-0.13
H_2	$2H^+ + 2e \longrightarrow H_2$	0.0
Cu	$Cu^{++} + 2e \longrightarrow Cu$	+0.34
Hg	$Hg^{++} + 2e \longrightarrow Hg$	+0.79
Ag	$Ag^+ + e \longrightarrow Ag$	+0.80
Au	$Au^{+++} + 3e \longrightarrow Au$	+1.50

fig. ECS

In ECS series, electrodes which lie above the hydrogen are more electropositive. They have tendency to lose electrons. So, they are easily oxidized and are good reducing agent. whereas electrodes which lie below in ECS are less electropositive. They have less tendency to lose electrons. So, they are easily reduced and are good oxidizing agent.

ECS is also called activity series.

Application of ECS

The applications of ECS are as follows:

1. To predict strength of oxidizing & reducing agent.
2. To construct galvanic cell.
3. To predict anode & cathode.
4. To predict whether the metal can replace hydrogen from acid or not.
5. To predict feasibility of reaction (spontaneity)

1. To predict strength of oxidizing & reducing agent

In electrochemical series, elements lying above are good reducing agent whereas elements lying below are good oxidizing agent.

2. To construct galvanic cell

Since electrodes lying above in ECS are easily oxidized, they are used as anode whereas electrodes lying below are easily reduced so they are used as cathode in galvanic cell.

3. To predict anode & cathode

Electrodes having low standard red^n potential value is easily oxidized so, electrodes having low st. red^n poten (they lie above in ECS) are taken as anode. Similarly, electrodes having high standard red^n potential are kept as cathode.

4. To predict whether the metal can replace H_2 from acid or not

Those metals which lie above than H_2 are more electro positive than H_2, so, they can replace H_2 from dilute mineral acid. For e.g. Na, Mg, Zn, Fe, Sn, etc. And the metals which lie below H_2 are less electropositive than H_2. So, they can't replace H_2 from dilute acid.

5. To predict feasibility of reaction (spontaneity)

ECS is used to predict whether the rxn is feasible or not. For this, first of all E°_{cell} is calculated. If its value is +ve, then rxn is feasible. If −ve, then rxn is not feasible.

e.g. $Cu + ZnSO_4 \longrightarrow CuSO_4 + Zn$

$\overset{0}{Zn} + \overset{+2}{Cu}SO_4 \longrightarrow \overset{+2}{Zn}SO_4 + \overset{0}{Cu}$

In 1st rxn, Cu is oxidized & Zn is reduced.

So, $E^\circ_{cell} = E^\circ_{red} - E^\circ_{oxd}$

$= -0.76 - 0.34$

$= -1.10$ V

−ve sign indicates rxn is not feasible. //

$\overset{0}{Zn} + \overset{+2}{Cu}SO_4 \longrightarrow \overset{+2}{Zn}SO_4 + \overset{0}{Cu}$

In this rxn, Zn is oxidized & Cu is reduced.

$E^\circ_{cell} = E^\circ_{red} - E^\circ_{oxd}$

$= 0.34 - (-0.76)$

$= 1.10\ V$

So, this rxn is feasible //

Q. Predict whether the following rxn are feasible or not?

i) $\overset{0}{Zn} + \overset{+1}{Ag^+} \longrightarrow \overset{0}{Ag} + \overset{+2}{Zn^{++}}$

In this rxn, Zn is oxidized & Ag is reduced.

$E^\circ_{cell} = E^\circ_{red} - E^\circ_{oxd}$

$= 0.80 - (-0.76)$

$= 1.56\ V$ (feasible)

ii) $\overset{0}{Ni} + \overset{+2}{H_2}SO_4 \longrightarrow \overset{+2}{Ni}SO_4 + \overset{0}{H_2} \uparrow$

In this rxn, Ni is oxidized & H_2 is reduced.

$E^\circ_{cell} = E^\circ_{red} - E^\circ_{oxd}$

$= 0.0 - (-0.25)$

$= 0.25\ V$ (feasible)

iii) $\overset{0}{Cd} + \overset{+2}{Cu}SO_4 \longrightarrow \overset{0}{Cu} + \overset{+2}{Cd}SO_4$

In this rxn, Cd is oxidized & ~~Cd~~ Cu is reduced.

$E^\circ_{cell} = E^\circ_{red} - E^\circ_{oxd}$

$= 0.34 - (-0.40)$

$= 0.74\ V$ (feasible)

Nernst Equation

Emf of a cell at standard condition can be calculated by using electrochemical series whereas Emf of cell at non-standard condition is determined by using Nernst Equation.

This eqn was proposed by Walter Nernst in 1859.

For general rxn : $aA + bB \rightleftharpoons cC + dD$, the Nernst eqn

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$= (E^\circ_{cathode} - E^\circ_{anode}) - \frac{8.314 \times T}{n \times 96500} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\therefore E_{cell} = (E^\circ_{cathode} - E^\circ_{anode}) - \frac{8.314 \times T}{n \times 96500} \times 2.303 \log \frac{[C]^c [D]}{[A]^a [B]} \quad \text{--- i)}$$

At 25°C (room temp),

$$E_{cell} = E^\circ_{cell} - \frac{8.314 \times (25+273)}{n \times 96500} \times 2.303 \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\therefore E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{--- ii)}$$

Eqns i) & ii) are required Nernst equations.

Application of Nernst Equation

1. It is used to calculate emf of cell at non-standard condition.
2. It is used to calculate concentration of reactant & product.
3. It is used to calculate temp. of the system.

[solid] = 1

Q. Calculate the emf of the following cell at 25°C.

$Zn/Zn^{++}(0.01M)//Ag^{+}(0.1M)/Ag$.

Given : st. reduction potential of Zn^{++}/Zn electrode = $-0.76V$

st. reduction potential of Ag^{+}/Ag electrode = $+0.80V$

Soln.

$E^{\circ}_{Zn^{++}/Zn} = -0.76V$ $\quad\quad E^{\circ}_{cell} = ?$

$E^{\circ}_{Ag^{+}/Ag} = +0.80V$

Here, Zn is anode & Ag is cathode

At anode, $Zn - 2e^{-} \longrightarrow Zn^{++}$

At cathode, $(Ag^{+} + e^{-} \longrightarrow Ag) \times 2$

Net cell reaction: $\underset{A}{Zn} + \underset{B}{2Ag^{+}} \longrightarrow \underset{C}{2Ag} + \underset{D}{Zn^{++}}$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log \frac{[Ag]^2 [Zn^{++}]^1}{[Zn]^1 [Ag^{+}]^2}$$

$$= (E^{\circ}_{cathode} - E^{\circ}_{anode}) - \frac{0.059}{2} \log \frac{\{1\}^2 \times \{0.01\}}{\{1\} \times 0.1^2}$$

$$= (0.80 - (-0.76)) - \frac{0.059}{2} \log \frac{1 \times 0.01}{0.1^2}$$

$$= 1.56 - 0$$

$\therefore E_{cell} = 1.56V$ #

Hence,

The emf of given cell is 1.56 Volt //

Q. Calculate the emf of the cell Zn/ZnSO4 (0.1M) // CdSO4
/Cd. Given : $E^\circ_{Zn^{++}/Zn} = -0.76\ V$
$E^\circ_{Cd^{++}/Cd} = -0.4V$ at 298 K

Soln.

$E^\circ_{Zn^{++}/Zn} = -0.76\ V$ $E_{cell} = ?$ $[Zn^{++}] = 0.1M$

$E^\circ_{Cd^{++}/Cd} = -0.4\ V$ $[Cd^{++}] = 0.01\ M$

In this cell, Zn is anode & Cd is cathode

At anode, $Zn - 2e^- \longrightarrow Zn^{++}$

At cathode, $Cd^{++} + 2e^- \longrightarrow Cd$

$$\underset{A}{Zn} + \underset{B}{Cd^{++}} \longrightarrow \underset{C}{Cd} + \underset{D}{Zn^{++}}$$

The emf of the cell at 298K is

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \frac{[Cd]\,[Zn^{++}]}{[Zn]\,[Cd^{++}]}$$

$$= (E^\circ_{cathode} - E^\circ_{anode}) - \frac{0.059}{2} \log \frac{1 \times 0.1}{1 \times 0.01}$$

$$= [-0.4 - (-0.76)] - \frac{0.059}{2} \log \frac{0.1}{0.01}$$

$$= 0.36 - 0.0295$$

$E^\circ_{cell} = 0.3305\ V$ //

Q. Predict whether the rxn $2Ag + Zn^{++} \longrightarrow 2Ag^+ + Zn$ is fea
or not? Given E° of $Ag/Ag^+ = 0.80\ V$
E° of $Zn^{++}/Zn = -0.763\ V$

Soln.

$E^\circ_{Ag^+/Ag} = -0.80V$

$E^\circ_{Zn^{++}/Zn} = -0.763\ V$

$\overset{0}{2Ag} + \overset{+2}{Zn^{++}} \longrightarrow \overset{+1}{2Ag^{+}} + \overset{0}{Zn}$

In this rxn, Ag is oxidized & Zn is reduced.

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= E^\circ_{Zn^{++}/Zn} - E^\circ_{Ag^{+}/Ag}$

$= -0.763 - (-0.80)$

$= 0.037\ V$ (+ve)

∴ The rxn is feasible //

Q. Predict whether the rxn is feasible or not:

$Ni + ZnSO_4 \longrightarrow NiSO_4 + Zn$

Given: $E^\circ_{Zn/Zn^{++}} = 0.76\ V$

$E^\circ_{Ni/Ni^{++}} = 0.24\ V$

Soln:

$\overset{0}{Ni} + \overset{+2}{Zn}SO_4 \longrightarrow \overset{+2}{Ni}SO_4 + \overset{0}{Zn}$

In this rxn, Ni is oxidized & Zn is reduced.

$E^\circ_{Zn^{++}/Zn} = -0.76\ V$

$E^\circ_{Ni^{++}/Ni} = -0.24\ V$

∴ $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= E^\circ_{Zn^{++}/Zn} - E^\circ_{Ni^{++}/Ni}$

$= -0.76 - (-0.24)$

$= -0.52\ V$ (−ve)

∴ The reaction is not feasible //

1A
3. A Galvanic cell consists of metallic zinc plate immers with 0.1 M zinc nitrate solⁿ and lead plate in 0.02 M lead nitrate solⁿ. calculate the emf of the cell at 25°C Write the cell rxn and cell notation.

Given : $E^\circ_{Zn^{++}/Zn} = -0.76\,V$ (oxidⁿ) anode $E^\circ_{Pb^{++}/Pb} = -0.13\,V$ (redⁿ) cathode

Solⁿ.

In this cell, Zn has less reduction potential value tha Pb. so, Zn is anode & Pb is cathode.

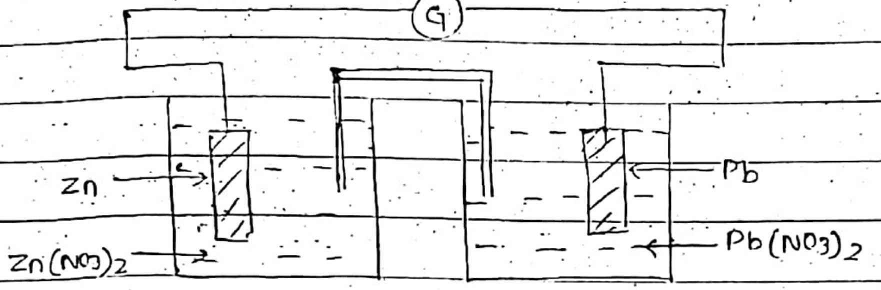


fig. Galvanic cell

Cell notation : $Zn / Zn(NO_3)_2\ (0.1M)\ //\ Pb(NO_3)_2\ (0.02M) / Pb$

At anode, $Zn - 2e^- \longrightarrow Zn^{++}$

At cathode, $Pb^{++} + 2e^- \longrightarrow Pb$

Net cell rxn : $\underset{A}{Zn} + \underset{B}{Pb^{++}} \longrightarrow \underset{C}{Pb} + \underset{D}{Zn^{++}}$

$$E_{cell} = \underset{(E_C^\circ - E_A^\circ)}{E^\circ_{cell}} - \frac{0.059}{n} \log \frac{[Pb]\,[Zn^{++}]}{[Zn]\,[Pb^{++}]}$$

$$= (-0.13 + 0.76) - \frac{0.059}{2} \log \frac{1 \times 0.1}{1 \times 0.02}$$

$$= 0.63 - 0.020619$$

$$= 0.6093\ V.$$

∴ The emf of the cell at 25°C is 0.6093 V //

Calculate the concentration of Ni^{++} in the cell at 25°C, if the emf is 0.601 V.

$$Ni/Ni^{++}\ (a = ?)\ //\ Cu^{++}(0.75\ M)\ /Cu$$

Given : $E^\circ_{Ni/Ni^{++}} = 0.25\ V$, $E^\circ_{Cu^{++}/Cu} = 0.34\ V$

Soln.

$E_{cell} = 0.601\ V$ $\qquad E^\circ_{Ni^{++}/Ni} = -0.25\ V$ (oxidn) anode

$[Ni^{++}] = ?$ $\qquad E^\circ_{Cu^{++}/Cu} = 0.34\ V$ (redn) cathode

In this cell, Ni is anode & Cu is cathode since ~~the~~ Ni has less reduction potential value than Cu.

At anode, $Ni - \cancel{2e^-} \longrightarrow Ni^{++}$

At cathode, $Cu^{++} + \cancel{2e^-} \longrightarrow Cu$

$$\underset{A}{Ni} + \underset{B}{Cu^{++}} \longrightarrow \underset{C}{Cu} + \underset{D}{Ni^{++}}$$

The emf of cell at 25°C is

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \frac{[Cu]\,[Ni^{++}]}{[Ni]\,[Cu^{++}]}.$$

$$0.601 = (E^\circ_C - E^\circ_A) - \frac{0.059}{2} \log \frac{1 \times [Ni^{++}]}{1 \times 0.75}$$

$$0.601 = (0.34 + 0.25) - \frac{0.059}{2} \log \frac{[Ni^{++}]}{0.75}$$

$$0.011 = \frac{-0.059}{2} \log \frac{[Ni^{++}]}{0.75}$$

$$\frac{-22}{59} = \log \frac{[Ni^{++}]}{0.75}$$

$$10^{-22/59} = \frac{[Ni^{++}]}{0.75}$$

$\therefore [Ni^{++}] = 0.32\ M$ //

Calculate the emf of the following cell at 25°C giving electrode rxn and cell rxn.

$Cd(s) / Cd^{++} (0.01M) \; // \; Cd^{++} (0.5M) / Cu(s)$

$E^\circ_{Cd^{++}/Cu} = -0.140V$ $\quad$ $E^\circ_{Cu^{++}/Cu} = 0.34 V$

Soln.

$E^\circ_{Cd^{++}/Cu} = -0.140 V$ (oxidn) anode $\quad [Cd^{++}] = 0.01M$

$E^\circ_{Cu^{++}/Cu} = 0.34 V$ (redn) cathode $\quad [Cu^{++}] = 0.5M$

At anode, $Cd - 2e^- \longrightarrow Cd^{++}$

At cathode, $Cu^{++} + 2e^- \longrightarrow Cu$

Net cell rxn : $Cd + Cu^{++} \longrightarrow Cu + Cd^{++}$

The emf of cell at 25°C is

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \frac{[Cu][Cd^{++}]}{[Cd][Cu^{++}]}$$

$$= (E^\circ_C - E^\circ_A) - \frac{0.059}{2} \log \frac{1 \times 0.01}{1 \times 0.5}$$

$$= (0.34 + 0.140) - (-0.0501)$$

$$= 0.5301 \text{ V} \; //$$

General Inorganic Chemistry (15 marks)
Ionization energy
Electron affinity
Electro negativity
s-block elements
p-block elements
transition elements

Vertical column : Group
No. of groups - 9 (18 columns)
subgroup A & B

Horizontal row : Period
No. of periods - 7

I .... VII group (A & B) ⇒ 14 ⇒ 14
VIII group (no subgroup but 3 columns) ⇒ 3 ⇒ 3
zero group ⇒ 1 ⇒ 1
18 columns

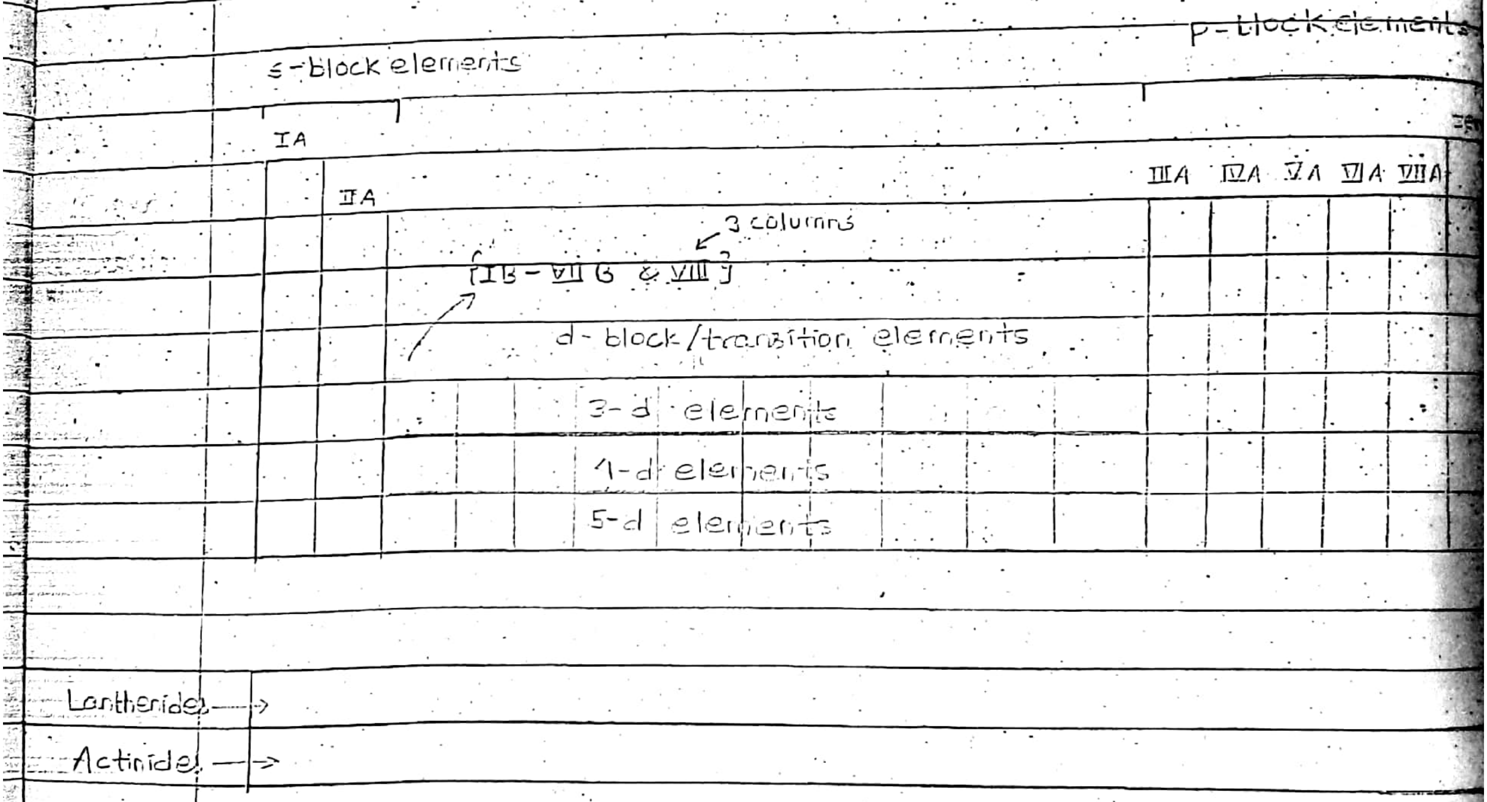
Period — no. of elements
1 ⇒ 2 , shortest period
2 ⇒ 8 , short "
3 ⇒ 8 , " "
4 ⇒ 18 , long "
5 ⇒ 18 , " "
6 ⇒ 32 , largest "
7 ⇒ incomplete , longest

2 columns (IA, IIA) ⇒ s-block elements

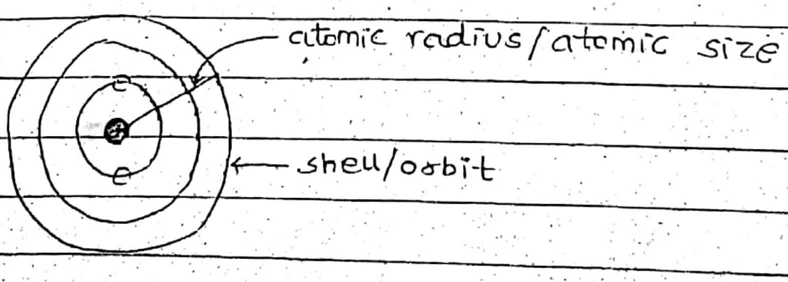
6 columns (IIIA, IVA, VA, VIA, VIIA & zero group) ⇒ p-block

10 columns (IB, IIB, IIIB, IVB, VB, VIB, VIIB & VIII) ⇒ d-b
elements (transition elements)

Lanthenides & Actinides ⇒ f-block elements
(inner transition elements)



Atomic size



Atomic radius

Atomic size can be expressed in terms of atomic radius. Atomic radius is defined as 'the distance between the centre of nucleus to the outermost shell of atom'.

Variation of atomic size in periodic table

1) Along period

Along period, there are constant no. of shells but there is gradual increase of nuclear charge (+ve charge). So, there is gradual increase in ENC (effective nuclear charge) on going left to right. As a result, there is gradual increase in contraction. So, atomic size of atom decreases on going left to right in period.

$_3Li$ $_4Be$ $_5B$ $_6C$ $_7N$ $_8O$ $_9F$

gradual ↑ in ENC →

gradual ↓ in atomic size

2) Along group

Along group, there is addition of shells along with increase in ENC. So, there is decrease in ENC on going top to bottom. As a result, there is less contraction. So, size of atom increases on going top to bottom along group.

$_3Li$	↓ in ENC
$_{11}Na$	↑ in atomic size
$_{19}K$	
Rb	
Cs	
Fr	

Ionization potential / Ionization energy (I.E)

The energy required to remove electron from outermost shell of gaseous, neutral, isolated atom in ground state is k/a ionization potential/energy. It is endothermic process. In other words, ionization energy can be defined as the energy required to form cation (+ve ion).

$M + IE_1 \xrightarrow{-e^-} M^+$ $IE_1 \Rightarrow$ 1st ionization energ

$M^+ + IE_2 \xrightarrow{-e^-} M^{++}$ $IE_2 \Rightarrow$ 2nd " "

$M^{++} + IE_3 \xrightarrow{-e^-} M^{+++}$ $IE_3 \Rightarrow$ 3rd " "

$IE_1 < IE_2 < IE_3$

Variation of I.E in periodic table

) Along period.

Li Be B C N O F

$\longrightarrow$ size decreases (↓)

$\longrightarrow$ ENC increases (↑)

$\longrightarrow$ I.E value ↑

Along period, there is decrease in atomic size on going left to right due to which there is ↑ in ENC. So, electrons are held more tightly by the nucleus. As a result, more energy is required to remove electrons from the outermost shell. Therefore, ionization energy increases on going left to right along period.

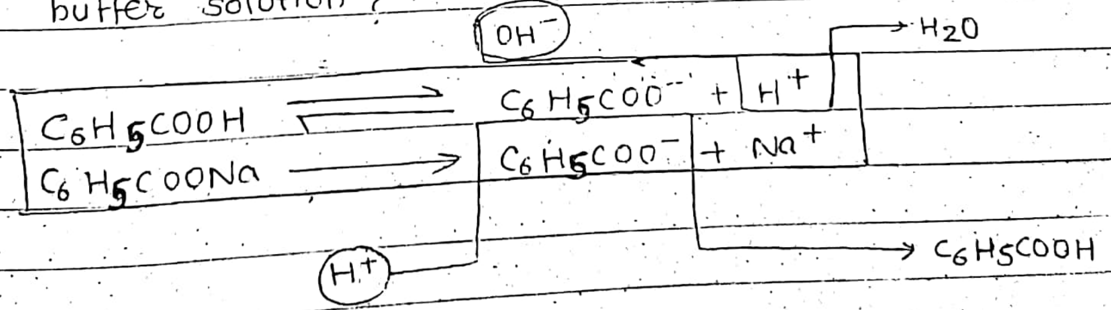
2) Along group

Along group, the size of atom increases due to increase in no. of shells. Due to this, the electrons are held loosely and ENC decreases. As a result, less energy is required to remove electron from the outermost shell & I.E. value also decreases on going top to bottom in group.

Li	size ↑
Na	ENC ↓
K	IE value ↓
Rb	
Cs	
Fr	

1. Why mixture of benzoic acid & sodium benzoate is called buffer solution?
2. Why mixture of ammonium chloride & ammonium hydroxide is buffer solution?

1) ⇒



An acidic ~~b~~ solution is prepared by mixing weak acid (C_6H_5COOH) with strong base (C_6H_5COONa). C_6H_5COOH is partially ionized whereas C_6H_5COONa is ~~weakly~~ completely ionized. When small amount of strong acid (HCl) is added, H^+ reacts with benzoate ion ($C_6H_5COO^-$)

to produce weak acid (CH_3COOH) which is composition o
buffer itself. So, there is no considerable change in PH val

Electron Affinity (EA)

The amount of energy released when an electron i added to outermost shell of neutral gaseous atom i its ground state is known as electron affinity. It is denoted by EA. It is exothermic process. It is also called energy required to form anion.

$$\underset{\text{atom}}{X} + e^- \longrightarrow X^- + EA$$

Variation of EA in periodic table

1) Along period

On going left to right in period of periodic table, there is gradual decrease in atomic size on going left to right due to which attractive power of nucleus become increases gradually. As a result, amount of energy released by addition of electron also increases. Therefore, electron affinity value graduall increases on going left to right in a period.

$$\underrightarrow{\text{Li} \quad \text{Be} \quad \text{B} \quad \text{C} \quad \text{N} \quad \text{O} \quad \text{F}}$$

Atomic size ↓

Electron affinity ↑

*

2) Along group

on going top to bottom along group in periodic table, there is increase in atomic size due to which attractive power of nucleus decreases gradually. As a result, amount of energy released by addition of electron also decreases. Therefore, electron affinity value decreases on going top to bottom in a group.

F
Cl
Br
I ↓

Atomic size ↑
EA ↓

Q. Electron affinity of F is less than that of Cl even though it has smaller size than Cl. Why?

- Since Fluorine has smaller size, there is high electron density. So, there is electronic repulsion. As a result, there is less tendency to attract electron. So, it has less electron affinity than Chlorine.

EA of F < EA of Cl
At. size of F ≤ At. size of Cl

Electroneg

Electronegativity (EN)

The tendency of atom in co-valently bonded atom molecule to attract shared pair of electron towar itself is known as electronegativity. It is measure in Pauling scale. Smaller the size, greater will b the electronegativity value.

Variation of electronegativity in periodic table.

1) Along period

On going left to right in a period, there is gradua decrease in atomic size. So, electron attracting tende also increases. Therefore, electronegativity value increases on going left to right along period in a periodic table.

$\text{Li} \quad \text{Be} \quad \text{B} \quad \text{C} \quad \text{N} \quad \text{O} \quad \text{F} \longrightarrow$

Atomic size ↓

Electronegativity value ↑

2) Along group

on going top to bottom in a group, there is increase in atomic size. So, electron attracting tendency decreases. Therefore, electronegativity value decreases on going top to bottom along group in a periodic table.

F
Cl
Br
I ↓

Atomic size ↑
EN value ↓

Most electronegative element : F – 4 Pauling scale
2nd " " " : O – 3.5 "
3rd " " " : Cl – 3 "
Least " " " : Cs – 0.7 "

~~3 d elements (Transition elements)~~

~~S-block elements~~

Atomic no.	Element	Electronic configuration
1	Hydrogen	$1s^1$
2	Helium	$1s^2$
3	Lithium	$1s^2 2s^1$
4	Beryllium	$1s^2 2s^2$
5	Boron	$1s^2 2s^2 2p^1$
6	Carbon	$1s^2 2s^2 2p^2$
7	Nitrogen	$1s^2 2s^2 2p^3$
8	Oxygen	$1s^2 2s^2 2p^4$
9	Fluorine	$1s^2 2s^2 2p^5$
10	Neon	$1s^2 2s^2 2p^6$
11	Sodium	$1s^2 2s^2 2p^6 3s^1$
12	Magnesium	$1s^2 2s^2 2p^6 3s^2$
13	Aluminium	$1s^2 2s^2 2p^6 3s^2 3p^1$
14	Silicon	$1s^2 2s^2 2p^6 3s^2 3p^2$
15	Phosphorus	$1s^2 2s^2 2p^6 3s^2 3p^3$
16	Sulphur	$[Ne] 3s^2 3p^4$
17	Chlorine	$[Ne] 3s^2 3p^5$
18	Argon	$[Ne] 3s^2 3p^6$
19	Potassium	$[Ne] 3s^2 3p^6 4s^1$

20	Calcium	[Ne] $3s^2 3p^6 4s^2$	
21	Scandium	[Ar] $4s^2 3d^1$	
22	Titanium	[Ar] $4s^2 3d^2$	
23	Vanadium	[Ar] $4s^2 3d^3$	expected
* 24	Chromium	[Ar] $4s^2 3d^4$	[Ar] $4s^1 3d$
25	Manganese	[Ar] $4s^2 3d^5$	~~[Ar]~~
26	Iron	[Ar] $4s^2 3d^6$	
27	Cobalt	[Ar] $4s^2 3d^7$	
28	Nickel	[Ar] $4s^2 3d^8$	expected
* 29	Copper	[Ar] $4s^3 3d^9$	[Ar] $4s^1 3d$
30	Zinc	[Ar] $4s^2 3d^{10}$	

Exceptional electronic configuration in Chromium and Copper is due to stable electronic configuration of half filled ($3d^5$) and fullfilled ($3d^{10}$) electronic configuration.

s-block elements

Those elements in which last electron enters in s-subshell are called s-block elements. In this s-block, elements of group IA and IIA are present. In this block, elements are ~~cha~~ categorized into alkali metals and alkaline earth metals. Electronic configuration: ns^{1-2}

The general properties of s-block elements are as follo

1) They are highly electropositive in nature i.e. they can loose electrons easily.

2) They are soft metals (light metals).

3) They are good reducing agent. That means they are easily oxidized.

4) They can form basic oxides like Na_2O, BaO, MgO, CaO, K_2O, etc. because these oxides can form alkali on dissolving in water.

5) They can form electrovalent compounds. ~~For~~

6) e.g. Li, Na, K, Rb, Cs, Fr, Ca, Mg, Be, Ba, etc.

p-block elements

Those elements in which last electron enters in p-subshell are called p-block elements. In this block, elements of group IIIA, IVA, VA, VIA, VIIA and zero are present. The electronic configuration of this block elements is: np^{1-6}

The general properties of p-block elements are as follows:

1) They are metalloids and non-metals.

2) They are electronegative in nature i.e. they have tendency to gain electrons.

3) They are good oxidizing agent. That means they are easily reduced.

4) They can form acidic oxides like CO_2, SO_2, I_2O_5, P_2O_5, etc. because these oxides can form acid on

dissolving in water.

5) e.g. C, N, O, F, Cl, B, I, P, S, etc.

d-block elements

Those elements in which last electron enters in d-subs are called d-block elements. In this block, elements of group IB, IIB, IIIB, IVB, VB, VIB, VIIB and VIII are present. ~~In~~ These elements are generally metals. d-block element are also called transition elements, because they exhibit transition behaviour between more electropositive s-block and more electronegative p-block elements. This block can be categorized into following 3 types :

1) 3d-elements (1st transition series)
2) 4d-elements (2nd " ")
3) 5d-elements (3rd " ")

Now, the general properties of d-block elements are as follows :

1) They are metals having high melting & boiling point with metallic lustre (shining).

2) Some of these metals are coinage metals.

3) Their electronic configuration is $ns^{1-2}(n-1)d^{1-10}$

4) They have variable oxidation state and valency.

5) They have catalytic property.

elements having incomplete d-orbital → form coloured compounds

6) They can form co-ordination compound / complex compound.

7) They can form colouring compound.

8) They have magnetic property i.e. Para, dia or ferro magnetism.
e.g. Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn

Detail study of properties of elements

1. Electronic configuration

Elements	Electronic configuration
Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
V	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$
Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
Co	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
Ni	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$
Cu	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
Zn	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

The electronic configuration of d-block elements is $ns^{1-2} (n-1)d^{1-10}$. The detail electronic configuration of these elements is given above. Among them, Chromium (at. no. 24) and Copper (at. no. 29) have exceptional electronic configuration due to stable half-filled ($3d^5$) and full-filled ($3d^{10}$) orbital.

Zn is not considered as true d-block elements eve though its last electron enters in d-subshell because it has full-filled electronic configuration i.e. $4s^2 3d^{10}$. Due to not being true d-block element, it can't show variable oxidation state i.e. it has only one oxidation state +2. And it has only one valency i.e. 2. Besides this, it cannot form coloured compound.

2. Variable oxidation state

Elements	Oxidation state
Sc	+2, +3
~~V~~ Ti	+2, +3, +4
~~Ti~~ V	+2, +3, +4, +5
Cr	+1, +2, +3, +4, +5, +6
Mn	+2, +3, +4, +5, +6, +7
Fe	+2, +3, +4, +5, +6
Co	+2, +3, +4, +5
Ni	+2, +3, +4
Cu	+1, +2, +3
Zn	+2

d-block elements exhibit variable oxidation state because they have 4s and 3d orbital having nearly equal energy. Therefore, electron may be lost either from 4s or 3d orbital during formation of chemical bond. Among them, Mn exhibit maximum oxidation number upto +7.

3. Formation of co-ordination compound

d-block elements have tendency to form co-ordination compound with several ligands like NH_3, H_2O, CN^-, Cl^-, etc. In co-ordination compound, ligand donates electron pair to central atom. The tendency of formation of co-ordination compound by transition element is due to following reason :-

1. They have relatively very small size of cation and have high positive charge. It makes more easy to accept lone pair of electron donated by ligand.

2. The transition element's ~~have~~ cation have vacant d-orbital due to which it becomes more easy to accept lone pair of electrons donated by ligand.

3. Since transition, elements show variable oxidation state, they can form co-ordination compound.

The structure of these co-ordination compound depends on number of ligands present in molecule. The structure may be square planar, linear, tetrahedral or octahedral. These structures are based on oxidation number of central atom.

oxidation no.	Structure
2	Linear
4	Tetrahedral
6	Octahedral

Some examples of co-ordination compound are:

$Ni(CO)_4$, $Co_2(CO)_8$, $Fe(CO)_5$, $[Ni(NH_3)_6]^{+3}$

4. Catalytic property:

~~The~~ Most of the transition elements can act as catalys They have vacant d-orbital and small cation. So, they can form unstable intermediate compound with reactan molecules, these intermediate compound follows the path having low activation energy. As a result, rate of reaction become high.

Some transition elements may provide large surface area on which reactant molecules get adsorbed and come closer to each other for the reaction.

Reactant + Transition element ⟶ unstable intermediate
(catalyst)

↓

Product + transition elemen
(catalyst)

Some examples of the r^{xn} are:

$$3H_2 + N_2 \xrightleftharpoons[Mo]{Fe} 2NH_3$$

$$SO_2 + O_2 \xrightleftharpoons{V_2O_5} SO_3$$

$$KClO_3 \xrightarrow[\Delta]{MnO_2} KCl + O_2$$

$$C_2H_4 + H_2 \xrightarrow[\Delta]{Ni} C_2H_6$$

5. Alloy formation

Transition metals have tendency to form alloy. Alloy is the homogeneous mixture of metals. Since transition metals have quiet similar size, they are suitable to fit in crystal lattice. As a result, tendency of alloy formation is high.

V. Imp.

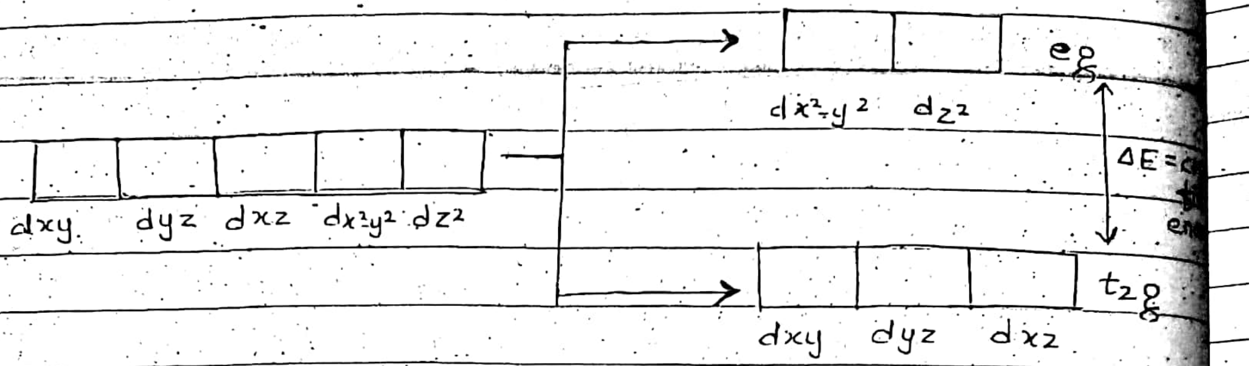
6. Formation of coloring compounds

The compounds formed by transition elements are coloured in solid state as well as in solution form. The compounds of s & p-block elements are white in colour.

The main reason of d-block element's compounds being coloured is incomplete d-orbitals of transition elements. All 5-orbitals of d-subshell have identical energy. When compound is formed, their energy donot remain same, they have different energy and is categorized into 2 types: e_g and t_{2g}.

During formation of compounds, electrons of d-orbital become excited and jump from t_{2g} to e_g by absorption of certain coloured from light beam (white colour). As a result, they form colouring compounds. The nature of colour depends on absorption of colour absorbed by transition element. This phenomenon is k/a d-d electronic transition. called If d-orbital is fulfilled or empty, then d-d electronic transition is not possible either due to empty or fulfilled d-orbital.

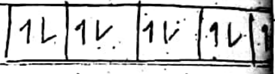
So, these compounds reflect white colour back and become white.

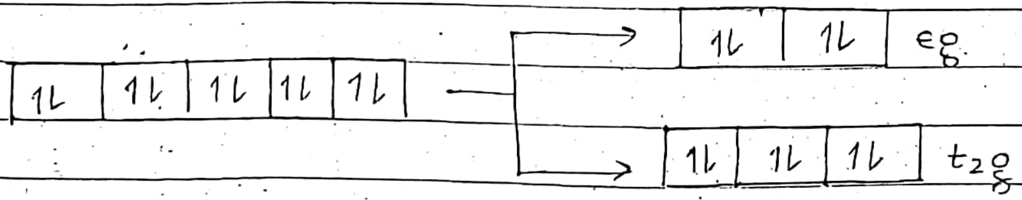


Q. Why $ZnSO_4$ is white in colour?

- Electronic configuration of Zn is $[Ar]\,4s^2\,3d^{10}$.

Electronic configuration of Zn^{++} (in $ZnSO_4$) is $4s^0 3d^{10}$.





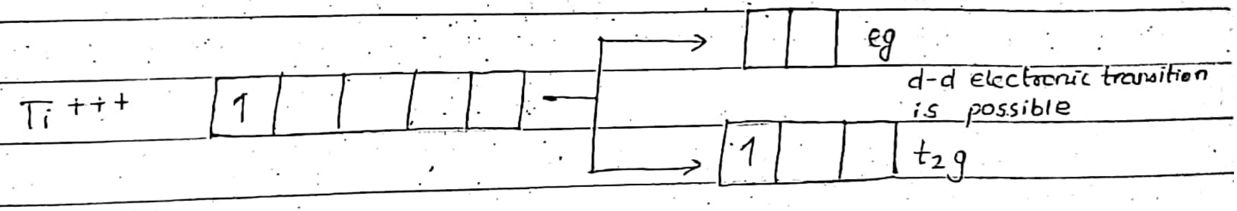
The electronic configuration of Zn^{++} in $ZnSO_4$ is $3d^{10}$ which is fullfilled electronic configuration. Due to this, there is no d-d electronic transition. As a result, $ZnSO_4$ reflects white colour and That's why, $ZnSO_4$ is white in colour.

Q. Why Zn is not considered as pure d-block element?

A. same answer as above

Q. $TiCl_3$ (Titanium chloride) is coloured whereas TiO_2 is colourless. Why?

- The electronic configuration of Ti is $4s^2 3d^2$ (22). In $TiCl_3$, electronic configuration of Ti^{+++} is $4s^0 3d^1$. Due to being incomplete d-orbital, there may occur d-d electronic transition. So, $TiCl_3$ is coloured whereas In TiO_2, electronic configuration of Ti^{++++} is $4s^0 3d^0$ (i.e. empty d-orbital). So, d-d electronic transition is not possible. That's why, TiO_2 is colourless.



magnetic property, they are classified into para, dia and ferro magnetic.

Para magnetic : those substances which are attracted by magnetic field are called para magnetic substances an phenomenon is called paramagnetism.

Dia magnetic : those substances which are repelled by magnetic field are called dia magnetic substances and phenomenon is called dia magnetism.

Ferro magnetic : those substances which are strongly attracted by magnetic field are called ferro magnetic substances and phenomenon is called ferromagnetism.

⇒ The paramagnetism is the property due to presence of unpaired electrons. Thus, most of the transition elements are paramagnetic. As the no. of unpaired electro increases, the paramagnetic property also increases.

Similarly, increase in no. of paired electrons increase the diamagnetic property.

The magnetic behaviour of element can be explained in terms of magnetic moment, which is calculated by using following formula:

magnetic moment $\boxed{\mu = \boxed{\sqrt{n(n+2)}}}$ Bm ↓ Bohr magneton

where, n = no. of unpaired electrons

⇒ Among 3-d elements, Mn^{+2} ion has maximum paramagnetic property because it has maximum unpaired electrons. The magnetic momentum of Mn is

3d5 | 1 | 1 | 1 | 1 | 1 |

no. of unpaired e^- = 5.

$\therefore \mu = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35} = 5.9160$ Bm

Q. If magnetic momentum is 3.9, what will be the no. of unpaired electrons?

Soln.

$\mu = 3.9$

We know,

magnetic momentum $\mu = \sqrt{n(n+2)}$

or, $3.9^2 = n^2 + 2n$

or, $n^2 + 2n = 15.21$

or, $n^2 + 2n - 15.21 = 0$

$\therefore n = 3.026, -5.026$

Hence, no. of unpaired electrons = 3

If $\mu = 0$, the element is diamagnetic. So,

paramagnetism $\propto \mu$

↑ in magnetic moment ↑ paramagnetism.

Q.1 Write the properties of s-block and p-block elements. (4+4)

2. Differentiate between electronegativity & electron affinity. (

3. What is ionization potential ? Write its variation in periodic table. Mention the factors affecting it. (8)

Factors affecting ionization potential

1- Atomic size
2. Electronic configuration
3. Screening / shielding effect
4. Nature of subshell

Q.4. What is electron affinity ? Explain the factors affecting it

5. Write short notes on : i) Electronic configuration and oxidation state of transition ele
ii) Co-ordination compounds formed by transition elements
iii) Colouring " " " "
iv) Magnetic behaviour of transition elements
v) Atomic radii of " "

6. Zn is not considered as transition element. Why ?

7. $SnCl_2$ is coloured compound But $SnCl_3$ is white. Why ?

8. Write short notes on:

Corrosion

In general, certain metals are slowly detoriated upon long exposure to moist atmosphere. For e.g. green coating on copper surface, dullness on lead surface, etc. All these phenomena are the result of formation of hydrated oxides of metal on surface. Hence, corrosion may be defined as the slow process of conversion of metal into their hydrated oxides by the action of ~~gases~~ and moisture present in the atmospheric air. The rate of corrosion of metals depends on following factors:

i) Nature of metal
ii) Presence of impurities, gases & moisture present in ~~iii)~~ atmosphere
iii) Presence of catalyst

Types of corrosion

Depending upon the mechanism of corrosion, there are 2 types of corrosion:

1. Dry corrosion
2. Wet corrosion

1. Dry corrosion

In this type of corrosion, the corroding agents are usually oxygen of air and acidic gases like HCl, SO_2, CO_2, etc. where direction reaction between corroding agents with metal surface takes place. The dry corrosion is further catagorized into 2 types:

a) Oxidation corrosion
b) Corrosion by other gases

Oxidation corrosion

In this corrasion, the direct oxidation of metal takes place by atmospheric oxygen in absence of moisture.

$$\underset{metal}{M} + \underset{oxygen}{O_2} \longrightarrow \underset{metal\ oxide}{M^{n+} + O^{n-}}$$

At ordinary temp, metals are slighlly attracted by oxygen. But alkali and alkaline earth metals are easily attacked by oxygen even at low temperature.

Corrosion by other gases

The corrosion by other gases occurs by direct oxidation of metal by acidic gases like HCl, SO_2, H_2S, Cl_2 etc. The magnitude of corrosion depends upon the affinity of metals with the gas. For e.g. AgCl, FeS, $SnCl_4$

2. Wet corrosion

This type of metal corrosion occurs in aqueous environme In this corrosion, anodic & cathodic area are created in the metal. Flow of current takes place in presence of aqueous environment along with some gases. Most common example of this type of corrosion is the formation of non-sticky brown coating over the surface of iron called rust having molecular formula $Fe_2O_3 \cdot xH_2$

Prevention of corrosion.

Corrosion can be prevented by the following ways.

1) Galvanization

It is the process of coating outer surface of active metal by less active metal which has low affinity towards corrosion. Generally, iron surface can be prevented by this process.

2) Oiling and greasing

To prevent metal surface from corrosion, they can be greased and oiled.

3) Enamel coating / Painting

To prevent from corrosion, metal surface can be coated by enamel.

4) Selection of material

To prevent from corrosion, metals used in construction can be selected in such a way which are far from corrosion and less reactive towards atmospheric gases.

Industrial Chemistry (7 marks)

- paint,
- lubricant,
- explosive

Explosives

An explosive is a substance or mixture that when ignited undergoes a rapid, violent chemical reaction that produce large amount of gas, heat, light, soun and high pressure. Such explosives have exothermic reactions. These reactions are difficult to control. They are used in different construction as well as destructi purpose. It may be used to propell projectiles.

Uses of explosives

1. Explosives are used for constructive rather than destructive purpose. They ~~are~~

2. They are used for blasting ore of metals, breaking down ~~p~~ coal.

3. They are also used for blasting rock or mountain for construction of tunnel, excavating earth surface for damp, etc.

Types of explosives

Explosives are classified into 3 types:

1) Primary explosive
2) Low explosive
3) High explosive

1. Primary explosive

It is also called initiating explosive or detonator. These are very sensitive which explode on receiving slight shock / fire. These are mainly used in small quantity to start or initiate the explosion of main explosive, which are comparatively less sensitive.

Some examples of primary explosive are:

Lead azide PbN_6

Tetracene $C_2H_7N_7O$

Diazodinitrophenol (DDNP), etc.

2. Low explosive.

These explosives are less sensitive than primary explosive. They donot explode suddenly. The chemical reaction taking place in such explosives are comparatively slow and time consuming. Mainly, these explosives are used to project projectiles like rocket, missiles.

e.g. Gun powder

Mixture of KNO_3, charcoal & sulphur

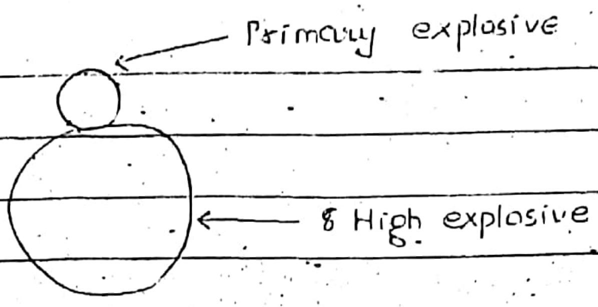
75% 15% 10%

3. High explosive

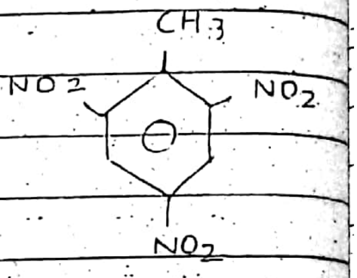
These explosives have higher energy than other explosives. However, they are quite stable and less sensitive to fire and mechanical shock. They need small amount of primary explosive.

e.g. Trinitrotoluene (TNT)

Trinitroglyceride (TNG), etc

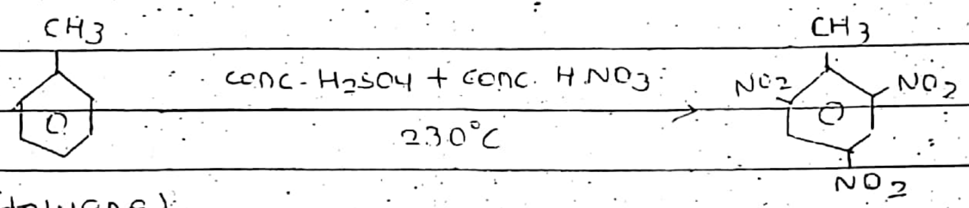


TNT



TNT.

It stands for Trinitrotoluene.
It can be prepared by nitration of toluene with conc. HNO_3 and conc. H_2SO_4 at 230°C.



(toluene)

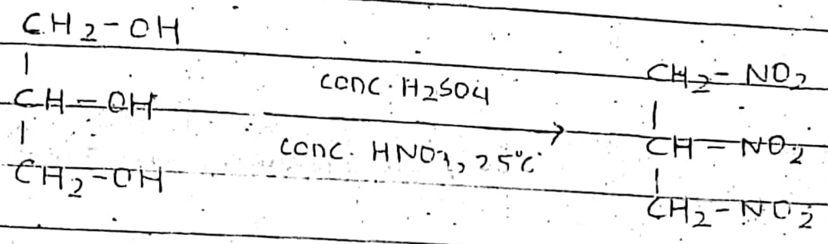
(TNT)

Uses of TNT

1) It is widely used in under water explosive and military purpose.
2) It is easy for loading in container because of its low melting point, less reactive & less sensitive.

3) It is safe in manufacture, transportation & storage.
4) It is non-hygroscopic as well as doesn't react with metal to form unstable compound.

TNG (Trinitroglyceride)



$$\begin{matrix} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{matrix} \xrightarrow[\text{conc. } HNO_3,\ 25^\circ C]{\text{conc. } H_2SO_4} \begin{matrix} CH_2-NO_2 \\ | \\ CH-NO_2 \\ | \\ CH_2-NO_2 \end{matrix}$$

(glycerol) (TNG)

TNG can be prepared by heating glycerol with mixture of conc. H_2SO_4 and conc. HNO_3 ~~at 25°C~~ (60% and 40% respectively) at 25°C.

Properties

1. TNG is pale yellow in colour.
2. It is oily liquid.
3. It can be exploded on receiving small amount of fire.
4. It is used to prepare dynamite. Dynamite is prepared by mixing TNG with inert absorbent such as wood, dust, starch, etc. The strength of dynamite depends on ratio of TNG / GNT (Glycerine trinitride) and inert absorbent.

Lubricants

The substance applied between 2 moving or sliding surfaces to reduce frictional resistance between them is known as lubricant. The main purpose of lubricant is to keep sliding surface apart so that frictional resistance can be minimized. And the process of reducing frictional resistance between moving surfaces by applying lubricant is k/a lubrication.

Functions of lubricants.

1. The main function of lubricant is to reduce friction.
2. It reduces the surface deformation.
3. It acts as coolant to carry out functions of machine
   It reduces the loss of energy in the form of heat
4. It reduces expansion of metal by frictional heat.
5. It reduces the maintenance and running cost of machine.

Classification of lubricants

Lubricants are classified into 3 types:

1. Liquid 2. Semi-solid 3. Solid lubricants

1. Liquid lubricants

A fluid applied between two sliding surface to reduce the friction between them is known as liquid lubricants. It is also called lubricating oil

The functions of liquid lubricants are as follows:

a) It acts as coolant.
b) It reduces the frictional force between 2 sliding surfaces.
c) It prevents corrosion.
d) It acts as sealing agent.

The characteristics of lubricating oil are as follows:

a) Most of the lubricating oil posses high viscosity, high oxidation resistance, low freezing point and low pressure.

b) They have heat stability, non-corrosive property.

Types of liquid lubricants

There are 3 types of liquid lubricants.

1) Vegetable oil

2) Petroleum oil

3) Blended oil

Vegetable oil

Vegetable oils were used before the invention of petroleum industry. These oils possess good oiliness which forms gummy and sticky substance in contact with air and they have tendency to hydrolyze. So, they are used for lubricating purpose.

Petroleum oil

They are obtained by distillation of petroleum. They are hydrocarbon; the length of hydrocarbon varies from 12 to 50 carbon atoms. The shorter carbon chain possess low viscosity than the longer chain. These are used because of their low cost, availability in large amount, quite stable but they possess poor oilyness. The oilyness of petroleum oil will be increased by addition of additives.

Blended oil

The lubricating oil mixed with some additives to improve the properties of lubricants are called blended oil e.g. The oilyness of lubricating oil increases by adding vegetable oil. It is also mixed with organic substances containing chlorine, sulphur, phosphorus to prevent the welding together of the sliding surface. It is mixed with polystyrene to increase the viscosity of oil. For example, Phenol and amino compounds are added to reduce oxidizing property of lubricants.

2. Semi-solid lubricants

These lubricants can be obtained by addition of thickening agents to lubricating oils. They are also called grease. Grease can be prepared by saponification of fat with alkali. The consistency of greeze is governed by the total amount of mineral oil present in it.

Q. Mention the conditions to use grease.

1. Grease can be used in that situation where oil cannot remain in place due to high load, low pressure, sudden jerk, etc.

2. Grease can be used at high temperature.

3. In place where seal is necessary against the

entry of dust, air, moisture, etc.
~~e.g.~~

4. e.g. In paper industry, textile as well as edible articles, lubricating oil is not used, so, grease is used.

3. Solid lubricants

These lubricants reduce the friction by separating 2 moving or sliding surfaces. They are used either in dry powder or mixed with oil or water e.g. Graphite powder or Molybdenum powder. Graphite is very soapy to touch, non-imflamable and donot oxidize up-to 375°C. Graphite is used in powder form as suspension of graphite in oil, which is used in internal combustion engine as well as food industry.

Paints

Paint is a viscous suspension of finely divided solid pigments in a fluid medium, which on drying yields an impermeable film of powder. When paints are applied on surface, they act as inert barrier and also give beautiful appearance. Some requirements/requisit of paints are as follows:

1) It should have high hiding power.
2) The film/layer of paint should not crack on drying.
3) It should form a good, impermeable and uniform

layer on the surface for the effective protection from corrosion.

4) It should be weather resistance.
5) It should be consistent for required purpose.

Some important constituents of paints are as follows:

1) Pigment
2) Medium
3) Thinner
4) Drier
5) Extender
6) Plasticizer

1. Pigment

The important property of pigment in a paint are colour lying power. For e.g. natural pigment and synthetic pigment. Natural pigments are chalk, mica, iron oxide, etc. Synthetic pigments are barium sulphate, Zinc oxide, Lead oxide, etc.

2. Medium

It is the medium of the paint. The main function of medium is to hold pigment on the surface of wall. For e.g. oil (soyabean oil, fish oil, petroleum oil, etc.)

3. Thinner

Thinner are added to paint for increasing viscosity when applied to wall surface. They are volatile substance which evaporates easily after application of paint. for e.g. turpentine oil, spirit, acetone, kerosene, ethyl alcohol, etc.

4. Drier

The substance which is added to paint for drying purpose are known as drier. Generally, napthanol is used as drier.

5. Extender

These are the materials which improve the properties of paint are ex-tender. For e.g. silica, $CaCO_3$, etc.

6. Plasticizer

They are sometimes used in paint to give elasticity to the layer and to prevent from cracking. For e.g. Triphenyl phosphate, tributyl phosphate, etc.

Types of paint

There are different types of paint. They are:

1. Varnish
2. Enamel
3. Emulsion paint
4. Special paint
5. Fire retardant paint
6. Anti fouling paint
7. Distempers

1. Varnish

It is the homogeneous dispersion solution of natural or synthetic resin. It is used as protective and decorative coating for surface.

produce lustre, hard and glossy appearance.

3. Emulsion paint

These are dispersion of synthetic resin in water. It contains pigment, medium, extender, preservative and anti foaming agent. The advantage of emulsion paint is that it is washable, it is easily drying and easily diluted with water.

4. Special paint

They are various in nature like heat resistant paint which contains metallic powder (e.g. Al, Zn, Sn, Graphite) which can withstand temperature upto red heat and is used in oven, aircraft, smoke stuck etc.

5. Fire retardant paint

It contains blinders which breakdown at elevated temperature producing non-imflammable gas like CO_2, NH_3, HCl (gas), etc. These paints contain PVC, chlorinated rubber, etc.

6. Anti-fouling paint

They are used in under water construction which contains anti-fouling agents like mercuric oxide, cupric oxide, pentachlorophenol. It is used in ship, boat, etc.

7. Distempers

They are special water paint containing chalk powd glue, colouring pigments and water as a solvent.

Besides these paints, there are also different types of paints such as cellulose paint, cement paint, aluminium paint, etc.

Polymers

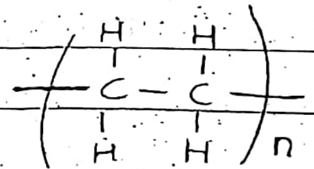
poly → many
mer → molecules /units.

Those macromolecules which are formed by small simple molecules are known as polymers. These small simple molecules are called monomers. The combination of simple molecules repeatedly two or more times in the same regular manner to form polymer is known as polymerization.

$$nM \xrightarrow{\text{polymerization}} \left(m-m-m-m\right)_n$$

monomer polymer

$$CH_2=CH_2 \xrightarrow{\text{''}}$$



$$\left(-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\right)_n$$

ethene
(monomer)

polyethene
(polymer)

Classification of polymer

There are different basis to classify polymer which are as follows:

A. On the basis of source of polymer, there are 2 types of polymer: 1) Natural polymer
2) Synthetic polymer

1. Natural polymer

The polymers which are obtained from nature i.e. plant and animal are called natural polymers.
e.g. starch, cellulose, rubber, paper, protein, etc.

2. Synthetic polymer

The polymers which are prepared by human beings are called synthetic polymers. e.g. Polyethene, Bakelite, PVC, Nylon, etc.

B. On the basis of monomer unit, there are 2 types of polymer : 1) Homo polymer
2) Hetero polymer / Co-polymer

1. Homo polymer

The polymer which ~~a~~ is formed by the combination of one type of monomer is called homo polymer. e.g. ethene, polyethene, PVC, etc.

2. Co-polymer

The polymer which is formed by the combination of 2 or more different types of monomer is called co-polymer. e.g. Bakelite (Formaldehyde + Phenol)
Nylon 6,6 (Adipic acid + Hexamethylene diamine)

C. On the basis of combination of atoms, there are 2 types of polymer : 1) Inorganic polymer
2) Organic polymer

1. Inorganic polymer

Those polymers which are formed by the combination of atoms other than carbon atoms are called inorganic polymers e.g. Silicon, Polyphosphazine, Polysulphur-nitride, etc.

2. Organic polymer

Those polymers which are formed by combination of carbon atoms are called organic polymers : e.g. PVC, Bakelite, etc.

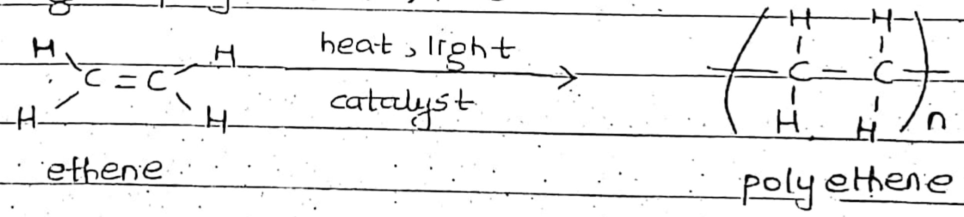
Types of organic polymer

There are 3 types of organic polymer. They are:

1) Additional polymer
2) Condensation polymer
3) Plastic polymer

1. Additional polymer

Those polymers which are formed by addition of monomers are k/a additional polymers. They are also called chain polymers and the phenomenon is k/a additional polymerization. Additional polymerization occurs due to application of heat, light, catalyst for breaking down of covalent bond of monomer. e.g. polyethene, PVC



$$H_2C=CH_2 \xrightarrow[\text{catalyst}]{\text{heat, light}} \left(-CH_2-CH_2- \right)_n$$

2. Condensation polymer

The polymers which are formed after condensation of monomers are k/a condensation polymers. And the phenomenon is called condensation polymerization. In this polymerization, the basic monomer combines through condensation reaction by elimination of simple molecule as a product. These eliminated molecules may be are like H_2O, NH_3, HCl, etc.

$$\underset{\text{aminoacid}}{NH_2-CH_2-COOH} + \underset{\text{aminoacid}}{NH_2-CH_2-COOH} \xrightarrow{-H_2O} NH_2-CH_2-CO-NH-CH_2COOH$$

polyaminoacid
(condensation polymer)

3- Plastic polymer

Those polymers which have high molecular weight and can be moulded into any desired form when subjected to heat and pressure in the presence of catalyst are known as plastic polymers. On the basis of moulding and non-remoulding, there are categorized into 2 types:

1) Thermoplastic polymer
2) Thermosetting polymer

1- Thermoplastic polymer

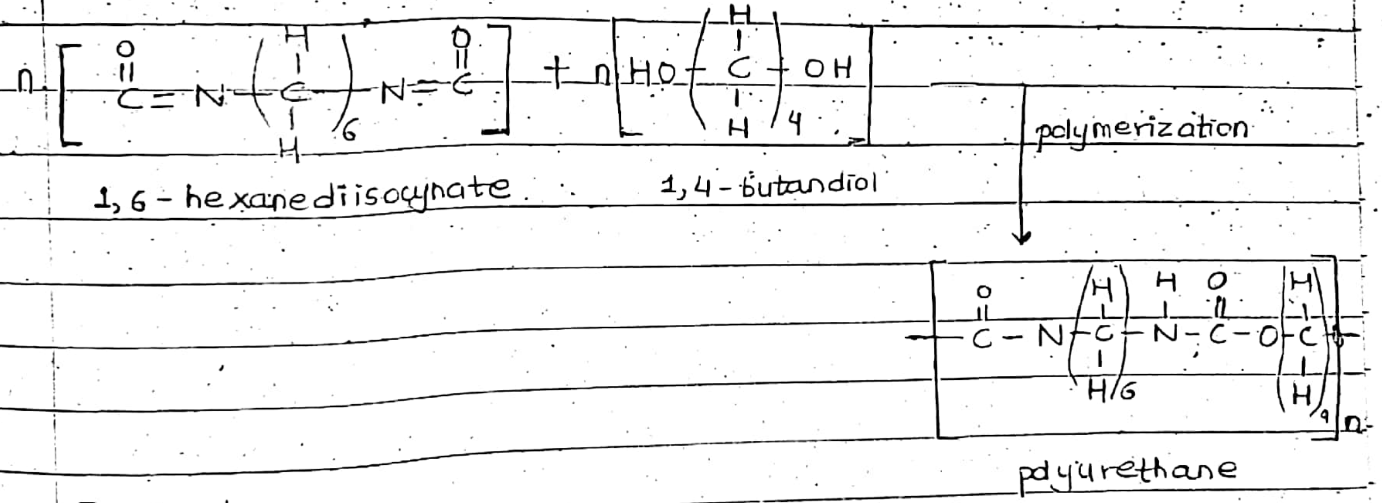
	Thermoplastic polymer	Thermosetting polymer
1.	These polymers are produced by addition polymerization.	These polymers are produced by condensation polymerization.
2.	They have linear molecular structure.	They have 3-dimensional molecular structure.
3.	They are easily soften on heating. ~~be~~ So, they can be re-moulded.	They donot soften on heating. But, they get hard on heating.
4.	Generally, they are soft, weak and less brittle.	Generally, they are hard, strong and more brittle.
5.	They are soluble in organic solvent.	They are insoluble in organic solvent.
6.	e.g. Polyethene PVC (hard thermoplastic polymer)	e.g. Bakelite

Some Important Polymers

1. PVC (Polyvinylchloride)
2. Teflon
3. Bakelite
4. Nylon
5. Polyster / Polystyrene
6. Polyurethane
7. Silicon
8. Rubber

Polyurethane

Preparation: It can be prepared by reacting diisocynate and diol. For e.g. 1,4-butanediol is treated with 1,6-hexanediisocynate. Then, polyurethane is produced.



Properties

1) Polyurethane is resistant to ozone, oxygen & water.
2) It is stable upto -40°F temperature (-40°C)

Uses

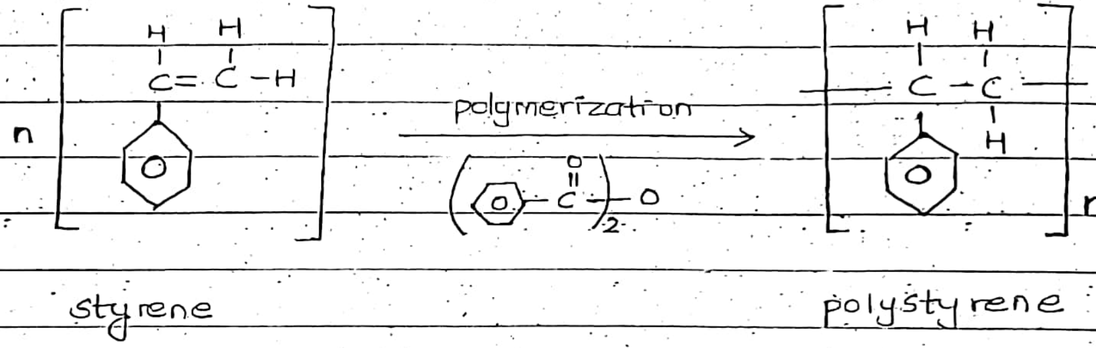
The uses of polyurethane are:

1) They are used as layer coating.
2) They are used in garment industry
3) They are used as synthetic leather
4) They are used to produce or manufacture different

types of utensils.

Polystyrene.

Preparation: It is prepared by free radical polymerization of styrene in presence of benzoyl peroxide.



Properties

1) It is hard, brittle and have density 1.05 gm/cc.
2) It is highly flammable and burns with orange yellow flame.
3) on oxidation, it produces CO_2 and H_2O
4) Its melting point is 240°C.
5) It is chemically inactive due to being single bond from double bond.

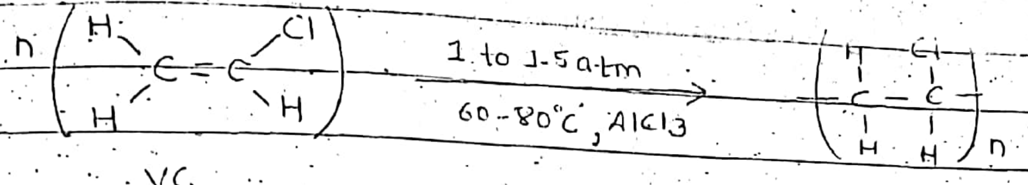
Uses

1) It is used to form container for food material.
2) It is used for making hot drink cups, different types of toys, combs household articles, etc.
3) It is used to manufacture tiles for floor.

Imp

PVC (Polyvinyl chloride)

Preparation: It can be prepared by heating vinyl chloride in presence of peroxide at 60-80°C between 1 to 1.5 atm pressure. It is hard thermoplastic polymer.



VC

PVC.

Properties

1. It is linear type of polymer.
2. It is hard and rigid but it can be made soft by adding phosphate ester.
3. It has low permeability of gases.
4. It is not recommended to use at temperature above 70°C. (bcoz it may crack & get destroyed above 70°C)

Uses

1. It is used as unplasticized PVC and plasticized PVC.

As unplasticized PVC:

Unplasticized PVC are used for manufacturing tank, helmet, refrigerate components. They are used for manufacturing tyres of cycles, motorcycles, etc.

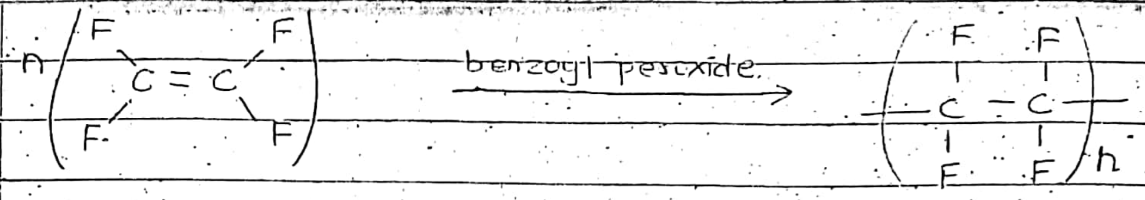
As Plasticized PVC:

Plasticized PVC are used for manufacturing raincoat, hard bags, curtain, clothes, toys, table cloths, belts, etc. They are also used to prepare insulating materials for wires & other electrical goods.

artificial flooring.

Teflon (PTFE)

Also called polytetra fluorcethylene. It is obtained by polymerization of tetrafluoroethylene under pressure in presence of organic peroxide as catalyst.



(Tetrafluoroethylene)   Teflon

Properties

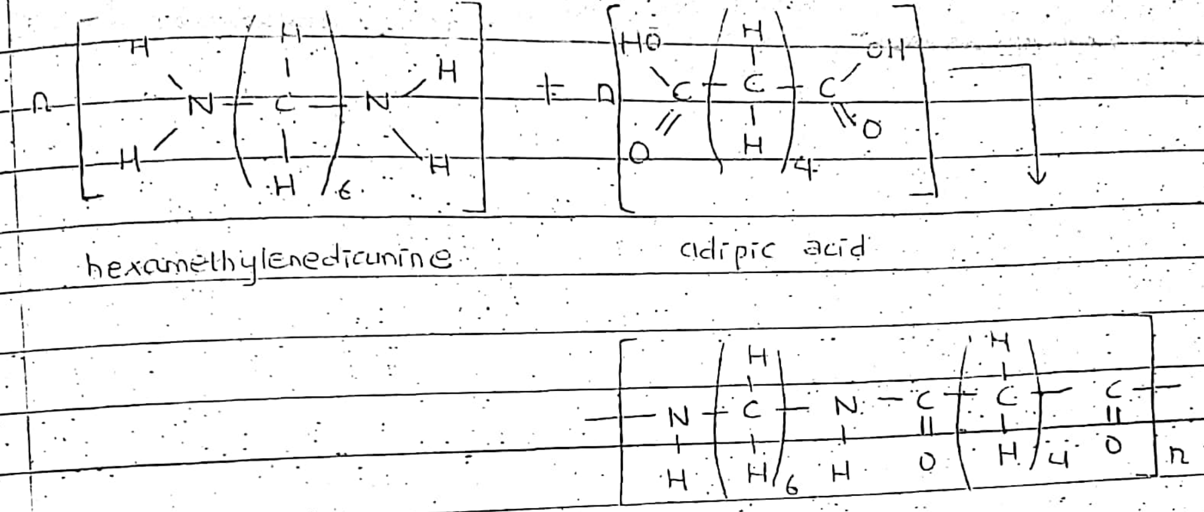
1. It is very hard having high resistance towards heat.
2. It is resistant towards chemical action of acid and base.
3. It is bad conductor of electricity.
4. It is insoluble in all solvents.
5. It is incombustible & used upto 300°C.
6. It is used in manufacturing insulating material for motor, transformer, cable wire, etc.

Uses

1. It is used in manufacturing insulating material for motor, transformer, cable wire, etc.
2. It is also used for making gaskets.
3. It is used in transformation of chemicals.
4. It is used for coating aesbestos.
5. It is used for making stoppers in burette.

Nylon 6,6

It is synthetic polymer having amide group. It is prepared by condensation polymerization of adipic acid with hexamethylene diamine.



hexamethylenediamine

adipic acid

6,6 - nylon

Properties

1. They have high melting point.
2. They are white in colour.
3. They are translucent.
4. They are insoluble in organic solvent but soluble in phenol & formic acid.

Uses

1. They are used to prepare brush.
2. They are used in making textiles.
3. They are used in making ropes.

Concept of Biodegradable, non-degradable and conducting polymer

Biodegradable polymer

Those polymers which are decomposed in natural, aerobic and anaerobic environment are called bi degradable polymers. Bio-degradation of polymer can be achieved by ability of micro-organism in the environment to metabolize the molecular structure. The use of bio-degradable polymer is that they are used in biotic environment. Some examples of biodegradable polymer is polylactic acid, polybutylene succinate, polyanhydride, polyvinyl alcohol, starch derivative, cellulose, etc.

Application of biodegradable polymer.

1. They are used in agricultural field for making fertilizer.
2. They are used in biomedical field.
3. They are used in waste management.

Generally, biodegradable polymers are organic materia which can be broken down by few living organisms.

Non-degradable polymer

Those polymers which don't undergo degradation / decomposition due to exposure to oxygen, ozone, moisture, heat, radiation, micro organism are known as non-degradable polymers. For example: Epoxy resin, polyurethane, etc. They are not decomposed by micro-organisms or other biological factor. Most of the synthetic polymers are non-degradable polymers. Xylon, nylon, polyester, etc are synthetic as well as non-degradable polymers.

Conducting polymer

In most of the polymers due to lack of free electrons, they are poor conductor of electricity. But within the past few years, polymers have been synthesized which posses electrical conductivity. They are called conducting polymers.

Conducting polymers are categorized into 4 types:

1) ICP (Intrinsically conducting Polymer)
2) DCP (Doped " ")
3) ECP (Extrinsically " ")
4) CCP (Coordination " ")

1. ICP (Intrinsically Conducting Polymer)
ICP consists of delocalized electron pair or residual charge due to which they conduct electricity. For e.g. Polyanilaine, Polypyrrole, Polythiophene, etc.

2. DCP (Doped Conducting Polymer)
DCP are obtained by exposing a polymer to a charge transfer agent in gas phase or in solution phase. For e.g. P-dopant, N-dopant

3- ECP

ECP conducts electricity due to presence of externally added ingradients ~~[illegible]~~ in them. Some external gradients are carbon powder, metallic fiber, etc.

4- CCP.

CCP are produced by combination of metal atom with polydenate ligand (ligand which donates more than 2 electrons) for e.g. Calcium & Magnesium complex.

Engineering application of conducting polymer

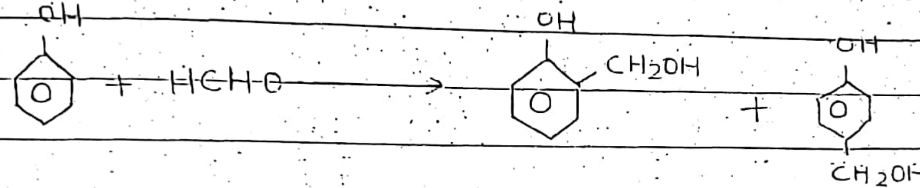
They are light in weight, easy to process, have good mechanical property. So, they are used in rechargable battery, in optical display device, in aircraft, in telecommunication systems, in solar cell, in transistor, diode, photovoltaic device, etc.

Imp Bakellite

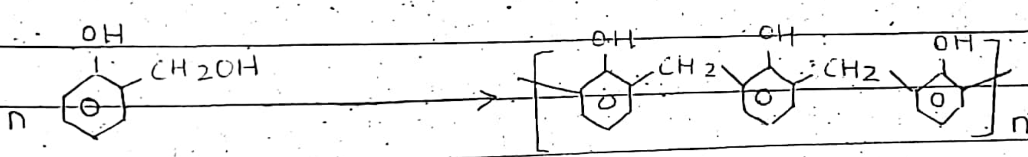
It is prepared by condensation polymerization of phenol with formaldehyde in presence of acid or alkali.

phenol + formaldehyde ⟶ Bakellite

Initially, ortho and para hydroxy methyl phenol is produced which react to form bakellite.



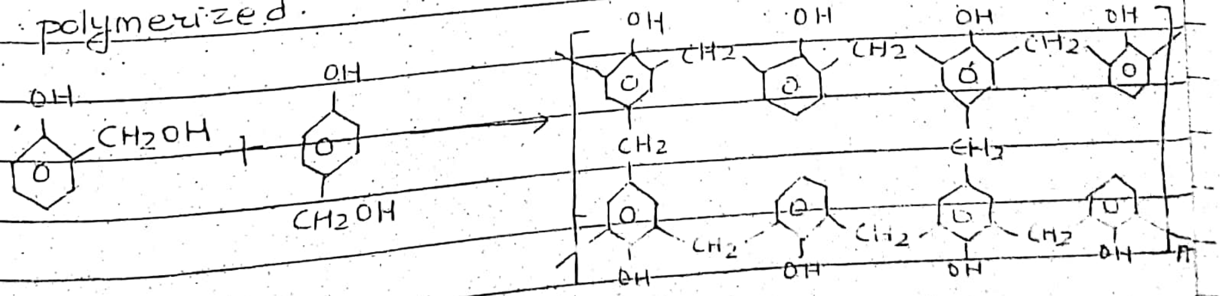
o-hydroxymethyl phenol p-hydroxy methyl phenol



o-hydroxymethyl phenol

linear polymer (Bakellite)

When same type of hydroxymethyl phenol reacts, linear polymer is produced, whereas, crosslinked polymer is formed when different type of hydroxy methyl phenol are polymerized.



Cross-linked polymer (Bakellite)

Properties

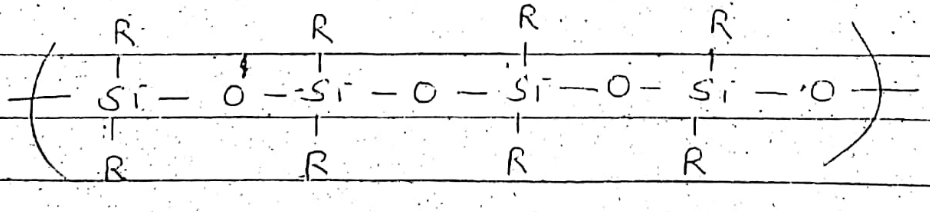
1. It is thermosetting polymer.
2. It is too rigid, very hard.
3. It has high resistance towards heat, water.
4. It ~~h~~ is insoluble solid.
5. It is unreactive towards many chemical reactions like acid-base.
6. It has highly insulating property.

Uses

1. They are used in manufacturing electric insulators like switch, plug, heater handle, etc.
2. They are used to make body parts of telephone, TV, radio, etc.
3. They are used in paints & variable varnish.
4. They are used to make parts of airplanecraft.
5. They are used to make handle of utensils which are used for heating purpose.

Silicon

It is inorganic polymer which contains alternate silicon, oxygen linkage. Organic radicals are attache with silicon atom.



$$\left(-\overset{R}{\underset{R}{|}}\!\!Si - O - \overset{R}{\underset{R}{|}}\!\!Si - O - \overset{R}{\underset{R}{|}}\!\!Si - O - \overset{R}{\underset{R}{|}}\!\!Si - O - \right)$$

Silicon

Preparation: Silicon polymer is prepared by reacting alkyl hallide or by reacting silicon halide with Grignard's reagent.

$Si + CH_3Cl \longrightarrow CH_3SiCl_3 + (CH_3)_2SiCl_2$

$SiCl_4 + CH_3MgCl \longrightarrow (CH_3)_3SiCl + (CH_3)_4SiCl + MgCl_2$

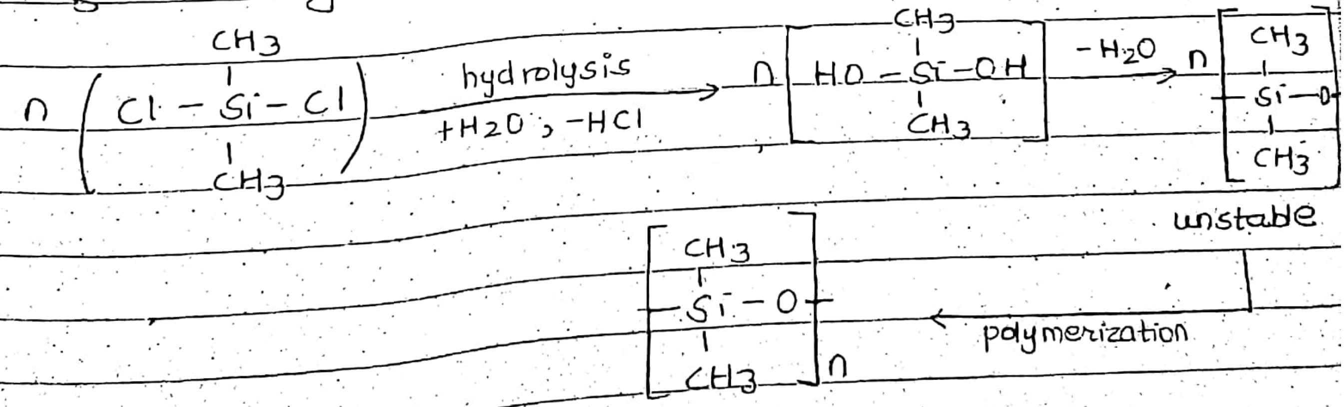
These polymers can be separated by fractional distillation

Types of Silicon polymer

1. Dimethyl silicon polymer dichloride
2. Trimethyl silicon chloride
3. Monomethyl silicon trichloride

1. Dimethyl silicon dichloride

It is bifunctional unit particle. After polymerization, it gives very long chain of polymer.



$$n\left(Cl-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-Cl\right) \xrightarrow[+H_2O,\ -HCl]{\text{hydrolysis}} n\left[HO-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-OH\right] \xrightarrow{-H_2O} n\left[-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-O-\right]$$

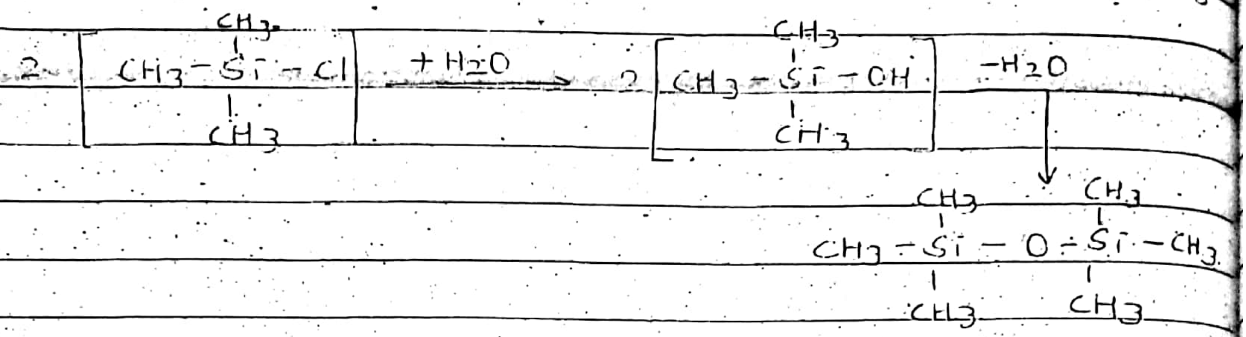
unstable

$$\xrightarrow{\text{polymerization}} \left[-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-O-\right]_n$$

Dimethyl silicondichloride polymer is also called silicon Rubber.

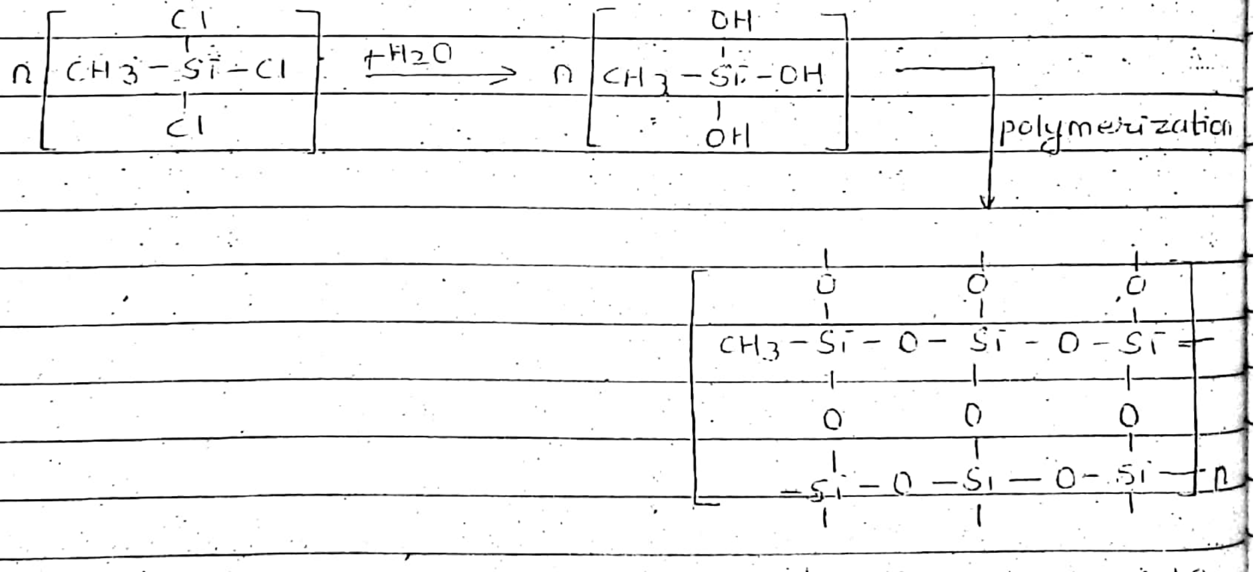
2. Trimethyl silicon chloride

It is a monofunctional silicon polymer. Hence, it is known as chain stopper. It has limited chain length.



3. Monomethyl silicon trichloride

It is trifunctional and give crosslinked polymer.



monomethyl silicon trichloride
(crosslinked)

Uses of different types of Silicon polymer

1. Silicon oil / Liquid silicon polymer

Generally they are dimethyl silicon polymer having low molecular weight. The silicon which possess low surface tension, very small change in viscosity, etc.

- They are used as high temperature lubricants as they are highly stable & non-volatile.
- They are used as cosmetic polisher.
- They are used as heat transfer.
- They are used in high vaccum pump.

2. Silicon grease

They are made by adding carbon black, silica, wood flour, marble flour, china clay to silicon oil. They are modified form of silicon oil.

- They are used as lubricant in aeroplane.
- They do not freeze at low temperature (-40°C) and don't melt upto 200°C. So, silicon is used in cold as well as hot circumstances.

3. Solid silicon

They are highly crosslinked polymer obtained by condensing bifunctional silicon polymer or trifunctional silicon polymer.

- They are used for making high temp. insulating materials & high voltage ins materials.
- They are mixed with paints, pigment & enamel

to make them resistance to the effect of high temperature, sunlight & chemicals.

4. Silicon rubber
They are obtained by mining high molecular weight of dimethyl silicon polymer, silica, carbon black / metal, etc. which causes formation of cross-linked between methyl group of adjacent chain.

- They are used in ceiling joints of aircraft and insulating electrical part like transistor which can't be heated.

Properties of silicon

1. They have high range of thermal stability (100°C - 250°C
2. They are able to repel water.
3. They ~~are~~ have excellent resistance to oxygen, ozene, UV-rays, etc.
4. They have low chemical reactivity.
5. They have low ionicity.
6. They don't support micro-biological growth.

Environmental Chemistry (15 marks)

Environment

- Biotic (Animals, plants, Microbial organisms)
- Abiotic (non-living things)

- The process of degradation of quality of abiotic components of environment is k/a pollution. Due to pollution, unwanted materials or things are mixed up in air, water, soil, sound, etc. On the basis of nature, pollution can be categorized into different types:

1) Air pollution 2) Water pollution 3) Soil pollution

(Defn, Causes, Effects, Remedies)

ozone layer depletion	Alkalinity
global warming	Hardness of water
greenhouse effect	DO (Dissolved oxygen)
acid rain	COD (Chemical oxygen Demand)
	BOD (Biological " ")

1) Air pollution

The process of degradation of quality of air of atmosphere by unwanted addition of pollutant particle and gases is k/a air pollution. Some examples of pollutant particles are: C, S, Pb (lead), P, etc and some examples of gases are: SO_2, CO, oxides of Nitrogen, oxides of Phosphorus, etc

Causes.

Urbanization

Industrialization (unmanaged establishment of industries, factories and so on)

Deforestation (less forest, CO_2 consumption less & increased CO_2 & other gases leads to air pollution)

Use of pesticides, insecticides, etc.

Effects

causes acid rain

air borne diseases

cultural monuments fade up due to acid rain

effects on plants & animals

Remedies

wellmanaged urbanization

plantation

less utilization of pesticides, fertilizers, etc.

preserve biodiversity

Ozone layer depletion

In stratosphere of atmosphere, there is a layer of ozone which is protective layer for earth. It protects earth from UV-radiation coming from sun. Nowadays, due to increase in CFC (chlorofluorocarbon) in atmosphere ozone layer is depleting. somewhere, there is formation of hole which is called ozone layer depletion & ozone layer hole formation.

CH_2Cl_2 } CFC
CH_3Cl

very powerful reagent / OA

$CFCl_3 \longrightarrow CFCl_2 + Cl^{\bullet}$ (nascent chlorine)
↓
newly born chlorine

$CFCl_2 \longrightarrow CFCl + Cl^{\bullet}$

$O_3 + Cl^{\bullet} \longrightarrow ClO^{\bullet} + O_2$

$ClO^{\bullet} \longrightarrow Cl^{\bullet} + O^{\bullet}_2$

$O^{\bullet} + O_3 \longrightarrow O_2 + O_2$

Effect of ozone layer depletion

- sea level rise
- global warming is caused (0.05-0.06°C temp. rise in
  (day to day ↑ in temp of earth's surface) Nepal) per year)
- it causes rise in sea level (temp ↑, glaciers melt, sea level ↑)
  (1.8mm rise in sea level per year on earth)
- it causes glaciers melting.
- it causes green house effect
- it causes skin cancer & other problems
- it destroys plants & animals

Global warming
The increase in average temp. of earth surface due to different types of pollution is known as global warming.

CFC doesn't trap heat

Green house effect

The phenomena of trapping of heat coming from sun due to effect of green house gases like CH_4, CO_2, perfluorocarbon, SCl6 (sulphur hexachloride), nitrous oxide & nitric oxide is k/a green house effect.

Due to green house effect, temp. of earth surfaces get rise up which causes global warming.

Acid rain

When air becomes polluted, gases like SO_2, CO, CO_2, P_2O_5, nitrogen oxides ~~a~~ increase in atmosphere. During rainy season, when rain falls, water reacts with these gases to form acids which fall on earth surface in the form of rain. This phenomena is k/a acid rain. It is the change in pH of rain water.

$$CO + H_2O \longrightarrow H_2CO_3$$
$$SO_2 + H_2O \longrightarrow H_2SO_3$$
$$N_2O_5 + H_2O \longrightarrow HNO_3$$
$$P_2O_5 + H_2O \longrightarrow H_3PO_4$$

2) Water pollution

-/

Hardness of water

Those water which cannot produce lather when reacts with soap is k/a hard waiter and the phenomena is hardness of water. Water becomes hard due to presence of soluble salts of Ca and Mg. These soluble salts of Ca and Mg can form precipitate with soap. As a result, lather is not formed.

perm-anent hardness {
$CaCl_2$, $MgCl_2$
$CaSO_4$, $MgSO_4$
$Ca(NO_3)_2$, $Mg(NO_3)_2$
} Causes of hardness of water
$Ca(HCO_3)_2$, $Mg(HCO_3)_2$ } → temporary hardness

Types of hardness

i) Temporary hardness
- can be removed by boiling
- caused by $Ca(HCO_3)_2$ & $Mg(HCO_3)_2$ (bicarbonates of Ca & Mg)

ii) Permanent hardness
- cannot be removed by boiling
- can be removed by some chemical process
- caused by chlorides, sulphates & nitrates of Ca & Mg.

· Methods to remove hardness of water ·

1) By boiling.

Temporary hardness can be removed by boiling.

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + H_2O + CO_2$$

$$Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3 + H_2O + CO_2$$

2) By reacting with $Ca(OH)_2$

- To remove temporary hardness

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$

3) By reacting with washing soda (Na_2CO_3)

- To remove permanent hardness

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + NaCl$$

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$

4) By Permutit process

- This process is used to remove all types of hardness by reacting with sodium zeolite (Na_2Z).

$$CaCl_2 + Na_2Z \longrightarrow CaZ + 2NaCl$$

Imp

Dissolve oxygen (DO)

The amount of oxygen available in nature water in dissolved form is k/a dissolve oxygen. It is important parameter to measure water pollution.

- In water pollution, to decompose organic materials, dissolve oxygen is used. Due to this, D.O decreases in water and plants & organisms can't survive well bcoz of lack of DO.

- According to WHO recommendation for drinking water, DO should be more than 1 ppm.

COD (Chemical Oxygen Demand)
BOD (Biological Oxygen Demand)

- COD (oxygen required to decompose all waste materials i.e. dead plants & animals)

- BOD (oxygen required to survive all aquatic plants & animals)

COD
BOD
DO
Hardness
Alkalinity
+
Note

} lab manual

Organic Chemistry (15 marks)

Reaction mechanism

i) Nucleophilic substitution reaction (SN^1 and SN^2)

ii) Elimination reaction (E_1 and E_2)

Nucleophile : -ve species or electron rich species (nucleus loving) e.g. Br^-, OH^-, CN^-, $\ddot{N}H_3$, $R\ddot{N}H_2$
+ve

i) Nucleophilic substitution reaction

Such type of reaction in which weak nucleophile or atom get substituted by strong nucleophile is known as nucleophilic substitution reaction.

For example: Hydrolysis of alkyl hallide in aqueous medi

$$RX + aq.\ \overset{KOH/}{NaOH} \longrightarrow ROH + NaX$$

$$CH_3Cl + aq.\ NaOH \longrightarrow CH_3OH + NaCl$$

$$\underset{\text{substrate}}{CH_3CH_2Br} + \underset{\text{nucleophile}}{aq.\ NaOH} \longrightarrow CH_3CH_2OH + NaBr$$

On the basis of reaction mechanism, nucleophilic substitu reaction can be categorized into 2 types:

a) SN^2 reaction

b) SN^1 reaction

a) SN^2 reaction mechanism

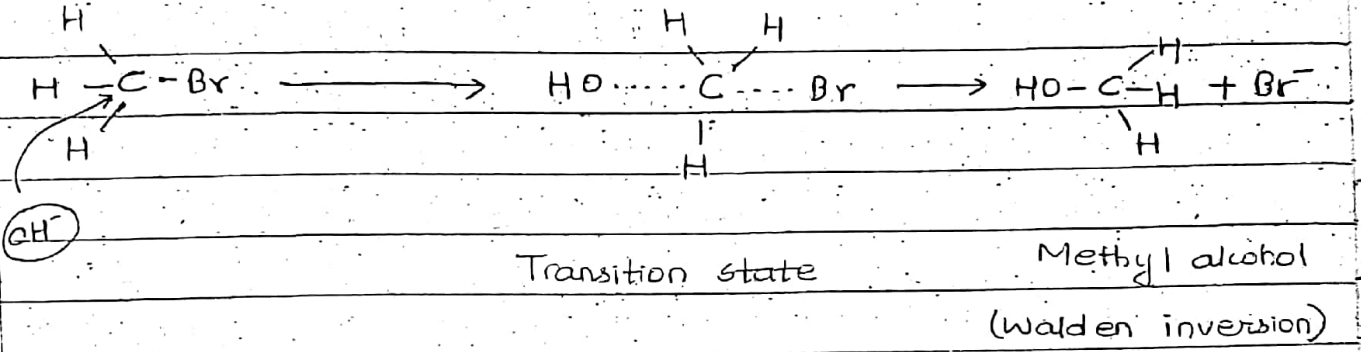
Such type of nucleophilic substitution reaction in which rate of reaction depends on concentration of both ~~reactan~~ substrate and nucleophile is k/a SN^2 reaction mechanism. It is also called bimolecular nucleophilic substitution reaction mechanism.

Generally, primary alkyl hallide (1° alkyl hallide) shows SN^2 reaction mechanism.

e.g. Hydrolysis of methyl bromide in aq. medium

$$\underset{\text{methyl bromide}}{CH_3Br} + NaOH\,(aq.) \longrightarrow CH_3OH + NaBr$$

Mechanism



First of all, nucleophile (OH^-) attack substrate carbon from opposite to that of Br-atom because Br-atom and OH^- both are electronegative. Naturally, they repel each other as much as possible. So, it is called back side attack. As a result, a transition state is formed as shown in figure. In this transition state, C-Br bond is starting to break whereas C-OH bond is starting to form. In this state, three C-H bonds are lie in a plane whereas C-OH and C-Br bonds are perpendicular to that plane.

Energy required to ~~cleave~~ detach C-Br bond is supplied from the energy released during formation of C-OH bond.

Finally, primary alcohol is produced having opposite configuration than that of alkyl hallide. It is called Walden inversion.

Q. Describe reaction mechanism of hydrolysis of methyl bromide / ethyl iodide / 1° alkyl hallide.

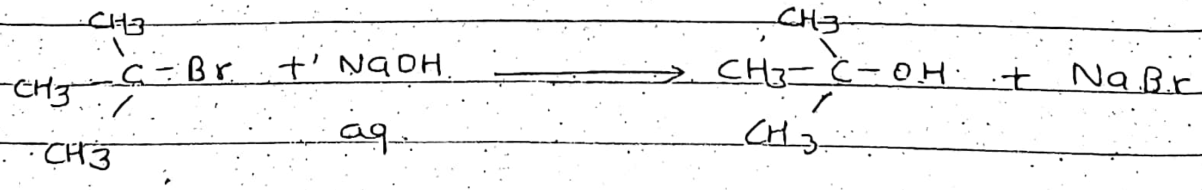
Q. Describe bimolecular nucleophilic substitution rxn mechanism with their molecular configuration.

b) SN^1 reaction mechanism

Such type of nucleophilic substitution reaction in which rate of chemical reaction depends only with concentration of substrate is k/a SN^1 reaction mechanism. It is also called unimolecular nucleophilic substitution reaction.

Generally, tertiary alkyl hallide (3° alkyl hallide) shows SN1 reaction mechanism.

e.g. Hydrolysis of tertiary butyl bromide



$$(CH_3)_3C-Br + NaOH \xrightarrow[aq]{} (CH_3)_3C-OH + NaBr$$

tert. butyl bromide

2-methyl-2-bromopropane

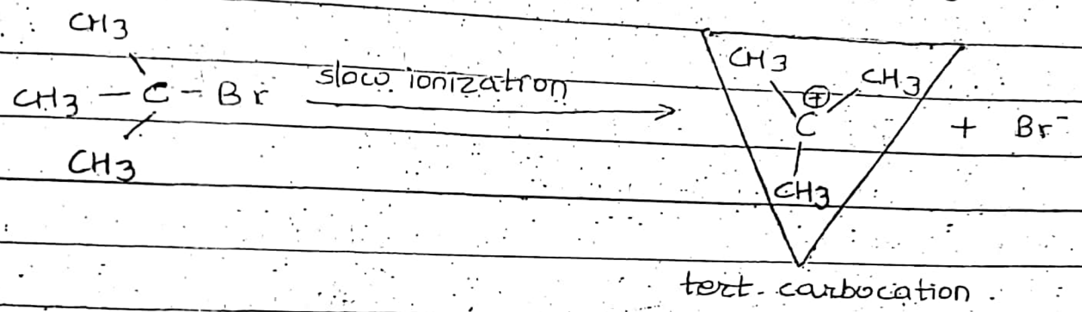
tert. butyl alcohol

Mechanisin

Mechanism of this rxn completes in 2 steps:

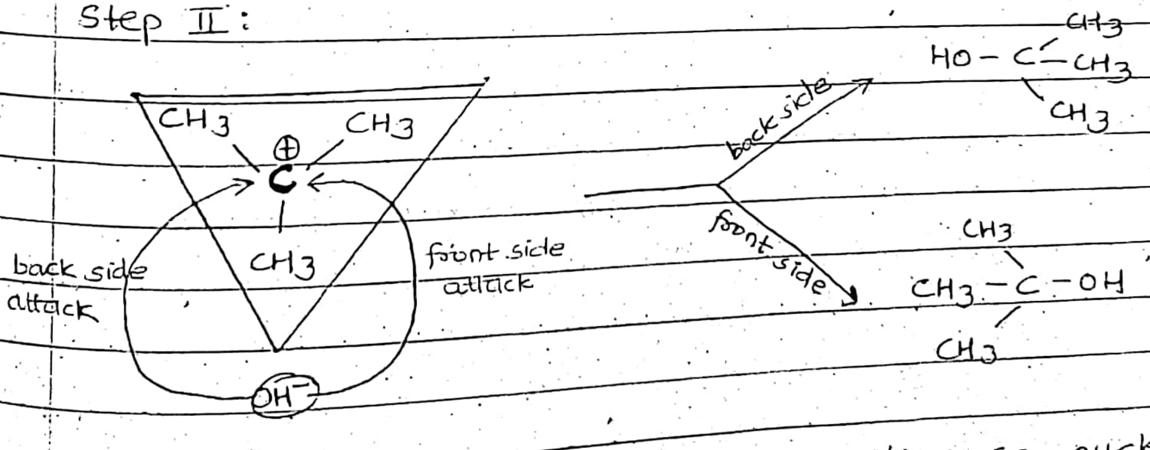
Step I:

In case of 3° alkyl hallide, there is presence of bulky group (CH_3) around the substrate carbon. Therefore, direct attack of nucleophile is not possible. It is called crowding effect. Therefore, slow ionization of substrate takes place to form tertiary carbo cation.



This tertiary carbocation is sp^2 hybridized having trigonal planar structure

Step II:



Tertiary carbocation is highly reactive so nucleophile can attack either from back side to form tertiary alcohol having inversion configuration or from ~~for~~ front side to form tertiary alcohol having retention configuration.

Factors affecting SN^1 & SN^2 reaction mechanism

1. Nature of solvent

Polar solvent favours SN^1 reaction mechanism because in SN^1 reaction mechanism, ionization takes place.

2. Nature of nucleophile

Strong nucleophile favours SN^2 reaction mechanism because in this reaction, nucleophile directly attack ~~to~~ substrate carbon.

3. Nature of substrate

Primary alkyl hallide favours SN^2 reaction mechanism whereas tertiary alkyl hallide favours SN^1 reaction mechanism. In case of secondary alkyl hallide, rxn mechanism depends on solvent & nucleophile. If strong nucleophile and non-polar solvent is present, it favours SN^2 reaction whereas ~~SN1~~ it favours SN^1 rxn in presence of weak nucleophile and polar solvent.

i) Elimination reaction

Such type of chemical reaction where atom or group of atoms are removed from two adjacent carbon in the substrate molecule to form C=C molecule without addition of any other atom or group of atoms is k/a elimination reaction. Double bonded carbon (C=C) molecule is formed.

On the basis of nature, there are 2 types of elimination reaction. They are:

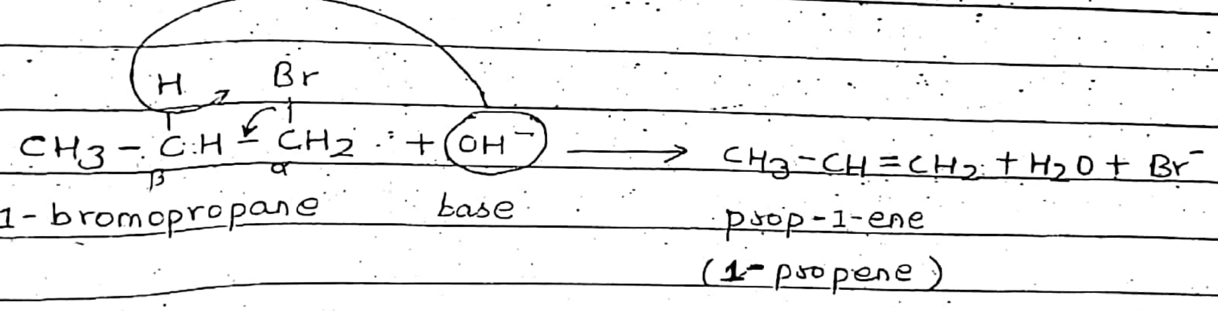
a) E_2 reaction (bimolecular elimination rxn)

Such type of elimination rxn in which rate of chemical rxn depends on concentration of substrate as well as base is k/a E bimolecular elimination rxn or E_2 rxn. Generally, dehydrohalogenation of primary alkyl hallide takes place by E_2 reaction mechanism.

e.g.

$$\underset{\text{substrate}}{CH_3-CH_2-CH_2-Br} + \underset{\text{base}}{\text{alc. KOH}} \longrightarrow CH_3-CH=CH_2 + H_2O + KBr$$

Mechanism



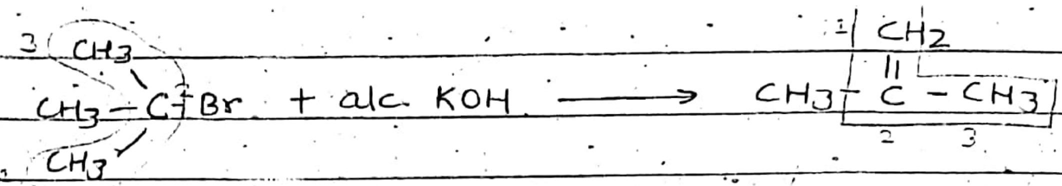
$$\underset{\text{1-bromopropane}}{CH_3-\underset{\beta}{\overset{H}{C}H}-\underset{\alpha}{\overset{Br}{C}H_2}} + \underset{\text{base}}{OH^-} \longrightarrow \underset{\text{prop-1-ene (1-propene)}}{CH_3-CH=CH_2} + H_2O + Br^-$$

Here, the base (OH^-) abstracts proton (H^+) from the β-carbon and at the same time, the hallide is removed with the formation of alkene.

b) E_1 reaction (unimolecular elimination rxn)

Such type of elimination rxn in which rate of reaction depends on concentration of substrate only is k/a unimolecular elimination rxn or E_1 rxn.

Generally, elimination of tertiary alkyl hallide in presence of alcoholic KOH shows E_1 reaction mechanism.



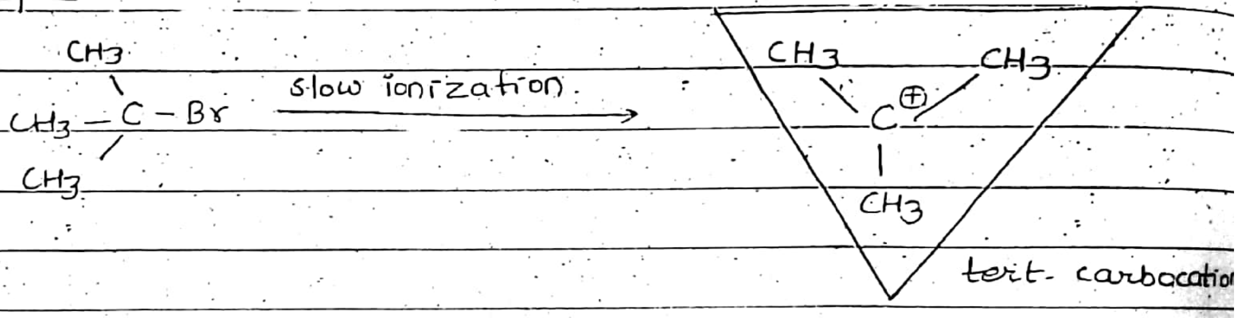
2-bromo-2-methyl propane

2-methyl prop-1-ene

Mechanism

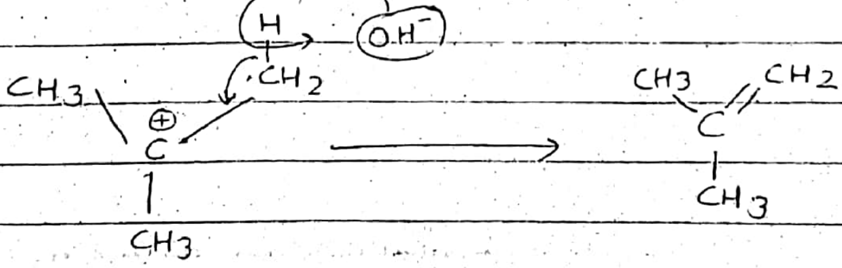
Mechanism of this rxn takes place in 2 steps:

Step I:



First of all, slow ionization takes place to form tertiary carbocation. In this case, direct abstract of proton is not possible due to presence of one hallide and 3 CH3-group around substrate carbon. That carbocation is very unstable.

Step II:



From carbocation, base can abstract proton immediately from β-carbon with the formation of alkene.

Factors affecting elimination reaction

1. Nature of solvent

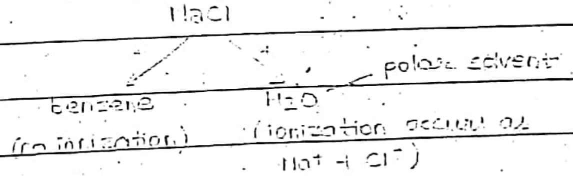
Polar solvent favours E_1 reaction mechanism because in E_1 reaction mechanism, ionization takes place.

2. Nature of base

Strong base favours E_2 reaction mechanism because in this r^{xn}, base directly abstracts proton from β-carbon.

Reactive intermediate

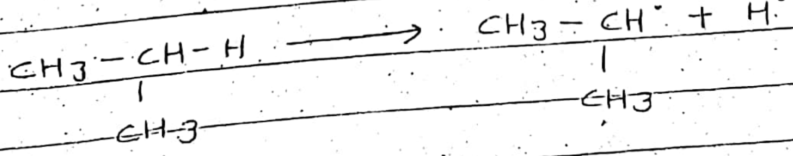
i) Free radical
ii) Carbocation
iii) Carboanion



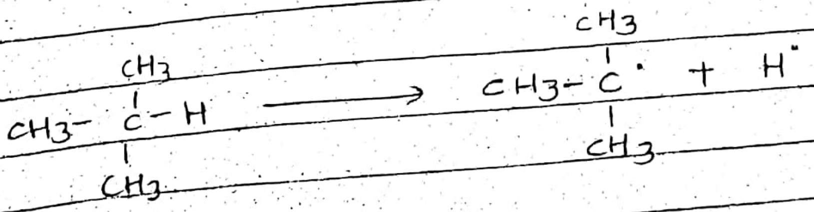
i) Free radical

CH_4

$CH_3-H \longrightarrow CH_3^{\bullet} + H^{\bullet}$



$CH_3-CH(CH_3)-H \longrightarrow CH_3-CH^{\bullet}(CH_3) + H^{\bullet}$



$CH_3-C(CH_3)_2-H \longrightarrow CH_3-C^{\bullet}(CH_3)_2 + H^{\bullet}$

Reactive intermediate

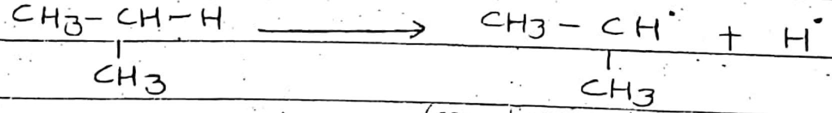
During chemical reaction, there is necessary to breaking of chemical bond. Due to breaking of bond, there may be formation of radicals or ions which are called intermediates. They are extremely short lived. In organic chemistry reactive intermediates are formed from substrate. On the basis of their nature, there are 3 types of reactive intermediates which are as follows:

i) Free radical

Those species which have carbon carrying one unpaired electron is known as free radical. It is also called carbon radical. Generally, carbon radical is formed by homolytic fission of bond. Homolytic fission occurs at high temperature in gas phase in non-polar solvent, by ultraviolet light.

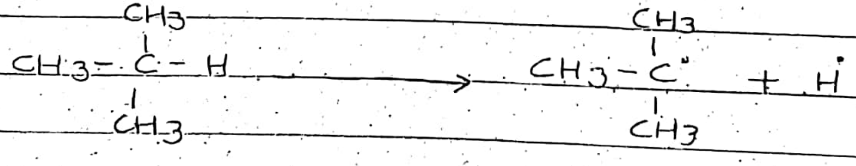
$$CH_3-H \longrightarrow \dot{C}H_3 + \dot{H}$$

(primary free radical)



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-H \longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{\dot{C}H}} + \dot{H}$$

(sec. free radical)



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-H \longrightarrow CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{\dot{C}}}}} + \dot{H}$$

(tert. free radical)

There are 3 types of free radicals: Primary free rad
Secondary "
Tertiary "

unstable → more reactive.
non-polar solvent → benzene

Free radicals are very reactive i.e. they are unstable. The reactivity of free radical depends on number of CH3-group present in radical. The stability of carbon radical increases with increase in number of alkyl group attached to the carbon containing unpaired electron due to hyper conjugation. So, stability order of carbon radical is as follows:

$$3° > 2° > 1° > \dot{C}H_3$$

$$\xleftarrow{\hspace{4cm}}$$

increase in stability of free radical
due to increase in delocalization of electron
(hyper conjugation)

$$\underrightarrow{3° < 2° < 1° < \dot{C}H_3}$$

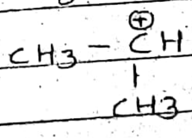
reactivity order increase

ii) Carbocation

Those reactive intermediate in which carbon carries ~~carbon carri~~ positive charge is k/a carbocation. Generally, they are formed by heterolytic fission of chemical bond. This type of fission occurs due to presence of polar solvent.

$\overset{\oplus}{C}H_3$

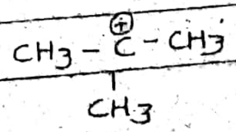
$CH_3CH_2^{\oplus}$



$CH_3-\overset{\oplus}{C}H-CH_3$

There are 3 types of carbocation:

- Primary carbocation
- Secondary carbocation
- Tertiary carbocation



$CH_3-\overset{\oplus}{C}(CH_3)-CH_3$

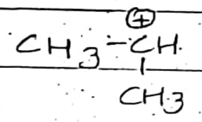
- Primary carbocation

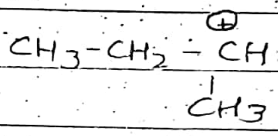
Those carbocation in which only one alkyl group is attached with positively charged carbon atom is k/a primary carbocation. ~~+ve~~ for e.g.

$CH_3\overset{\oplus}{C}H_2$, $CH_3CH_2\overset{\oplus}{C}H_2$

- Secondary carbocation

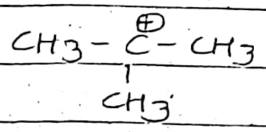
Those carbocation in which two alkyl groups are attached to positively charged carbon atom is k/a secondary carbocation. For e.g.

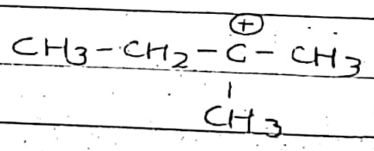

$$CH_3-\overset{\oplus}{\underset{CH_3}{CH}}$$


$$CH_3-CH_2-\overset{\oplus}{\underset{CH_3}{CH}}$$

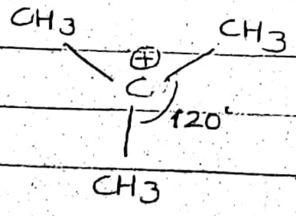
- Tertiary carbocation

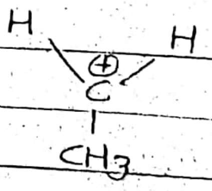
Those carbocation in which 3 alkyl groups are attached to positively charged carbon atom is k/a tertiary carbocation. For e.g.


$$CH_3-\overset{\oplus}{\underset{CH_3}{C}}-CH_3$$


$$CH_3-CH_2-\overset{\oplus}{\underset{CH_3}{C}}-CH_3$$

Carbocations are sp^2 hybridized so they have trigonal planar structure.





Stability of carbocation

- The reactivity of carbocation depends on alkyl group present in that carbocation. Reactivity of carbocation decreases with increase in no. of alkyl groups present in carbocation because ↑ in no. of alkyl group ↑s the electron release on positively charged C-atom. As a result, intensity of positive charge decreases and stability increases. Hence, reactivity decreases.

iii) Carbanion

Those reactive intermediate in which negative charge contained by carbon atom is k/a carbanion. It is due to heterolytic fission of chemical bond. ~~It~~ This type of fission is due to presence of polar solvent.

There are 3 types of carbanion:

- Primary carbanion
- Secondary carbanion
- Tertiary carbanion

Primary carbanion

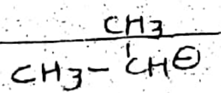
Those carbanion in which only one alkyl group is attached with -vely charged C-atom is k/a primary carbanion.

For e.g. $CH_3-\overset{\ominus}{C}H_2$, $CH_3-CH_2-\overset{\ominus}{C}H_2$

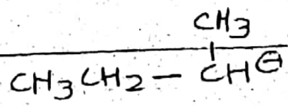
Secondary carbanion

Those carbanion in which two alkyl groups are attached to -vely charged C-atom is k/a secondary carbanion.

For e.g.



$CH_3-\overset{CH_3}{\overset{|}{C}}H^{\ominus}$,

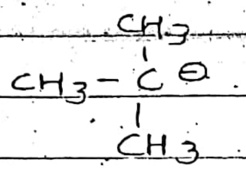


$CH_3CH_2-\overset{CH_3}{\overset{|}{C}}H^{\ominus}$

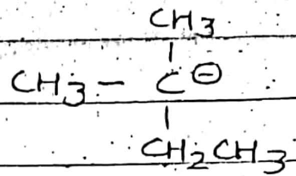
- Tertiary carbanion

Those carbanion in which 3 alkyl groups are attached to -vely charged C-atom is k/a tertiary carbanion.

For e.g.



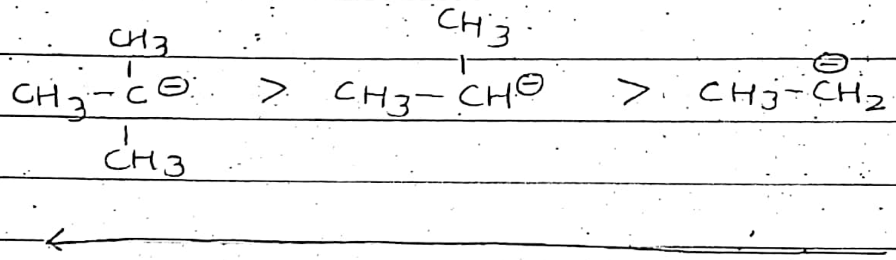
$CH_3-\overset{CH_3}{\underset{CH_3}{C^{\ominus}}}$,



$CH_3-\overset{CH_3}{\underset{CH_2CH_3}{C^{\ominus}}}$

Stability of carbanion

Stability of carbanion depends on no of alkyl group attached with -ve charged C-atom. Increase in no. of alkyl group increases the stability due to increase in delocalization of electron by resonance structure.



$CH_3-\overset{CH_3}{\underset{CH_3}{C^{\ominus}}} > CH_3-\overset{CH_3}{CH^{\ominus}} > CH_3-\overset{\ominus}{CH_2}$

increase in stability

Isomerism

Those molecules having same molecular formula but different in structural arrangement ~~is~~ are k/a isomers. And the phenomenon is k/a isomerism.

Isomerism ~~bear~~ is broadly classified into 2 types:

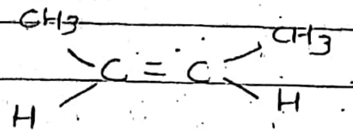
1) structural isomerism (Geometrical isomerism)
2) Stereo isomerism

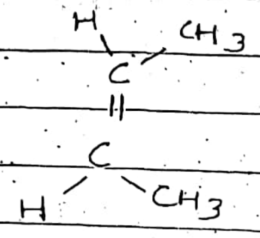
Stereoisomerism

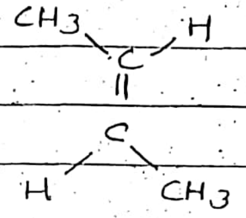
Those molecules having same molecular formula but different orientation in space (having different configuration) are known as stereoisomers. There are 2 types of stereo isomers:

a) Geometrical stereoisomers
b) Optical stereoisomers

a) Geometrical ~~isom~~ stereoisomers





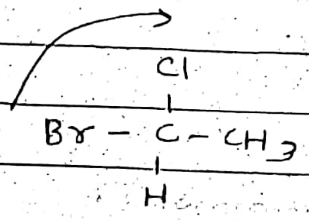


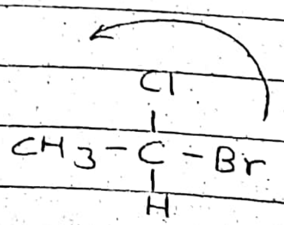
Cis molecule   Trans molecule

b) Optical stereoisomers

The molecules having same molecular formula but different activity towards plane polarized light is k/a optical isomers. And this phenomenon is k/a optical stereoisomerism. The isomers that rotate plane polarized light in clockwise direction is known as dextro (+) rotatory molecule (↷).

The isomers that can rotate plane polarized light in anticlockwise direction is known as laevo (−) rotatory molecule (↶).





+ molecule   − molecule

Rubber & Vulcanization of rubber

Those polymers having elastic property upto 300% are known as rubber. Rubber can be stretched upto 4 to 10 times its original length. As soon as the stretching, it will be returned to its original position. Rubber are also called Elastomers (polymer having elastic property). At unstretched condition, rubber molecules are not straight but they become straight at stretched condition. Therefore, rubber is elastic in nature. The rubber found in nature are called natural rubber. The basic component of natural rubber is latex which is dispersion of isoperene (type of hydrocarbon).

This isoperene polymarized to give long coil chain of rubber. The molecular weight of rubber is about 1,00,000 - 1,50,000 amu. Generally, rubber is made of sap of wide range of plants.

Vulcanization of rubber

Rubber has some drawbacks like

i) ~~i)~~ It has plastic nature i.e. it becomes soft at high ~~ii)~~ temperature. It is usable ~~enly~~ only between 10-60°C.

ii) It is weak.

iii) It has water absorption capacity.

iv) It is less resistant towards non-polar solvent i.e. easily soluble in non-polar solvent.

v) It is easily attacked by oxidizing agent.

vi) It has swelling soiling property.

vii) It is little durable.

To improve these properties / drawbacks of rubber, it is compounded with different chemicals like sulphur, H_2S, benzoyl chloride, etc. In most cases, rubber is mixed with sulphur to improve its quality. By mixing ~~In~~ sulphur, rubber becomes heat resistant upto 140°C. The process of increasing quality of rubber by compounding with different chemicals is k/a vulcanization of rubber.

For example: tyre rubber (vulcanized rubber)
In tyre rubber, 3-5% sulphur is mixed with natural rubber whereas in battery case rubber, there is 30% sulphur.

Advantages of vulcanization

1) By this process, rubber becomes good tensile i.e. it will be durable.

2) Due to vulcanization, rubber ~~become~~ ~~water~~ lose the capacity to absorb water.

3) Due to vulcanization, rubber becomes high resista to oxidizing agent.

4) Rubber becomes high electrical resistant.

5) Rubber becomes resistant to organic solvents like petrol, benzene, carbon tetrachloride, etc.

6) Due to vulcanization, rubber becomes usable between −40°C to 100°C.

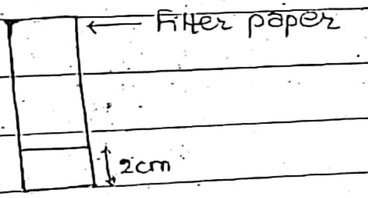
7) Due to vulcanization, rubber becomes air resistant

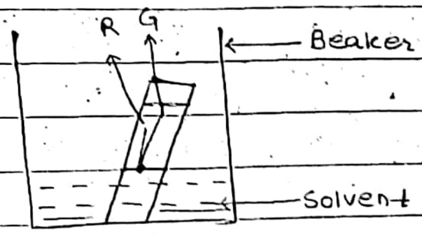
Analytical Chemistry

Chromatography (Lab manual)

R-Red
G-Green

1) Paper chromatography

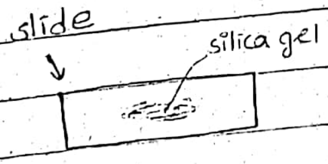




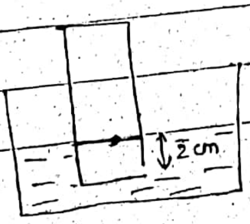
Capillary tube

$$\text{Retention factor } (R_f) = \frac{\text{dist. travelled by colour}}{\text{total dist. travelled by solvent}}$$

2) Thin layer chromatography



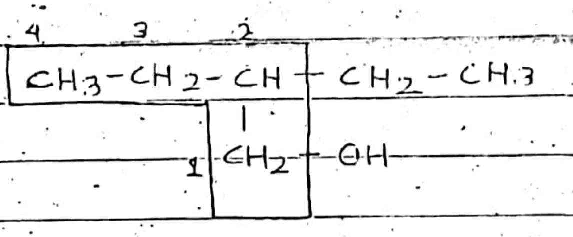
suitable chemical substance
(silica gel) → solidified form



Engineering chemistry: Jain & Jain

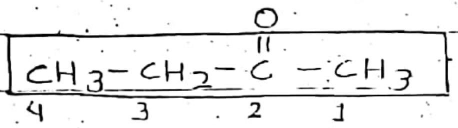
Nuclear Magnetic Resonance (NMR)

Cement - silica + clay

1)


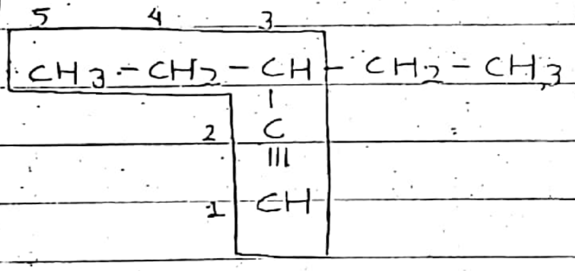
$$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{\underset{\underset{1\;CH_2-OH}{|}}{CH}}-CH_2-CH_3$$

⇒ 2-ethylbutan-1-ol

2)


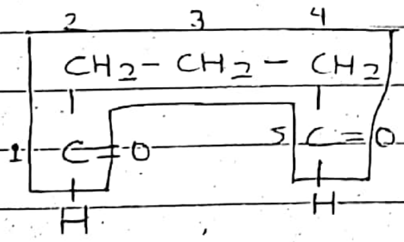
$$\underset{4}{CH_3}-\underset{3}{CH_2}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{1}{CH_3}$$

⇒ Butan-2-one

3)


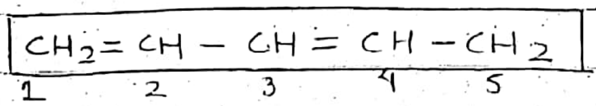
$$\overset{5}{CH_3}-\overset{4}{CH_2}-\overset{3}{\underset{\underset{\underset{\underset{1\;CH}{|||}}{2\;C}}{|}}{CH}}-CH_2-CH_3$$

⇒ 3-ethylpent-1-yne

4)


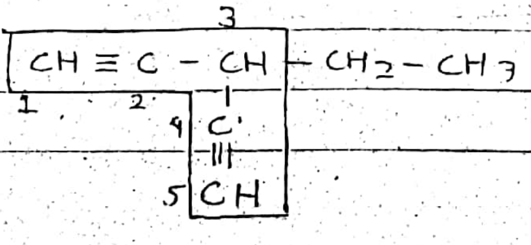
$$\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_2},\quad \underset{\underset{H}{|}}{\overset{1}{C}}=O,\quad \underset{\underset{H}{|}}{\overset{5}{C}}=O$$

⇒ Pentane - 1,5-dial

5)


$$\underset{1}{CH_2}=\underset{2}{CH}-\underset{3}{CH}=\underset{4}{CH}-\underset{5}{CH_2}$$

⇒ Penta-1,3-diene

6)


$$\underset{1}{CH}\equiv\underset{2}{C}-\overset{3}{\underset{\underset{\underset{\underset{5\;CH}{|||}}{4\;C}}{|}}{CH}}-CH_2-CH_3$$

⇒ 3-ethylpenta-1,4-diyne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