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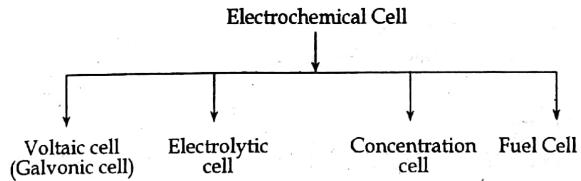
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Chapter 1

Electro-Chemistry and Buffer

1. Electrochemical cell

A device which is used to convert the chemical energy into electrical energy by redox reaction is known as electrochemical cell. It is classified as



1.1 Electrolytic cell

An electrolytic cell is a device in which chemical reaction is occurred by passing electric current through it. It consists of a voltmeter and two electrodes connected with a battery (cell). These two electrodes connected are dipped into electrolytes i.e. electrolytic solution as shown in the figure. The electrode which is connected with +ve terminal of battery is called anode and -ve terminal of battery is called cathode. And when electricity is passed through the electrodes then dissociation of electrolyte takes place when anion moves towards anode and gets oxidized whereas cation moves towards cathode and gets reduced.

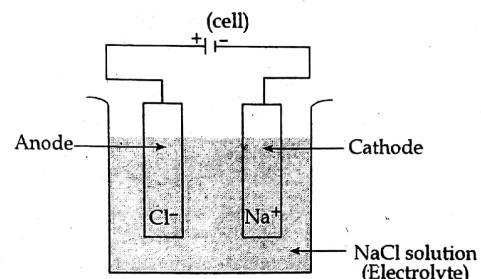
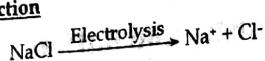
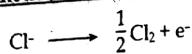


Fig. Electrolytic cell

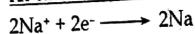
Reaction



At anode (oxidation)



At cathode (Reduction)



Electrolytes

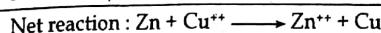
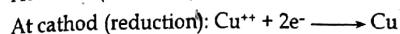
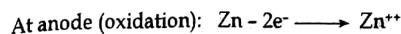
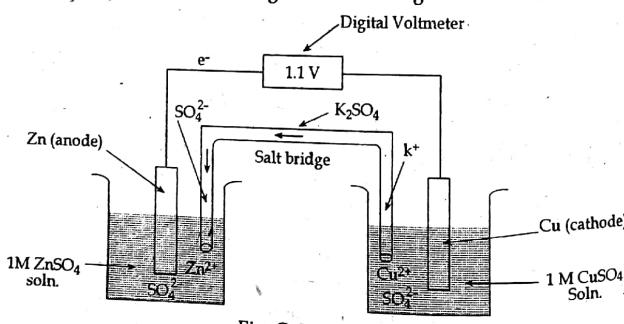
The compounds which ionise in aqueous solⁿ and conduct electricity through it are called electrolytes. It is classified as

- (a) **Strong electrolyte:** which ionise completely in dilute aq. solution.
e.g. HCl, NaCl, NaOH, H₂SO₄, strong acids, strong bases etc.
- (b) **Weak electrolyte:** which doesn't ionize completely in dilute aqueous solution.
e.g. CH₃COOH, NH₄OH, AgCl, weak acid and bases, etc.

1.2 Galvanic cell (Voltaic cell)

A galvanic cell, in which electrical current is generated by a spontaneous redox reaction. It is also known as voltaic cell or Daniel cell.

Let us construct a voltaic cell which consists of two electrodes, two electrolytes and a salt bridge as shown in figure.



Standard condition for galvanic cell

- Temperature should be 25°C
- Concentration of electrolyte should be 1M.

Salt bridge

This is U-shaped tube containing concentrated solution of inert electrolytes like KNO₃, NH₄NO₃ etc. in a gel of agar-agar. The main function of salt bridge are:

- To complete the electrical circuit by allowing the ions to flow from one to other solⁿ.
- To maintain the electronical neutrality of the solution.
- To minimize the junction potential.

Tips to remember

At anode	At cathode
- oxidation occurs	- Reduction occurs
- negative sign	- Positive sign
- electrons are produced	- Electrons are consumed

1.3 Single electrode Potential

When a metallic rod is dipped into the solution of same metal salt, the metallic ion from the metal comes into equilibrium with solution leaving behind the equivalent number of electron on metal surface And metal gets negatively charged. To neutralise the charge, positive ions come near the surface i.e. Solid- liquid layer interface. On that surface certain potential arises due to the development of oppositely charged layer. Hence, the potential which is developed due to the separation of charge in solid _liquid interface is called single electrode potential.

If the single electrode potential is measured at standard condition ie. temp-25.c, concentration of electrolyte 1M and pressure is 1 atm (for gaseous electrode), then it is known as standard single electrode potential.

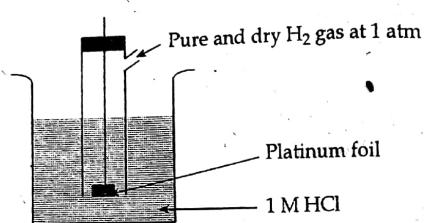
1.4 Normal standard Hydrogen Electrode (NHE/SHE)

Fig: Normal Hydrogen electrode

When an inert metal like platinum foil is dipped into standard solution i.e. 1M HCl electrolyte solution at 25° C and pure, dry H₂ gas at 1 atm passed through the solution then this system is known as standard normal hydrogen electrode (NHE). At 25 °C the standard electrode potential is zero volt. Therefore, NHE is used as reference electrode to measure the standard electrode potential of the given electrode.

If NHE is anode then half cell notation as - pt/H₂ (1 atm), H⁺ (1M) ||

If NHE is cathode cell notation as || H⁺ (1M), H₂ (1 atm) pt

1.5 E.m.f. of cell (Standard)

Emf of cell (standard) is calculated as

$$E_{\text{cell}}^{\circ} = E_C^{\circ} = E_A^{\circ}$$

Where,

E_C° = reduction potential at cathode

E_A° = reduction potential at anode

Also it can be calculated as

$$E_{\text{cell}}^{\circ} = E_{\text{Anode}}^{\circ} + E_{\text{Cathode}}^{\circ}$$

$$\therefore E_{\text{cell}}^{\circ} = E_A^{\circ}(\text{oxidation}) + E_C^{\circ}(\text{reduction})$$

1.6 Nernst Equation

The Nernst equation is given by

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log Q$$

Where,

Q = ratio of concⁿ of products and reactions equilibrium electrode
 $r \times n$.

Uses:

- By Nernst equation, emf of unknown cell can be calculated.
- pH of solution can be calculated.
- Potential of cell at non-standard condⁿ. can be calculated.
- Unknown concentration of cell can be determined.

1.7 Electrochemical series

The systematic arrangement of various electrodes arranged in series in order of increasing their reduction electrode potential is known as electrochemical series. It depends upon the standard reduction potential.

Application**a) Determination of comparative rate of reaction:**

By electrochemical series, we can compare the rate of reaction from standard EMF calculates between and different set of electrodes the higher value of EMF, higher the rate of reaction.

b) Construction of galvanic cell:

The electrode with low value of reduction potential is used as anode and the electrode with higher value of reduction potential is used as cathode and from the Nernst's eqⁿ, galvanic cell can be designed and its EMF is calculated.

c) Spontaneity of redox reaction:

If emf is positive then the reaction is spontaneous.

d) Determination of strength of agent:

The strength of oxidising as well as reducing agent, the movement of redox reaction and the speed (slow or fast) of the reactions can be determined by electrochemical series.

Numerical Examples

1. Calculate the emf of the following cell at 25°C
 $E^\circ \text{Fe}^{+++}/\text{Fe}^{++} = +0.77 \text{ V}$, $E^\circ \text{Sn}^{++}/\text{Sn} = -0.14 \text{ V}$
 in which $[\text{Fe}^{++}] = 0.4 \text{ M}$, $[\text{Fe}^{+++}] = 0.1 \text{ M}$
 $[\text{Sn}^{++}] = 0.2 \text{ M}$.

[IOE 2070 Bhadra]

Solution:

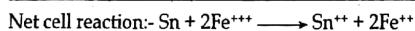
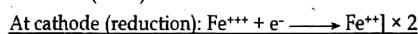
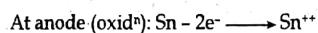
Here,

The reduction potential of electrodes are given.

$$E^\circ \text{Fe}^{+++}/\text{Fe}^{++} = +0.77 \text{ V}$$

$$E^\circ \text{Sn}^{++}/\text{Sn} = -0.14 \text{ V}$$

Therefore,



$$\therefore E^\circ_{\text{Cell}} = E^\circ_C - E^\circ_A$$

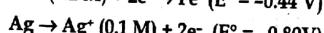
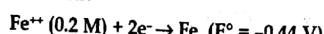
$$= 0.77 - (-0.14)$$

$$= 0.91 \text{ V}$$

The emf of cell at 25°C is calculated as using Nernst eqn.

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{Cell}} - \frac{0.0591}{2} \log \frac{[\text{Fe}^{++}]^2 [\text{Sn}^{++}]}{[\text{Fe}^{+++}]^2} \\ &= 0.91 - \frac{0.0591}{2} \log \frac{(0.4)^2 (0.2)}{(1)^2} \\ &= 0.91 + 0.044 \\ &= 0.954 \text{ V} \\ \therefore E_{\text{Cell}} &= 0.954 \text{ V} \end{aligned}$$

2. Calculate the emf of the cell obtained froms given electrode reactions.



[IOE 2073 Back]

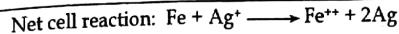
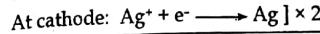
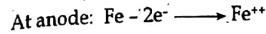
Solution: Here,

The reduction potential of electrodes are:

$$\text{Fe}^{++}/\text{Fe} \quad E^\circ_A = -0.44 \text{ V}$$

$$\text{Ag}^+/\text{Ag} \quad E^\circ_C = 0.80 \text{ V}$$

Therefore,



$$\therefore E^\circ_{\text{Cell}} = E^\circ_C - E^\circ_A$$

$$= 0.80 + 0.44$$

$$= 1.24 \text{ V}$$

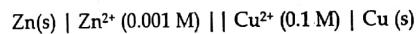
Using Nernst eqn,

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{Cell}} - \frac{0.0591}{2} \log \frac{[\text{Fe}^{++}]}{[\text{Ag}^+]^2} \quad [\because \text{consider, at } 25^\circ \text{C}] \\ &= 1.24 - \frac{0.0591}{2} \log \frac{[0.2]}{[0.1]^2} \\ &= 1.24 - 0.038 \\ &= 1.20 \text{ V} \end{aligned}$$

3. Calculate the emf of a cell at 25°C when the concentration f ZnSO_4 and CuSO_4 are 0.001 M and 0.1 M respectively. The standard potential of cell is 1.2 volts. [2073 Chaitra]

Solution:

Cell notation is

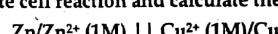


$$E_{\text{cell}} = E^\circ_{\text{cell}} + \frac{0.0592}{n} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$$

$$= 1.2 + \frac{0.0592}{2} \log \frac{0.1}{0.001}$$

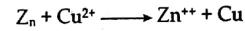
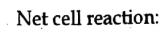
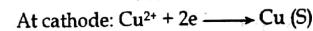
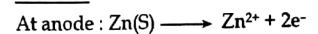
$$= 1.259 \text{ Volt.}$$

4. Write cell reaction and calculate the emf of the cell,



$$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$$

$$E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ Volt.}$$

Solution:Reaction

8 ... A Refresher Solution of Eng. Chemistry (B.E. I Yr I Part)

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{Cu}^{++}/\text{Cu}}^{\circ} - E_{\text{Zn}^{++}/\text{Zn}}^{\circ} \\ &= 0.34 - (-0.76) \\ &= 1.10 \text{ Volt} \end{aligned}$$

5. What is concentration of Ni^{2+} in the cell at 25°C . If the emf is 0.601 Volt?



$$\text{Given: } E_{\text{Ni}/\text{Ni}^{2+}} = 0.25 \text{ V}$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$$

Solution:

$$E_{\text{cell}} = E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ} + \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ni}^{2+}]}$$

$$\text{or, } 0.601 = 0.34 - (-0.25) + \frac{0.0592}{2} \log \frac{(0.75)}{a}$$

$$\text{or, } 0.011 = \frac{0.0592}{2} \log \frac{0.75}{x}$$

$$\text{or, } \log \frac{0.75}{x} = 0.37162$$

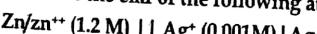
$$\text{or, } \frac{0.75}{x} = 10^{0.37162}$$

$$\text{or, } \frac{0.75}{x} = 2.532$$

$$\therefore x = 0.319 \text{ M}$$

Hence, concentration of $\text{Ni}^{2+} = 0.319 \text{ M}$.

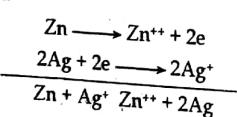
6. Calculate the emf of the following at 25°C



$$E_{\text{Zn}/\text{Zn}^{++}}^{\circ} = 0.76 \text{ V}$$

$$E_{\text{Ag}/\text{Ag}^{+}}^{\circ} = 0.80 \text{ V}$$

Solution:



$$E_{\text{cell}} = (E_C^{\circ} - E_A^{\circ}) - \frac{0.0591}{2} \log \frac{[\text{Zn}^{++}]}{[\text{Ag}^{+}]}$$

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$$= 0.80 - (-0.76) - \frac{0.0591}{2} \log \frac{1.2}{(0.001)^2} = 1.380 \text{ volt.}$$

Note: Given oxidation potential should be converted to reduction potential i.e. gain of electron.

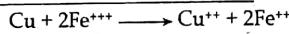
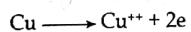
Reduction potential = - oxidation potential.

7. The emf of a cell of standard $\text{Fe}^{++}/\text{Fe}^{+++}$ electrode and Cu^{++}/Cu electrode is 0.41V. Find out the Cu^{++} ion concentration in the cell.

$$E_{\text{Fe}^{++}/\text{Fe}^{+++}}^{\circ} = -0.77 \text{ V}$$

$$E_{\text{Cu}^{++}/\text{Cu}}^{\circ} = 0.3 \text{ V}$$

Solution: Reaction



Next reaction

$$E_{\text{cell}}^{\circ} = 0.77 - 0.3 = 0.43 \text{ Volt}$$

From Nernst equation

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \\ &= 0.43 - \frac{0.0591}{2} \log \frac{[\text{Fe}^{++}]^2 [\text{Cu}^{++}]}{[\text{Fe}^{+++}]^2} \end{aligned}$$

$$\text{or, } 0.41 = 0.43 - \frac{0.0591}{2} \log \frac{(1)^2 [\text{Cu}^{++}]}{(1)^2}$$

$$\text{or, } 0.02 = \frac{0.0591}{2} \log [\text{Cu}^{++}]$$

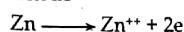
$$\therefore [\text{Cu}^{++}] = 4.751 \text{ M.}$$

8. What will be the emf of the cell at 30°C $\text{Zn/Zn}^{++} (0.001 \text{ M}) \parallel \text{Fe}^{++} (0.005 \text{ M}) \mid \text{Fe}$.

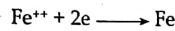
$$E_{\text{Fe}^{++}/\text{Fe}}^{\circ} = -0.44$$

$$E_{\text{Zn}^{++}/\text{Zn}}^{\circ} = -0.76$$

Solution: At anode



At cathode



$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_C^{\circ} - E_A^{\circ} \\ &= 0.44 - (-0.76) = 0.32 \text{ V} \end{aligned}$$

10 ... A Refresher Solution of Eng. Chemistry (B.E. I Yr I Part)

We know,

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{RT}{nF} \log Q \\ &= 0.32 - \frac{8.34 \times (273 + 30)}{2 \times 96500} \times 2.30 \log Q \\ &= 0.32 - 0.0306 \log \frac{[\text{Zn}^{++}]}{[\text{Fe}^{++}]} \\ &= 0.32 - 0.03006 \times \log \frac{(0.001)}{0.005} \\ &= 0.34 \text{ Volt.} \end{aligned}$$

9. Calculate the emf of the redox reaction and give cell notation.

Given: $E_{\text{Fe}^{++}/\text{Fe}^{+++}}^{\circ} = -0.77 \text{ V}$

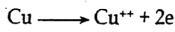
$$E_{\text{Cu}^{++}/\text{Cu}}^{\circ} = 0.34 \text{ V}$$

$$[\text{Fe}^{++}] = 0.2 \text{ M}$$

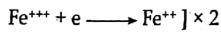
$$[\text{Fe}^{+++}] = 1 \text{ M}$$

$$\text{and } [\text{Cu}^{++}] = 0.1 \text{ M}$$

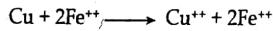
Solution: At anode



At cathode



Net cell reaction



$$E_{\text{cell}}^{\circ} = E_{\text{C}}^{\circ} - E_{\text{A}}^{\circ}$$

$$\approx 0.77 - 0.34$$

$$= 0.43 \text{ V}$$

Applying Nernst's equation,

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log Q \\ &= 0.43 - \frac{0.0591}{n} \log \frac{[\text{Cu}^{++}][\text{Fe}^{++}]^2}{[\text{Fe}^{+++}]^2} \\ &= 0.43 - \frac{0.0591}{n} \log \frac{0.1 \times 0.2^2}{1^2} \\ &= 0.5 \text{ V} \end{aligned}$$

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10. The emf of the cell $\text{Zn}(\text{S})/\text{Zn}^{++}$ (aq. 0.1 M) || cd^{2+} (aq. M_1) | $\text{cd}(\text{S})$ has been found to be equal to 0.3305 V at 299 K. Calculate the value of M_1 .

$$E_{\text{Zn}^{++}/\text{Zn}}^{\circ} = -0.76 \text{ V}$$

$$E_{\text{cd}^{2+}/\text{cd}}^{\circ} = -0.40 \text{ V}$$

Solution: The cell reaction can be written as



Here, n (number of electron involved) = 2

Using Nernst's equation

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{++}][\text{cd}]}{[\text{Zn}][\text{cd}]^2}$$

$$\text{or, } 0.3305 = -0.40 - (-0.76) - \frac{0.0591}{n} \log \frac{0.1 \times 1}{1 \times M_1}$$

$$\text{or, } 0.0295 = \frac{0.0591}{2} \log \frac{0.1}{M_1}$$

$$\text{or, } 0.999 = \frac{0.1}{M_1}$$

$$\text{or, } 10^2 = \frac{0.1}{M_1}$$

$$\text{or, } M_1 = 0.01 \text{ M}$$

11. Calculate the emf of the cell Zn/ZnSO_4 (0.1 M) || cdSO_4 (0.01 M) | cd

$$E_{\text{Zn}^{++}/\text{Zn}}^{\circ} = -0.76 \text{ V}$$

$$E_{\text{cd}^{2+}/\text{cd}}^{\circ} = -0.40 \text{ V at } 25^\circ\text{C}$$

How does emf of the above cell will alter on

1. Increasing concentration of ZnSO_4 .
2. Increasing temperature.

Solution:

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{C}}^{\circ} - E_{\text{A}}^{\circ} \\ &= 0.40 - (-0.76) \\ &= 0.36 \text{ V} \end{aligned}$$

Applying Nernst's equation,

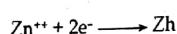
$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{2.303RT}{nF} \log \frac{[\text{ZnSO}_4][\text{cd}]}{[\text{cdSO}_4][\text{Zn}]} \\ &= 0.36 - \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \times \log \frac{0.1}{0.01} \\ &= 0.330 \text{ volt} \end{aligned}$$

12 ... A Refresher Solution of Eng. Chemistry (B.E. I Yr I Part)

- (i) Increasing concentration of ZnSO_4 emf decreases.
 (ii) Increasing temperature emf decreases.
12. A Zn- rod placed in 0.1M solution of ZnSO_4 , at 25°C . Assuming that the salt is dissociated to the extent at 95% at this dilution. Calculate the potential of the electrode at this temperature.

$$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$$

Solution:



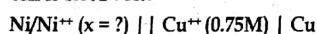
From the question

$$[\text{ZnSO}_4] = \frac{95}{100} \times 0.1 \\ = 0.095 \text{ M}$$

Using Nernst's equation,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Zn}]}{[\text{Zn}^{2+}]} \\ = -0.76 - \frac{0.0591}{2} \log \frac{0.1}{0.095} \\ = -0.79 \text{ volt}$$

13. What is the concentration of Ni^{2+} ion in the cell at 25°C if emf of the cell is 0.601 volt?



Solution:

$$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.25 \text{ volt}$$

$$E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = 0.34 \text{ volt}$$

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

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

Net rxn: $\text{Ni} + \text{Cu}^{2+} \longrightarrow \text{Ni}^{2+} + \text{Cu}$

$$E_{\text{cell}}^{\circ} = 0.34 - (-0.25) \\ = 0.59 \text{ volt}$$

Using Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Ni}^{2+}]}{[\text{Cu}^{2+}]} \\ = 0.59 - \frac{0.0591}{2} \log \frac{x}{0.75}$$

Electro-Chemistry and Buffer ... 13

$$\text{or}, -0.37 = \log \frac{x}{0.75}$$

$$\text{or}, x = 0.32 \text{ M.}$$

Buffer and pH

1.8 Buffer

A buffer solution is one kind of solution which resist the change in pH by the addition of small amount of acid and base

1.8.1 Types of buffer

There are two types of buffer.

a) Acidic buffer:- It is the mixture of weak acid and its salt with strong conjugate base.

example:- $\text{HCOOH} + \text{HCOONa}$

b) Basic buffer:- It is the mixture of weak base & its salt with strong acid.

example:- blood, sea water, $\text{NH}_4\text{OH} + \text{NH}_4\text{NO}_3$.

1.8.2 pH

The negative logarithm of H_3O^+ (or H^+) concentration is called pH solution.

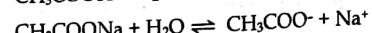
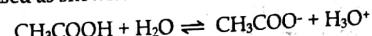
$$\text{i.e. } \text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{Note: } \text{pH} + \text{pOH} = 14$$

The pH value for acid, neutral and base are less than 7, equal to seven and greater than 7 respectively.

1.9 Mechanism of acidic buffer

The mechanism of buffer action can be explained with the help of common ion effect and Le-chatelier's principle. To give the mechanism of buffer action let us consider the acidic buffer of acetic acid and sodium acetate. Being a weak electrolyte acetic acid is partially ionised and sodium acetate is strong electrolyte, and is completely ionised as shown in reaction.



In general equation,

- (a) $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ (feebley ionised)
- (b) $\text{NaH} \rightleftharpoons \text{Na}^+ + \text{A}^-$ (completely ionised)

Case I When base is added:-

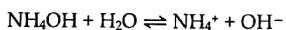
In this buffer system if we add small amount of strong base like NaOH , OH^- ion of the base combines with H^+ -ions of the acid to give water molecules. Due to this, the amount of H^+ ions in the system will be decreased and equilibrium state of equation (a) should be disturbed but according to Le-chatelier principle this disturbance is minimised by shifting the equilibrium state of towards forward direction i.e. more amount of acetic acid will be ionised to fulfill the decreased amount of H^+ -ion and therefore pH remains constant.

Case II: When acid is added:-

When acid is added to this solution the concentration of H_3O^+ ion in the solution increases which alters the dynamic equilibrium. The equilibrium shifts towards left. This happens when H^+ ion combines with CH_3COO^- to make CH_3COOH backward. This maintains the pH .

1.9.2 Mechanism of Basic Buffer

The mechanism of basic buffer can be understand by taking an example. Consider a basic buffer solution formed by mixing ammonia solution and ammonium chloride. The rxn is



This makes dynamic equilibrium



Case I: When acid is added:-

When acid is added in this buffer, H^+ -ion is introduced in solution which combines with OH^- ions in solution. This consumes OH^- ions from solution. The dynamic equilibrium shift toward right to compensate the consumed amount of OH^- ion making constant pH .

Case II: When base is added:-

When small amount of base is added to this solution. Extra OH^- ion is introduce into solution. The extra OH^- combines with NH_4^+ ion in solution shifting equilibrium backward. This makes constant pH .

1.10 Formula

(i) $\text{pH} = \text{p}^{K_a} + \log \frac{[\text{salt}]}{[\text{acid}]}$ for acidic buffer

where,

K_a is ionization constant of acid

$$K_a = \frac{[\text{H}_3\text{O}^+] [\text{A}^-]}{[\text{HA}]}$$

(ii) $\text{pOH} = \text{p}^{K_b} + \log \frac{[\text{salt}]}{[\text{base}]}$

where,

K_b is ionization constant of base

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

Numerical Examples

1. 50 ml of 0.2 M acetic acid is mixed with 50ml of 0.2 M sodium acetate solution. What will be the pH of the mixture?

$$K_a = 1.85 \times 10^{-5}$$

Solution:

$$\text{Total volume of solution} = 100 \text{ M}$$

$$[\text{Acid}] = \frac{0.2 \times 50}{100} = 0.1 \text{ M}$$

$$[\text{base}] = \frac{0.2 \times 50}{100} = 0.1 \text{ M}$$

$$\text{p}^{K_a} = -\log K_a = 4.732$$

$$\text{pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 4.732 + \log \frac{[0.1]}{[0.1]}$$

$$= 4.732 + 0$$

$$\therefore \text{pH} = 4.732$$

2. 30 ml of 0.10 M NaOH is added to 100 ml of 0.10 M solution of acetic acid. Calculate pH of the buffer solution.

$$(K_a \text{ for } \text{CH}_3\text{COOH} = 1.8 \times 10^{-5})$$

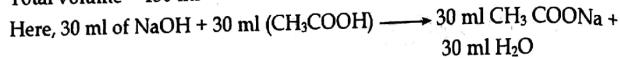
Solution:

Reaction



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Total volume = 130 ml



Acid remain untreated = 100 - 30

$$= 70 \text{ ml}$$

$$\therefore [\text{CH}_3\text{COOH}] = \frac{0.1 \times 70}{130}$$

$$= 0.05395$$

$$[\text{CH}_3\text{COONa}] = \frac{0.3 \times 30}{130}$$

$$= 0.06923$$

$$p^H = -\log K_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

$$= -\log (1.9 \times 10^{-5}) + \log \frac{0.06923}{0.05395}$$

$$= 4.8129$$

3. What is the p^H of the solution when 0.2 mole of HCl is added to one litre of solution containing 1M each of CH_3COOH and acetate ion. Assume total volume as one litre. (K_a of $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$) (K_b for $\text{CH}_3\text{COO}^- = 1.0 \times 10^{-5}$).

Solution:

When 0.2 M HCl is added to solution. 0.2 M H^+ ion from HCl combines with CH_3COO^- ion from solution to make concentration of $\text{CH}_3\text{COOH} = 1.2 \text{ M}$ (because 1M CH_3COOH is already present).

$$[\text{CH}_3\text{COOH}] = 1.2 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = 0.8 \text{ M}$$

$$p^H = -\log K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$= -\log (1.8 \times 10^{-5}) + \log \frac{[1.2]}{[0.8]}$$

$$= 4.921$$

4. Find out the how much sodium acetate should be used to prepare 1200 ml of a buffer which 0.1 N with respect to acetic acid has p^H of 5.2.

Solution:

Assume amount of $\text{CH}_3\text{COOH} = x$

We have total volume = 1200 ml

Then volume of 0.1 N $\text{CH}_3\text{COOH} = 1200 - x$

Since CH_3COOH is monobasic acid,

Molarity = Normality

$$\text{Now, } p^H = K_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

$$\text{or, } 5.2 = 4.74 + \log \frac{x}{0.1}$$

$$\text{or, } 0.46 = \log \frac{x}{0.1}$$

$$\text{or, } x = 10^{0.46} \times 0.1$$

$$\text{or, } x = 2.88 \times 0.1 = 0.288 \text{ M}$$

We know,

$$\text{Molarity} = \frac{\text{wt. in gm}}{\text{mol. wt.}} \times \frac{1000}{\text{volume in ml}}$$

$$\text{or, } 0.288 = \frac{\text{Wt. in gram}}{82} \times \frac{1000}{1200}$$

$$\therefore \text{Wt. of } \text{CH}_3\text{COONa} = 28.33 \text{ gm.}$$

5. What is the p^H of the solution when 0.2 mole NaOH is added to one litre of the solution containing one mole of each NH_3 and NH_4Cl . $K_b = 1.8 \times 10^{-5}$. Assume the total volume remains one litre.

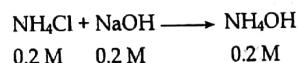
Solution:

$$[\text{NaOH}] = 0.2 \text{ NaOH}$$

$$[\text{NH}_3] = 1 \text{ M}$$

$$[\text{NH}_4\text{Cl}] = 1 \text{ M}$$

Reaction:



Now,

$$[\text{NH}_4\text{Cl}] = 1 - 0.20 = 0.8 \text{ M}$$

$$[\text{NH}_4\text{OH}] = 0.2 \text{ M}$$

Applying Henderson's equations:

$$p^{\text{OH}} = p^{\text{Kb}} + \log \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_4\text{OH}]}$$

$$= 4.74 + \log \frac{0.8}{0.2}$$

$$= 5.34$$

$$\therefore p^H = 14 - p^{\text{OH}} = 14 - 5.34 = 8.66$$

6. 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.

Solution:

200 ml of 0.1 M CH_3COOH

400 ml of 0.2 M CH_3COONa

Total volume = 200 + 400

$$= 600 \text{ ml}$$

$$[\text{CH}_3\text{COOH}] = \frac{0.1 \times 200}{600} = 0.033 \text{ M}$$

$$[\text{CH}_3\text{COONa}] = \frac{0.2 \times 200}{600} = 0.133 \text{ M}$$

Applying Henderson's equation,

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= 4.74 + \log \frac{[0.133]}{[0.0333]} = 5.34$$

7. A litre of solution contains 0.1 mole of acetic acid and 0.1 mole sodium acetate. What is change in pH of the solution after addition 0.02 mole of NaOH. $[\text{Ka} = 1.5 \times 10^{-5}]$

Solution:

$$[\text{CH}_3\text{COOH}] = 0.1 \text{ M}$$

$$[\text{CH}_3\text{COONa}] = 0.1 \text{ M}$$

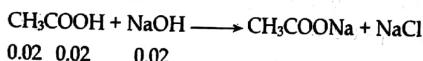
$$[\text{NaOH}] = 0.02 \text{ M}$$

Before addition of NaOH,

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

$$= -\log (1.8 \times 10^{-5}) + \log \frac{0.1}{0.1} = 4.74$$

After addition of NaOH



$$[\text{CH}_3\text{COOH}] = 0.1 - 0.02 = 0.08 \text{ M}$$

$$[\text{CH}_3\text{COONa}] = 0.1 - 0.02 = 0.12 \text{ M}$$

Using Henderson's equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

$$= -\log (1.8 \times 10^{-5}) + \log \frac{0.12}{0.08}$$

$$= 4.92$$

$$\text{Change in pH} = 4.74 - 4.92$$

$$= -0.18$$

8. A buffer contains 0.1 mole per litre of both NH_4Cl and NH_3 . Calculate the pH of the solution when 0.001 mole of HCl is added to it. [PU 2070]

Solution:

Here, given,

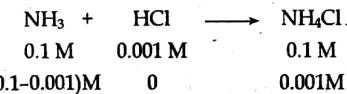
Concentration of salts base and acid

$$[\text{NH}_4\text{Cl}] = 0.1 \text{ M}$$

$$[\text{NH}_3] = 0.1 \text{ M}$$

$$[\text{HCl}] = 0.001 \text{ M}$$

Rxn



After the addition of HCl

$$[\text{NH}_3] = 0.1 - 0.001 = 0.099 \text{ M}$$

$$[\text{NH}_4\text{Cl}] = 0.001 + 0.1 = 0.101 \text{ M}$$

Now,

By Henderson's equation,

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_3]}$$

$$= 4.74 + \log \frac{[0.101]}{[0.099]}$$

$$= 4.75$$

Now,

$$\text{pH} = 14 - \text{pOH}$$

$$= 14 - 4.75 = 9.25$$

9. Calculate the pH of the solution formed by adding 0.4 g of NaOH on 500 ml 0.2 M acetic acid. $\text{p}K_a$ for acid = 4.74 [IOE 2073 Magh]

Solution:

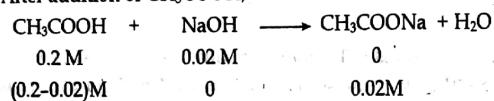
Given that,

500 ml of 0.2 M CH_3COOH (acetic acid)

$$\therefore [\text{CH}_3\text{COOH}] = 0.2 \text{ M}$$

$$\text{Molarity of NaOH} = \frac{0.4}{500} \times \frac{1000}{40} \\ = 0.02 \text{ M}$$

After addition of CH_3COOH ,



$$\therefore [\text{CH}_3\text{COONa}] = 0.02 \text{ M}$$

Now,

$$\begin{aligned} p^{\text{H}} &= p^{\text{Ka}} + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} \\ &= 4.74 + \log \frac{[0.02]}{[0.18]} \end{aligned}$$

$$\therefore p^{\text{H}} = 3.78$$

10. 0.005 mole wt KOH is added to 400 ml of 0.1 M CH_3COOH . Calculate the p^{H} of the mixture. Given $p^{\text{Ka}} = 4.74$. [2074 Back]

Soln: Given that

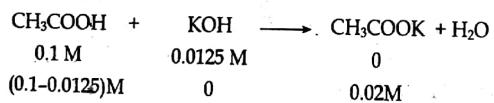
$$p^{\text{Ka}} = 4.74 \text{ for acid}$$

We know,

$$\begin{aligned} \text{molarity of KOH} &= \frac{0.005}{400} \times 1000 \\ &= 0.0125 \text{ M} \end{aligned}$$

$$\text{and } [\text{CH}_3\text{COOH}] = 0.1 \text{ M}$$

After addition



$$\therefore [\text{CH}_3\text{COOK}] = 0.0125 \text{ M}$$

Now, by Henderson's eqn

$$\begin{aligned} p^{\text{H}} &= p^{\text{Ka}} + \log \frac{[\text{CH}_3\text{COOK}]}{[\text{CH}_3\text{COOH}]} \\ &= 4.74 + \log \frac{[0.0125]}{[0.0875]} \therefore = 3.89 \end{aligned}$$

Exam Question Solutions

1. What is buffer solution? Write the mechanism acidic buffer. [TU 2063 Baishakh]

Ans: See theory portion.

2. Write the difference between galvanic and electrolytic cell and write the cell notation, cell reaction and emf of Cu - Ag cell. [TU 2063]

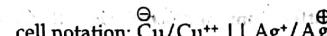
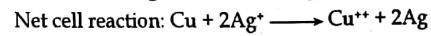
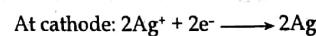
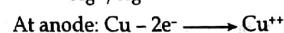
Ans:

Electrolytic cell	Galvanic cell
1. It is based on the chemical effect of electric current.	1. It is based on the electric effect of chemical reaction.
2. There is no cell notation.	2. It can be represented by cell notation like $\text{Zn}^\ominus / \text{Zn}^{++} (1\text{M}) \parallel \text{Cu}^{++} (1\text{M}) / \text{Cu}^\oplus$
3. It is non-spontaneous.	3. It is spontaneous.
4. It gives more emf.	4. It gives less emf.
5. No salt bridge is used.	5. The salt bridge is used.

Cell notation

$$E_{\text{Cu}^{++}/\text{Cu}}^\circ = +0.34$$

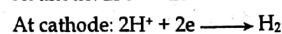
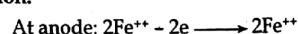
$$E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80$$



$$\text{emf} = (0.80 - 0.34)\text{V} = E_C (\text{Reduction}) - E_A (\text{Reduction}) = 0.46 \text{ V}$$

3. Calculate the reduction potential E for the Fe^{+++} (Fe^{++}) electrode when Fe^{++} ion concentration is half of Fe^{++} ion concentration at 25°C . [TU 2063]

Solution:



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Net equation: $\text{Fe}^{++} + 2\text{H}^+ \longrightarrow 2\text{Fe}^{+++} + \text{H}_2$

$$E_{\text{cell}}^{\circ} = E_{\text{C}}^{\circ} - E_{\text{A}}^{\circ}$$

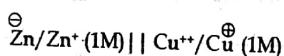
$$= 0.77$$

4. How does electrode potential originate? Define standard electrode potential? Write cell notation and cell reaction for Zn - Cu cell.

[TU 2067 Ashadh]

Ans: See theory portion.

Cell Notation:



5. What is buffer solution? Calculate the pH of resulting solution when 0.005 mole of KOH is added to 200 ml of 0.1 N acetic acid solution. ($\text{pK}_a = 4.74$)

Ans: For definition: See theory portion.

Numerical part:



Since, Molarity of KOH is less

$$0.005 + 0.005 \longrightarrow 0.005 + 0.005$$

$$[\text{CH}_3\text{COOK}] = 0.005 \text{ M}$$

$$[\text{CH}_3\text{COOH}] = 0.1 \text{ M} - 0.005 \text{ M} = 0.005 \text{ M}$$

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

$$= 4.74 + \log \frac{0.005}{0.005}$$

[Note: For any reaction 1 mole reactant give 1 mole of product. Here 0.005 mole is limiting reactant]

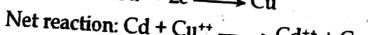
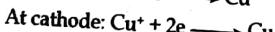
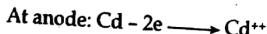
6. How does a galvanic cell differ from an electrolytic cell? Calculate the emf of the following cell at 25°C giving electrode reaction and cell reaction.



$$E_{\text{Cd}^{++}/\text{cd}}^{\circ} = -0.140 \text{ V}, E_{\text{Cu}^{++}/\text{Cu}}^{\circ} = 0.34 \text{ V}$$

[TU 2068 Bhadra]

Solution:



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$$E_{\text{cell}}^{\circ} = E_{\text{C}}^{\circ} - E_{\text{A}}^{\circ}$$

$$= 0.34 - (-0.140) = 0.48 \text{ Volt}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303}{nF} \log Q$$

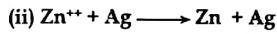
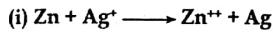
$$= 0.48 - \frac{2.303 \times 8.314 \times 248}{2 \times 96500} \times \log \left(\frac{0.01}{0.5} \right)$$

$$= 0.530 \text{ volt}$$

7. What is buffer solution? Discuss the mechanism of buffer with suitable example. [TU 2068]

Ans: See theory portion.

8. Define a galvanic cell. What are the function of salt bridge in a galvanic cell. Predict the feasibility of the following reaction.

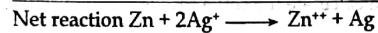
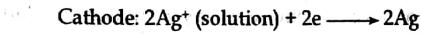
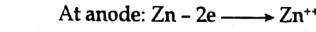
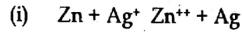


Given: $E_{\text{Zn}^{++}/\text{Zn}}^{\circ} = -0.76 \text{ V}, E_{\text{Ag}/\text{Ag}}^{\circ} = 0.80 \text{ V}$ [TU 2068 Bhadra]

Ans: A galvanic cell can be defined as the cell which generates electric current by a spontaneous redox reactions.

Functions of salt bridge

- To form a close circuit by providing medium to flow ions from one solution to other.
- To maintain the neutrality in the two cells.
- To minimize junctional potential.



$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0.80 - (-0.70) = 1.56 \text{ volt}$. since the emf is + ve the reaction is feasible.

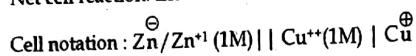
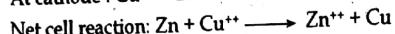
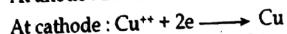
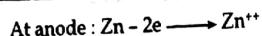
- (ii) This process is reverse of (i), not feasible.

9. How does electrode potential originate? Define standard electrode potential. Write cell notation and cell reaction of Zn - Cu cell. [TU 2069 Bhadra]

Ans: First part: See theory portion.

* Zn - Cu cell

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10. What is meant by buffer solution? Calculate the concentration of sodium formate HCOONa that must be present in 0.10 M solution in 0.1 M solution of formic acid to produce a pH of 3.80 ($K_a = 1.8 \times 10^{-4}$). [TU 2069 Bhadra]

Ans: A buffer solution is a kind of solution which resist change of pH even by adding small amount of acid or base.

We know,

$$pH = pK_a + \log Q$$

$$\text{or, } pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{or, } 3.80 = -\log(1.8 \times 10^{-4}) + \log \frac{x}{0.10}$$

$$\therefore (x) = 0.105 \text{ M.}$$

11. (a) What is normal hydrogen electrode?

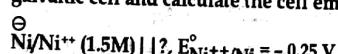
Ans: See theory portion.

- (b) Calculate the emf of the following cell at 25°C.

$$E_{\text{Fe}^{+++}/\text{Fe}^{++}}^{\circ} = -0.77, E_{\text{Sn}^{++}/\text{Sn}}^{\circ} = 0.14 \text{ V in which } [\text{Fe}^{+++}] = 0.4 \text{ M}, [\text{Fe}^{++}] = 0.1 \text{ M } [\text{Sn}^{++}] = 0.2 \text{ M} \quad [\text{TU 2069 Bhadra}]$$

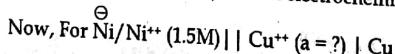
Ans: See numerical example on page no 6.

12. With the help of electrochemical series complete the following galvanic cell and calculate the cell emf.

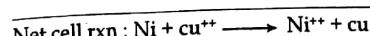
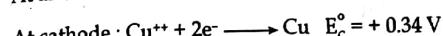


Ans: In galvanic cell, the electrode which has low value of reduction potential is always made 'anode' and electrode having high value of reduction potential is made cathode.

In our case anode is given and we have to find out the cathode. Let's take $\text{Cu}^{++} (a = 0) / \text{Cu}$ as cathode since it has higher reduction potential than that of Ni/Ni^{++} in electrochemical series.



Electro-Chemistry and Buffer ... 25

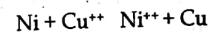


$$\therefore E_{\text{cell}}^{\circ} = E_c^{\circ} - E_a^{\circ} = 0.34 - (-0.25) = 0.59 \text{ V}$$

Now, using Nernst equation:

$$E_{\text{cell}}^{\circ} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Ni}^{++}][\text{Cu}]}{[\text{Ni}][\text{Cu}^{++}]}$$

We have the next reaction,



1 vol. 1 vol.

1.5 M 1.5 M

$$\text{So, } [\text{Ni}^{++}] = [\text{C}^{++}] = 1.5 \text{ M}$$

$$\therefore E_{\text{cell}}^{\circ} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{1.5 \times 1}{1 \times 1.5}$$

$$\text{or, } E_{\text{cell}}^{\circ} = E_{\text{cell}}^{\circ} - 0$$

$$\therefore E_{\text{cell}}^{\circ} = 0.59 \text{ V.}$$

13. The K_a of propanoic acid is 1.34×10^{-5} . What is the pH of a solution containing 0.5 M propanoic acid and 0.25 M sodium propionate? What will be the pH of this solution after 0.1M HCl has been added to the buffer? [2068 Magh]

Ans: Given, K_a of propanoic acid = 1.34×10^{-5}

$$\therefore pK_a = -\log[1.34 \times 10^{-5}] = 4.87$$

$$[\text{C}_2\text{H}_5\text{COOH}] = 0.5 \text{ M}$$

$$[\text{C}_2\text{H}_5\text{COONa}] = 0.25 \text{ M}$$

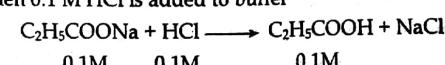
$$\text{pH of buffer} = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= pK_a + \log \frac{[\text{C}_2\text{H}_5\text{COONa}]}{[\text{C}_2\text{H}_5\text{COOH}]}$$

$$= 4.87 + \log \left(\frac{0.25}{0.5} \right)$$

$$= 4.57$$

When 0.1 M HCl is added to buffer



0.1M 0.1M 0.1M

$$\text{Total concentration of acid } [\text{C}_2\text{H}_5\text{COOH}] = 0.5 + 0.1 = 0.6 \text{ M}$$

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Concentration of Salt $[C_2H_5COONa] = 0.25 - 0.1 = 0.15 \text{ M}$

$$\begin{aligned} p^H &= p_{K_a} + \log \frac{[\text{salt}]}{[\text{acid}]} \\ &= 4.87 + \log \left(\frac{0.15}{0.6} \right) \\ &= 4.87 - 0.6 \\ &= 4.268 \end{aligned}$$

14. Derive Henderson equation for buffer solution. What is the p^H of resulting mixture obtained by mixing of 100CC of 0.2N HCl and 50CC of 0.5M ammonia solution, K_b for ammonia is 1.8×10^{-5} .

[2070 Chaitra]

Ans: For derivation: See theory part.

Numerical part:

Given,

$$\begin{aligned} \text{Volume of HCl} (V_1) &= 100 \text{ ml}, \\ \text{Strength of HCl} (S_1) &= 0.2 \text{ N} = 0.2 \text{ M} \\ \text{Volume of NH}_3 (V_1) &= 50 \text{ ml} \\ \text{Strength of NH}_3 (S_2) &= 0.5 \text{ M} \\ K_b \text{ for ammonia} &= 1.8 \times 10^{-5} \\ pK_b &= -\log [1.8 \times 10^{-5}] = 5.25 \end{aligned}$$

$$\begin{aligned} \text{Here, Total volume } (V_{\text{mix}}) &= V_1 + V_2 \\ &= 100 + 50 = 150 \text{ ml} \end{aligned}$$

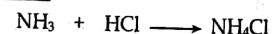
For HCl

$$[HCl] = \frac{V_1 \times S_1}{V_{\text{mix}}} = \frac{100 \times 0.2}{150} = 0.1333 \text{ M}$$

For NH₃

$$[NH_3] = \frac{V_2 \times S_2}{V_{\text{mix}}} = \frac{50 \times 0.5}{150} = 0.16667 \text{ M}$$

Reaction:



1 Vol. 1 Vol. 1 Vol.

0.1333M 0.1333M 0.1337M

$$\therefore [NH_3] = 0.1667 - 0.1333 = 0.0334 \text{ M}$$

$$\therefore [NH_4Cl] = 0.1333 \text{ M}$$

Now, Using Henderson's equation,

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

Electro-Chemistry and Buffer ... 27

$$\begin{aligned} &= 5.25 + \log \left(\frac{0.1333}{0.0334} \right) \\ &= 5.25 + 0.601 \\ &= 5.851 \\ \therefore p^H &= 14 - p^{OH} \\ &= 14 - 5.851 \\ &= 8.149 \end{aligned}$$

15. How can you measure the standard reduction potential of Zn electrode? Hydrogen electrode at 1 atm is connected with Zn electrode in which the emf of the cell is found to be 0.61 V at 25°C. If $[Zn^{2+}] = 1.0 \text{ M}$. Calculate H^+ in hydrogen electrode. [2070 Chaitra]

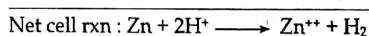
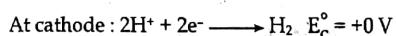
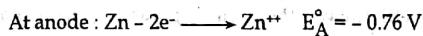
Ans: For 1st part: see the theory portion.

2nd part: Numerical part

Given,

$$\begin{aligned} E_{\text{cell}} &= 0.61 \text{ V} \\ [Zn^{2+}] &= 1.0 \text{ M} \\ [H^+] &=? \end{aligned}$$

The electrode reaction can be given as:



$$\begin{aligned} \therefore E_{\text{cell}}^\circ &= E_C^\circ - E_A^\circ \\ &= 0 - (-0.76) \\ &= +0.76 \text{ V} \end{aligned}$$

Now, using Nernst equation:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^\circ - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[H^+]^2} \\ \text{or, } 0.61 &= 0.76 - \frac{0.0591}{2} \log \frac{1.0}{[H^+]^2} \\ \text{or, } \frac{0.0591}{2} \log \frac{1.0}{[H^+]^2} &= 0.76 - 0.61 \\ \text{or, } 0.0295 \log \frac{1.0}{[H^+]^2} &= 0.15 \\ \text{or, } [H^+]^2 &= 8.228 \times 10^{-6} \\ \therefore [H^+] &= 2.8085 \times 10^{-3} \text{ M} \end{aligned}$$

16. What is buffer solution? Calculate the pH of 500CC of 0.2M CH₃COOH solution when 2gm of sodium acetate is added [K_a for CH₃COOH = 1.8 × 10⁻⁵] [TU 2071 Shrawan]

Ans: For definition See theory part.

Given,

Volume of solution = 500 ml

Strength of acid [CH₃COOH] = 0.2M

Weight of salt CH₃COONa = 2gm

$$\text{Molarity of CH}_3\text{COOH} = \frac{2}{\frac{60}{87}} = 0.0488 \text{ M}$$

K_a for CH₃COOH = 1.8 × 10⁻⁵

$$\therefore P_{K_a} = -\log(1.8 \times 10^{-5}) = 3.715$$

$$\begin{aligned} \therefore \text{pH of solution} &= P_{K_a} + \log \frac{[\text{salt}]}{[\text{acid}]} \\ &= 3.745 + \log \left(\frac{0.0488}{0.2} \right) \\ &= 3.132 \end{aligned}$$

17. What is Daniell cell? Answer the following question using equation (a) and (b)

$$(a) \text{Fe}^{++} (0.2 \text{M}) = \text{Fe}^{+++} + e (0.1 \text{M}), E^{\circ} = -0.77 \text{ V}$$

$$(b) \text{Cu}^{++} (0.3 \text{M}) + 2e = \text{Cu}, E^{\circ} = -0.34 \text{ V}$$

(i) Net cell reaction

(ii) Spontaneity of redox reaction

(iii) Cell notation

(iv) Emf of cell.

[TU 2071 Shrawan]

Ans: Daniell cell: See theory part.

Numerical:

$$\text{At anode: Cu} - 2e \longrightarrow \text{Cu}^{++}, E_A^{\circ} = 0.34 \text{ V}$$

$$\text{At cathode: Fe}^{+++} + e \longrightarrow \text{Fe}^{++} \times 2, E_C^{\circ} = 0.77 \text{ V}$$

$$\text{Net cell reaction: Cu} + 2\text{Fe}^{+++} \longrightarrow \text{Cu}^{++} + 2\text{Fe}^{++}$$

$$(i) \text{Net cell reaction: Cu} + 2\text{Fe}^{+++} \text{ Cu}^{++} + 2\text{Fe}^{++}$$

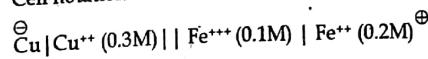
$$E_{\text{cell}}^{\circ} = E_C^{\circ} - E_A^{\circ}$$

$$= 0.77 - 0.34$$

$$= 0.43 \text{ V}$$

(ii) Here, the standard emf of cell is positive the reaction is spontaneous.

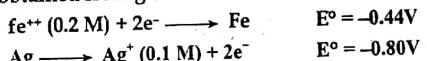
(iii) Cell notation:



Using Nernst equation

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log Q \\ &= 0.43 - \frac{0.0591}{2} \log \frac{[\text{Cu}^{++}][\text{Fe}^{++}]^2}{[\text{Cu}][\text{Fe}^{+++}]^2} \\ &= 0.43 - \frac{0.0591}{2} \log \left(\frac{0.3 \times (0.2)^2}{1 \times (0.1)^2} \right) \\ &= 0.43 - 0.0023 \\ &= 0.427 \text{ V} \end{aligned}$$

18. What is non-standard electrode potential? Calculate the emf of the cell obtained from given electrode reactions.



[IOE 2073]

Ans: Non-standard electrode potential:

The single electrode potential, when measured at non-standard condition (i.e. concentration of electrolyte is not equal to 1M and temp. is also not exactly 25°C), then it is called Non-standard electrode potential.

Numerical

See the solⁿ. of example on page no. 6.

19. Define buffer. Derive Hederson's equation for acidic buffer. Calculate the pH of the solⁿ. formed by adding 0.4 g of NaOH on 500 ml 0.2 M acetic acid. p_{Ka} for acidic acid = 4.74. [TU 2072]

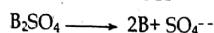
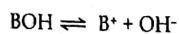
Ans: First part: See theory portion and

See the solⁿ. of example on page no. 19.

20. Derive Henderson's equation for basic buffer solution.

[TU 2072 Ashwin]

Ans: To derive the expression of Henderson's equation for basic buffer solution, we have to consider a weak base 'BOH' and its strong salt as B₂SO₄ which ionise as



Now, by law of mass action. Equilibrium constant 'K' is given as

$$K_b = \frac{[\text{B}^+] [\text{OH}^-]}{[\text{BOH}]} \quad \dots \dots \dots \text{(i)}$$

Where,

K_b = ionization constant of base.

Let $[\text{B}^+] = [\text{Salt}]$

$[\text{BOH}] = [\text{Base}]$

From eqn. (1), we get

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

Taking log on both sides

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

Taking -ve sign on both sides, we get

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

$p_{\text{OH}} = p_{\text{Kb}} + \log \frac{[\text{salt}]}{[\text{base}]}$ is required expression.

Chapter 2

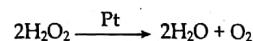
Catalyst

2.1. Catalyst

The substances which alters the rate of chemical reaction without undergoing any change in mass and composition at the end of the reaction is known as catalyst and the phenomenon is called catalysis.

For example,

platinum increases the rate of decomposition of hydrogen peroxide as



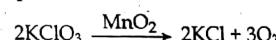
Here,

pt = catalyst

2.2. Classification of Catalysis

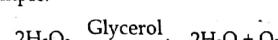
- a. Positive catalysis: The catalyst which increase the rate of reaction is known as positive catalyst and phenomenon is called positive catalysis.

Example:



- b. Negative catalysis: The catalyst which decreases the rate of reaction is called Negative catalyst and this phenomenon is known as negative catalysis.

Example:



- c. Auto catalysis: Sometimes one of the product of any reaction acts as a catalyst for further reaction. Thus, the product which catalyses the reaction is called auto catalyst. And the phenomenon in which one of the products of reaction itself acts as catalyst is known as auto catalysis.

Example:



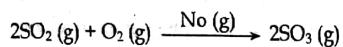
In this reaction, the product formed by hydrolysis of ethyl acetate, acetic acid acts as catalyst for reaction.

d. **Induced catalysis:** When one reaction influences the rate of other reaction which does not occur under ordinary condition the phenomenon is known as induced catalysis.

2.3.1 Homogeneous Catalysis

The phenomenon in which both catalyst and reactants are in same phase (i.e. gas/gas or solid/solid or liquid/liquid) is known as Homogeneous catalysis.

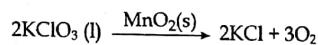
Example:



2.3.2 Heterogeneous Catalysis

The phenomenon in which the reactants and catalyst both are in different phase (i.e. like solid/liquid, gas/liquid etc.) is known as heterogeneous catalysis.

Example:



2.4 Catalytic Promoters

The substance which is not a catalyst itself but promotes the activity of a catalyst is known as catalytic promoters.

Example:

In the process of manufacture of ammonia, AS_2O_3 is used for Fe catalyst as promoters.

2.5 Catalytic poisoning

The substance which blocks the activity of catalyst is known as catalytic poison and such process is known as catalytic poisoning. For example: In process of manufacture of NH_3 , Heber's process, H_2S gas acts as poison.

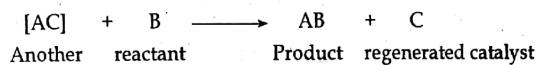
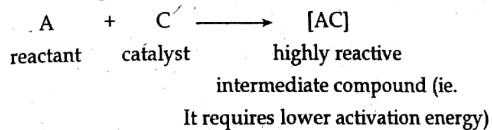
Note: Activation Energy:- Every substance or reactants need minimum amount of energy to make chemical reaction. Thus, the molecules do not react unless they attain a minimum amount of energy required to make a chemical reaction is known as the activation energy.

2.6 Theory of Catalysis

2.6.1 Intermediate Compound Formation Theory

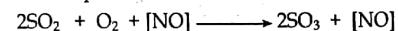
According to this theory, a catalyst initially combines with one of the reactants forming an intermediate compound. This intermediate compound is highly reactive. Hence it reacts with the second reactant to form the product and thereby the catalyst is regenerated.

Let a reaction between two reactants A and B in presence of a catalyst C. According to this theory, the reactions take place as

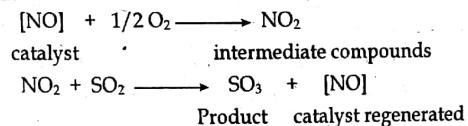


Lets us take an example to clear the concept about this theory.

Example: Catalytic oxidation of SO_2 in presence of $[\text{NO}]$ as catalyst in the chamber process for manufacture of sulfuric acid.

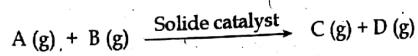


Mechanism



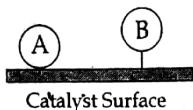
2.6.2 The Adsorption Theory

This theory mainly explain the mechanism of heterogeneous catalytic processes, specially those reactions between gaseous reactants catalysed by a solid catalyst. The reaction is initiated by adsorption of the reactant molecules on the surface of the catalyst. According to adsorption theory, for a general heterogeneous catalytic reaction such as:

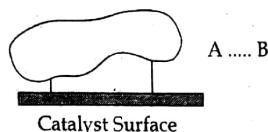


This theory involves mainly four steps.

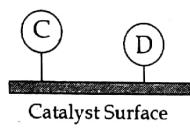
Step 1: Adsorption of reactant molecules on the catalytic surface by weak Vander waal force.



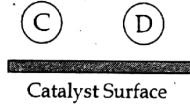
Step 2: Formation of an unstable and intermediate activated complex.



Step 3: Decomposition of the unstable activated complex.

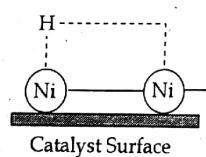


Step 4: Desorption of the stable products.

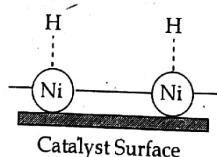


Example: Let take stepwise mechanism for the hydrogenation of ethene to ethane in presence of Ni catalyst.

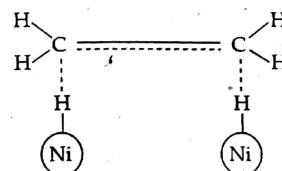
Step 1: Adsorption of hydrogen molecules on the catalyst surface due to residual valence bonds of Ni atoms.



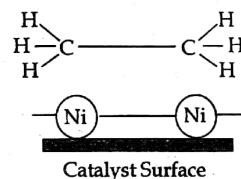
Step 2: The bond length of H-H bond is lesser than the bond length Ni-Ni, the H-H bond is stretched, weakened and hence broken into atoms.



Step 3: H atoms are attached to ethene molecules by partial chemical bonds, thus forming an unstable activated complex.



Step 4: The unstable activate complex is decomposed to the product (ethane) and the catalyst surface is released.



2.7 Application of Catalyst

- Catalyst is used to manufacture of ammonia in industry.
- Catalyst can be used to manufacture of chlorine.
- Used to manufacture of H_2 from water gas and steam.
- Use to manufacture of H_2SO_4 acid, HNO_3 acid.
- Catalyst is also used to manufacture of vegetable oil.

Exam Questions Solutions

1. Show your acquaintance to homogeneous and heterogeneous catalysis. Describe the intermediate compound formation theory of catalysis. [TU 2072 Ashwin]

Ans: Homogeneous & heterogeneous catalysis

See theory portion.

2nd part: See theory portion.

2. What is autocatalysis? Distinguish between positive and negative catalysis with examples. How does poison paralyze the activity of catalyst. [TU 2073 & 2074 P.U. Back]

Ans: 1st part:

See the (theory portion) definition of autocatalysis.

2nd part:

See the part of positive and negative catalyst.

3rd part:

See the part of positive of catalytic poisoning.

- 3.** What are the catalytic promoter and catalytic poison? Explain their activity on the basis of adsorption theory of catalysis. [2071 Shrawan]

Ans: Catalytic promoter:

The substance which is not a catalyst itself but promotes the activity of a catalyst is known as catalytic promoters.

Example:

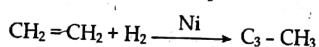
In the process of manufacture of ammonia, AS_2O_3 is used for Fe catalyst as promoters.

Catalytic poisoning:

The substance which blocks the activity of catalyst is known as catalytic poison and such process is known as catalytic poisoning, for example: In process of manufacture of NH_3 , Heber's process, H_2S gas acts as poison.

Activity of promoter

The promoter may increase the number of peaks and cracks on the surface of the host lattice of the catalyst and thus increases the number of defects. It helps, to increase the concentration of adsorbed reactant molecules on the surface of the catalyst thereby increase the rate of reaction. According to adsorption theory, reactants gets adsorbed by catalyst (promoter) and then activated complex is formed which is highly unstable. After that, activated complex gets rearranged and forms product and then product desorbs from surface of catalyst (promoter) and gives suitable final product. The example of Hydrogenation of ethene in presence of Ni catalyst is shown as



Activity of catalytic poison

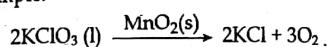
Poisons are adsorbed on the surface of the catalyst instead of reactant molecules, which will reduce the activity of catalyst by decreasing the concentration of the reactant. The activity of Ni catalyst in the reaction between ethene and hydrogen is paralyzed by CO molecular because it has greater affinity of adsorption.

- 4.** What is heterogeneous catalysis? Giving a suitable example. Explain the mechanism of heterogeneous catalysis write two criteria for choosing a catalyst for industrial purpose. [2070 Chaitra]

Ans: Heterogeneous catalysis:

The phenomenon in which the reactants and catalyst both are in different phase (i.e. like solid/liquid, gas/liquid etc.) is known as heterogeneous catalysis.

Example:



Mechanism:

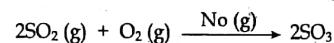
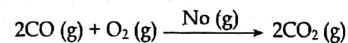
See the theory part (i.e. theory of catalysis) 2.6.2.

- 5.** Write a short notes on homogeneous catalysis. [2068 Magh Back]

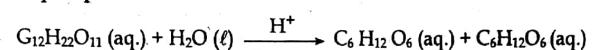
Ans: Homogeneous catalysis

The chemical reaction in which the catalyst and the reactants are in the same phase is called homogeneous catalysis. In this system, catalyst is thoroughly mixed with reactants. Some examples of homogeneous catalysis are given below:

Gas phase



Liquid phase



- 6.** (a) Give an account how a catalyst increase the speed of a reaction. [2070 Magh]

Ans: For any reaction of completion to give product reactant must have effective collision between reactant. This means reactants must have collision with a certain minimum amount of kinetic energy called as activation energy.

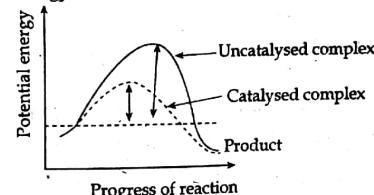
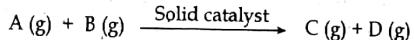


Fig: Activation energy graph

From the figure, we can see that the reactant has energy before crossing the barrier known as activation energy to give product with lower energy than reactant. And as shown in the figure of uncatalysed reaction has higher activation energy than catalysed reaction. Therefore, catalyst lowers the activation energy of reactants by providing an alternative path of reaction with lower activation energy and rate of reaction is faster when activation energy is low. It is cleared that the catalyst increase the speed of reaction.

- (b) Describe the adsorption theory of catalysis with a suitable example. [2070 Magh]

Ans: This theory mainly explain the mechanism of heterogeneous catalytic processes, specially those reactions between gaseous reactants catalysed by a solid catalyst. The reaction is initiated by adsorption of the reactant molecules on the surface of the catalyst. According to adsorption theory, for a general heterogeneous catalytic reaction such as:



7. What do you mean by catalytic poisoning? Explain the adsorption theory of catalysis with an example. [TU 2070 Bhadra]

Ans: Catalytic poisoning:

The substance which blocks the activity of catalyst is known as catalytic poison and such process is known as catalytic poisoning. For example: In process of manufacture of NH_3 , Heber's process, H_2S gas acts as poison.

2nd part: See the theory portion.

8. Explain the following terms

- (a) Homogeneous catalysis
- (b) Catalytic poisoning
- (c) Promoters

Ans: See the theory portion.

[TU 2069 Bhadra]

9. What is meant by catalysis? Point out its importance. Discuss intermediate compound formation theory. [2068 Bhadra]

Ans: Catalysis:

See theory parts.

Its importance

- (i) Catalyst control rate of reaction.
- (ii) Energy and time can be saved by use of catalysis.
- (iii) It prevents explosive kind of fast reaction.
- (iv) It is regenerated again and can be used again and again.
- (v) It increases the rate of reaction if original process is slow.

Intermediate compound formation

See theory portion.

10. What is meant by homogeneous catalysis? Describe the intermediate compound formation theory of catalysis with a suitable example list the criteria for choosing a catalyst for industrial application. [2067, 2070]

Ans: Homogeneous catalysis

See theory portion.

Intermediate compound formation theory

See theory part on 2.6.1.

Criteria for choosing a catalyst for industrial application

- Catalyst should be economic.
- It should be stable.
- It should be less poisoning.
- It should be easily available.
- it should give desired product as major product.

Chapter 3

Environmental Chemistry

3.1 Air pollution

Air pollution may be defined as the presence in the outdoor atmosphere of one or more contaminants or combination thereof in such quantities and of such duration as may be, or may tend to be injurious to human, plant or animal life.

3.2 Air Pollutant

(a) According to origin

(i) Primary pollutants

CO, NO_x, SO₂ and hydrocarbons.

(ii) Secondary pollutant

Those pollutants which are derived from primary pollutants due to chemical or photo chemical reactions. e.g.- ozone, peroxy-acetyl nitrate (PAN), photo -chemical smog etc.

(b) According to chemical composition

(i) organic pollutants e.g.- Hydrocarbons, aldehydes, ketones, amines and alcohols.

(ii) Inorganic pollutants:

Carbon compounds (e.g. CO and Carbonates)

Nitrogen compounds (e.g. NO_x and NH₃)

Sulphur compounds (e.g. H₂S, SO₂, SO₃ & H₂SO₄)

Halogen compounds (e.g. HF, HCl & metallic fluorides)

Oxidizing agents (e.g. O₃).

Inorganic particles (e.g. flyash, silica, asbestos and dusts from transport, mining, metallurgical and other industrial activities)

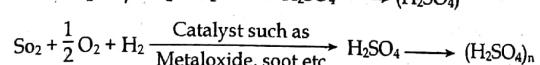
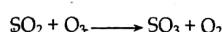
(c) According to state of matter:

(i) Gaseous pollutants: CO, NO_x and SO₂.

(ii) Particulate pollutants: Smoke, fumes, dust, mist fog, smog and sprays.

1. Sulphur dioxide (SO₂)

Combustion of any sulphur-bearing material produces SO₂ accompanied by a small quantity of SO₃. This mixture is usually denoted as SO_x. Nearly 67% of the global SO_x pollution is due to volcanic activity. It is mainly formed due to combustion fuels like petroleum & coal.



Gerosol

Effects: Increased breathing rate, suffocation, aggravation of asthma, respiratory irritation of throat, sensory irritation of throat and eyes.

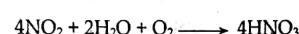
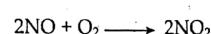
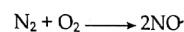
Remedy:

- (i) Removing of SO_x from fuel gases before letting them out into the atmosphere.
- (ii) Removing of sulphur from fuels used for combustion.
- (iii) Utilizing low sulphur fuels.
- (iv) Generation of power by alternative energy.

2. Oxides of Nitrogen (NO_x)

Out of the eight possible oxides of nitrogen, only N₂O, NO and NO₂ are the important constituents of the atmosphere.

Sources: Automobile exhausts, coal-fired and gas-fired furnaces, boilers, explosive industry, fertilizer industry, manufacture of HNO₃ etc.



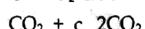
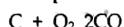
Effects: Respiratory irritation, headache, bronchitis, pulmonary emphysema, lungs problem (oedema), loss of appetite, corrosion of teeth.

Remedy:

- (i) Use of two stage catalytic converters in industry.
- (ii) Combustion of fuel in power plants with excess supply of air at relatively low temperature.

3. Carbon monoxide (CO)

The atmospheric air contains 0.1 to 0.12 ppm of carbon monoxide.



Sources: Incomplete combustion of fuels, automobile exhaust, jet engine emissions, blast furnace, mines and tobacco smoking.

Effects: Toxicity, blood poisoning, increased prone to accidents, CO combines with hemoglobin, is useless for respiratory purposes and hence leads to death.

Remedy:

- (a) Modification of engine design
- (b) Fuel modification and development of substitute fuels
- (c) Treatment of exhaust gases
- (d) Exhaust gas recirculation

4. Particulates

Particulates (solid or liquid) are important constituents of atmosphere. About zero million tones of particulate matter per year released from natural agencies such as volcanic eruptions, wind and dust storms, salt spray etc. Manmade activities such as burning of wood, coal, oil and gaseous fuels, industrial activities etc.

Fine particulate matter having size $<3\text{m}$ which can penetrate through nose and throat, reach the lungs and cause breathing problems and irritation of the lung capillaries.

Particulates present in the atmosphere may influence the climate through formation of clouds and snow. They also may absorb solar radiation and reduce visibility.

Particulate matter can be removed from gaseous effluents from industries with help of devices such as cyclone collectors, settling chambers, wet scrubbers and electrostatic precipitators.

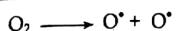
Ozone

Ozone layer is the layer of pale blue gas which is mainly found in stratosphere. This gas is an allotrope of oxygen.

• Formation of ozone layer

It is a photochemical reaction in which O_2 molecule gets split into two nascent oxygen by UV rays then it again combines with O_2 which causes formation of O_3 molecule e.e. ozone.

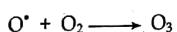
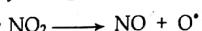
Reactions:



* O^\bullet = nascent oxygen



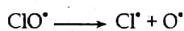
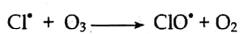
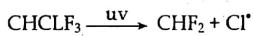
It is also formed in lower atmosphere due to decomposition of NO_2 gas by sunlight.



Depletion of ozone layer

It is also a photochemical reaction in which ozone layer gets destroyed by following gases CO, NO, NO_2 , CH_4 . The main gases that causes depletion of ozone layer are CFC like CFC_3 , $CHClF_3$, CF_2Cl etc.

Process: CFC are chlorine containing compounds which absorbs UV rays from the sun and decomposes to give Cl atom which destroys ozone.

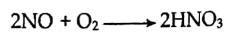
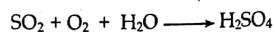


Acid Rain

As the name refers acid rain that is the rain water which contains small amount of acid. It happens due to presence of CO_2 in atmosphere which gets dissolved into rain water during raining thus formation of acidic rain. Its pH value is 5.63.



The acid rain mainly causes due to polluted environment which contains oxides of sulphur SO_x and nitrogen NO_x . During raining these oxides are dissolved in rain droplets resulting in the formation of sulphuric acid and nitric acid and the mixture of these acids and water is called acid rain. Its pH value is lower than 5.7.



Effects:

1. Damage to buildings and moments
2. Acidification of soil
3. Potential effects on aquatic systems
4. Corrosive damage to steel, zinc, oil based paints and automobile coatings.
5. Effects on human health.

Water Pollution

Water pollution is the contamination of water bodies (e.g. lakes, rivers, oceans, aquifers and ground water). This form of environmental degradation occurs when pollutants are directly or indirectly discharged into water bodies without adequate treatment to remove harmful compounds.

Sources or parameters

Following are the sources or parameters of water pollution:

(i) **Natural parameter**

Water gets polluted from natural wastes like decomposed animals and degraded / weathered product of agricultures.

(ii) **Human activities**

This parameter includes domestic activities and industrial activities:

(a) **Domestic activities:** It includes the waste water which contains human faces, kitchen wastes, organic water solution that helps in breeding of bacteria and fungi.

(b) **Industrial activities:** It includes the waste from factory and refineries. These waste contains several chemical that drained into streams which cause pollution. These type of waste decrease the BOD & COD of water.

(iii) In metropolitan city the surface runoff rain water also gets discharged into rivers and cause water pollution.

Causes of water pollution

- (i) Mixing of organic decomposed waste into river.
- (ii) Use of insecticides and pesticides in agriculture.
- (iii) Untreated sewer water discharging into rivers.
- (iv) Untreated management or surface runoff in urban areas.

Effects

1. It cause water based disease like typhoid, cholera, dysentery, eye disease etc.
2. use of pesticides and insecticides although it increases the crop production but it effect on human health.
3. The eco-system disturbed.
4. Aquatic life/system gets destroyed.

Remedies

1. Use of sewer treatment plant before it discharges into water bodies.
2. Control use of fertilizer, insecticides and pesticides.
3. Treatment of industrial waste water.
4. Managed surface runoff in urban areas.

Soil Pollution

Soil pollution as part of land degradation is caused by the presence of xenobiotic (human-made) chemicals or other alteration in the natural soil environment. It is typically caused by industrial activity, agricultural chemicals or improper disposal of waste.

Cause

1. Industrial activity
2. Agricultural activity
3. Waste disposal
4. Accidental oil spills
5. Acid rain

Effects

1. Effects on human health
2. Effect on growth of plants and crops
3. Decreased soil fertility
4. Toxic dust
5. Change in soil structure

Remedies

1. Treatment of industrial waste.
2. Control use of fertilizer, pesticides & insecticides in crop production.

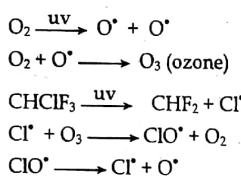
3. Control of water pollution.
4. Managed and durable construction of oil reservoir tanks.
5. Control of air pollution.
6. Treatment of waste water.

Exam Question Solutions

1. (a) What are chlorofluorocarbons? Give their photolytic reaction in the upper atmosphere. [TU 2067 Asadh]

Ans: Chlorofluorocarbons are the derivatives of methane, with F, Cl and hydrogen atom forming compounds like CFCl_3 , CHClF_3 , CF_2Cl etc. which also causes depletion of ozone layer.

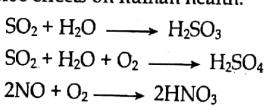
In the upper atmosphere there is depletion of ozone layer due to these gases.



- (b) Why oxides of sulphur and nitrogen are assumed as air pollutants?

[TU 2067]

Ans: The oxides of sulphur and nitrogen are assumed as air pollutants because the oxide SO_x and NO_x cause air pollution acid rain and have adverse effects on human health.



2. Point out the four major pollutants of water their adverse effect on human health and also mention their possible remedies. [TU 2067 Ashadh]

Ans: Following are the four major water pollutants:

1. Industrial wastes
2. Sewer water
3. Agriculture waste
4. Suspended solid and sediments

Effects

1. It causes water based diseases like typhoid, cholera, dysentery, eye burn etc.
2. Use of pesticides and insecticides has adverse effect on human health and causes malaria, kalaazar and typhoid.
3. Aquatic life get destroyed.
4. The eco-system get disturbed.

Remedies

1. Use of sewer treatment plant before it discharges into water bodies.
2. Control use of fertilizer, insecticides and pesticides.
3. Treatment of industrial waste water.
4. Managed surface runoff in urban areas.

3. Brief discusses sources of organic and inorganic substances responsible for water pollution. Point out adverse effects and possible remedies. [TU 2068 Bhadra]

Ans: Organic sources of water pollution

The organic sources includes:

- (a) **oxygen demanding wastes**
These include domestic and animal sewage, bio-degradable organic and food wastes also agricultural run-off.
- (b) **Disease causing waste**
These include pathogenic micro organism.
- (c) **Synthetic organic compounds**
These are the man made material such as synthetic pesticides, synthetic detergents, food additives, insecticides, paints, synthetic fiber etc.
- (d) **Sewage and agriculture runoff**
Sewage and runoff from agricultural lands supply plant nutrients which may stimulate the growth of algae and other aquatic weeds in the receiving water bodies. This unwieldy plant growth results in the degradation of the value of the water body.

Inorganic pollutions

These pollutants includes mineral acids, inorganic salts, finely divided metals or metal compounds, trace elements, cyanides, sulphates, nitrates and complexes of metal with organics present in natural water.

Adverse effect

- Causes various diseases like typhoid, cholera, dysentery etc.
- Aquatic life get destroyed.
- Eco-system get disturbed.
- Soil pollution

Remedies

- Waste water treatment.
- Proper treatment of industrial waste
- Control use of fertilizer, insecticides & pesticides.

4. (a) What is global warming? Give its cause and consequences.

[TU 2069 Bhadra]

Ans: Global warming also referred to as climate change, is the observed century scale rise in the average temperature of the Earth's climate and its related effects.

Causes

- Mainly due to air pollutants like CO₂.
- Unmanaged running of large industry and refineries.
- Power plant running
- Deforestation.
- High range of CFC production
- Ozone layer depletion.

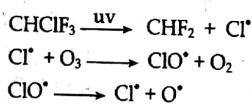
Consequences

- Average temperature rise of earth's climate.
- Melting of Northern & Southern ice bergs.
- Loss of eco-system
- Adverse effects on human health.

(b) What is photochemistry behind ozone layer depletion? In the ozone layer in presence of UV rays CFC releases free Cl^{*} atom which catalytically dissociate O₃ molecules.

[TU 2069 Chaitra]

Ans: CFC are chlorine containing compounds which absorbs UV rays from the sun light and decomposes to form Cl^{*} atom which destroy 5 ozone



It is supposed that one Cl^{*} atom can destroy 100000 ozone molecules.

5. Point out the sources of radioactive substances responsible for environmental pollution. Give their adverse effects and protective measures. [TU 2069 Bhadra]

Ans: The radioactive pollutants may originate from the following anthropogenic activities:

- Mining and process of ores e.g. Uranium tailings.
- Increasing use of radioactive isotopes in research, agriculture, industrial and medical e.g. I¹³¹, P³², CO⁶⁰ etc.
- Radioactive materials from testing and use of nuclear weaponry e.g. Sr⁹⁰, Cs¹³⁷.
- Radioactive materials from nuclear power plants and nuclear reactors e.g. Sr⁹⁰, Cs¹³⁷ etc.

Adverse effect

- Sr⁹⁰ which emanates from testing of nuclear weapons, accumulates in bone and teeth and cause serious disorders in human being.
- Skin problems.
- Decrease in human fertility system & genetic disorder.
- Embalance of environmental health.

Remedies

- Use of high protective material in these type of plant.
- Discouraging the use of radio isotopes.
- Use of lead jacket in effected radioactive area.

6. Briefly discuss any two sources of organic and inorganic substances responsible for water pollution point out their possible remedies.

[TU 2069 Chaitra]

Ans: See the solution of TU 2068 Bhadra on page no 48.

7. How do exhaust of internal combustion engine pollute air. Give the possible remedies.

We all know, the internal combustion engine are run by fuel gases and fuel oil which produces air pollutant gases like CO, NO & SO₂ which air pollution. These pollutants present in air causes lungs irritation and respiratory problems to human and animal as well.

Possible remedies

- Modification of IC engine
- Decreasing of sulphur content in fuels.
- Plantation.

50 ... A Refresher Solution of Eng. Chemistry (B.E. | Yr | Part)

8. What is the photochemistry behind ozone layer depletion?

Ans: See answer of Q.4(b), TU 2068 Bhadra on page 48.

9. What are major gases responsible for causing green house effect? How are they released in atmosphere? Give an account of the global effort to control the release of these gases.

Ans: The gases that are responsible for the green house effect are CO_2 , water vapour, CH_4 and manmade chlorofluorocarbons (CFC's).

Carbon dioxide is released by volcanoes, burning of plants as well as human activities such as deforestation and combustion of fossil fuels. Methane is released from coal mines, decomposition of organic matters.

Chlorofluorocarbons (CFC's) are used as coolants in refrigeration, propellants in aerosol sprays etc.

Globale effort to control these gases

1. Control use of fossil fuels.
2. Plantation
3. Pollution control
4. Minimization in use of old IC engines vehicles.
5. Proper treatment of industrial fog, smoke etc.

10. What are the main source of water pollution? Write the effect of water pollution on mankind. Mention the measures to control water pollution. [TU 2069 Bhadra]

Ans: Refer theory part

11. Point out the major sources of soil pollution, their effect and their possible remedies. [TU 2070 Bhadra]

Ans: Sources of soil pollution

- (1) Industrial activity
- (2) Agricultural activity
- (3) Waste disposal
- (4) Accidental oil spills
- (5) Acid rain

Effects

- (1) Effects on human health
- (2) Effects on growth of plant and crops.
- (3) Decreased soil fertility
- (4) Toxic dust
- (5) Change in soil structure

Remedies

- (1) Treatment of industrial waste.
- (2) Control use of fertilizer, insecticides pesticides.
- (3) Control of water pollution.
- (4) Managed and durable construction of oil tanks.
- (5) Treatment of waste water before disposal to soil.

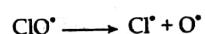
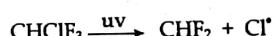
12. Give four familiarity with water pollution. Write CFC involves for ozone layer depletion and harmful effects. [TU 2070]

Ans: Water pollution means water contamination due to the disposal of waste water, use of fertilizer, agricultural runoff, acid rain, oil and other disease causing elements to water bodies.

Due to the water pollution it has adverse effect on human as well as animal life. It causes various water born disease like typhoid, cholera, dysentery etc to human.

CFC's are chlorine containing compounds which absorbs UV rays from sun and decomposes to give Cl atom which destroys ozone.

Reaction:



Harmful effect:

- (1) Globale warming
- (2) Due to free entry of solar radiation through holes of ozone layer causes skin cancer.
- (3) Increase green house effect.

13. Give an account on the sources of organic and inorganic substances responsible for water pollution with its adverse effects and possible remedies. [TU 2070 Magh]

Ans: See the answer Q.No. 3 (TU 2068 Bhadra) on page no 47.

14. What do you mean by soil pollution? Mention its major sources, adverse effect and possible remedies. [TU 2070 Magh]

Ans: Soil pollution as a part of land degradation is caused by the presence of xenobiotic (human-made) chemicals or other alteration in the natural soil environment. It is typically caused by the industrial activity, agricultural chemicals or improper disposal waste.

Second part:

Sources of soil pollution

- (1) Industrial activity
- (2) Agricultural activity
- (3) Waste disposal
- (4) Accidental oil spills
- (5) Acid rain

Effects

- (1) Effects on human health
- (2) Effects on growth of plant and crops.
- (3) Decreased soil fertility
- (4) Toxic dust
- (5) Change in soil structure

Remedies

- (1) Treatment of industrial waste.
- (2) Control use of fertilizer, insecticides pesticides.
- (3) Control of water pollution.
- (4) Managed and durable construction of oil tanks.
- (5) Treatment of waste water before disposal to soil.

15. What are the source of NO_2 and SO_2 pollutants in air? How do they play role in acid rain? Give two possible remedies of acid rain. [2068 Magh]

Ans: Sources of NO_2 are as follows

- Automobile exhaust
- coal fire and gas fired furnace

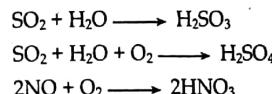
- boilers
- Explosive industries
- Fertilizer industry
- Manufacture of HNO_3

Sources of SO_2 are as follows:

- Combustion of coal
- Combustion of petroleum products
- Burning of refuse
- Petroleum industry
- Oil refining
- Power houses
- Sulphuric acid plants
- Metallurgical operations.

The SO_2 and NO_2 present in atmosphere combines with rain droplets during raining thus the formation of acid rain.

Reactions:



Remedies

- Control of air pollution
- Modification of IC engines

16. Write major sources of water pollution. How does CO_2 act as pollutants of the atmosphere? [2070, Chaitra]

Ans: First part: See theory part

Remaining part:

Carbon dioxide (CO_2) is the primary green house gas which is emitted from natural as well as human activities. CO_2 is naturally present in atmosphere but due to human activities its concentration is gradually increasing which causes alteration of environmental cycle. Now a day most of CO_2 is produced from fossile fuel combustion like coal, gas, petroleum etc.

Due to the increase in % of CO_2 in atmosphere increases green house effect and leads to rise in average temperature of earth's climate.

This pollution causes

- (i) Reduction of ozone layer
- (ii) Ecosystem change
- (iii) Increased extreme weather
- (iv) Sea level rise etc.

17. Discuss about the air pollution caused by oxides of nonmetals.

[TU.2071 Shrawan]

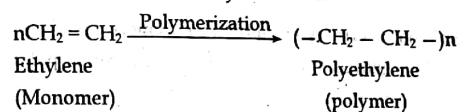
Ans: See theory part.

Chapter 4

Engineering Polymers

Introduction

The word "Polymer" is derived from two Greek words, Poly (Many) and mers (parts or units). A polymer is a large molecule formed by combining small molecules. The individual small molecules from which the polymers is formed are known as "Monomers" and the process by which the monomer molecules are linked to form big polymer molecule is called "Polymerization".



Synthetic Polymers

Addition polymers	Condensation polymers
1. Polymers that are formed by the combination or addition of monomers without formation of any other simple molecule. e.g. water, alcohol, Ammonia etc.	1. Formed by the condensation of monomers along with the formation of other simple molecule like water, alcohol, ammonia etc.
2. Monomers are unsaturated compounds. e.g. alkenes, alkynes and its derivatives.	2. Monomers are of different type.
3. Structure: simple chain or simple branch chain. $\begin{array}{c} 0 \\ \\ 0 \\ \\ 0 \\ \\ 0 \\ \\ 0 \\ \\ 0 \end{array}$	3. Structure: cross linked $\begin{array}{c} 0000000 \\ \\ 0 \\ \\ 0000000 \\ \\ 0 \\ \\ 0000000 \\ \\ 0 \end{array}$
4. Formed by one step reaction.	4. Formed by two step reaction.

5. Mostly thermoplastics (Recyclable)	5. Mostly thermosetting plastics.
6. May dissolve in organic solvent.	6. Does not dissolve in solvents.
7. Less brittle.	8. More brittle
8. E.g. Polythene, PVC, polystyrene etc.	8. E.g. Nylon 6, 6, Bekelite etc.

Inorganic Polymers

The molecules are linked with organic molecules like P, Si, S etc. In this kind of polymers, central atom is P, Si, S but other groups are organic group.

General characteristics of inorganic polymers

- (i) They generally melt but don't burn except polymer containing sulphur.
- (ii) They are cross linked so that makes them hard and brittle.
- (iii) They dissolve in polar solvent.

Classification of inorganic polymers

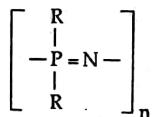
They are of following

- (1) Polyphosphazines
- (2) Sulphur based polymer
- (3) Silicones

(1) Polyphosphazines

These are the inorganic polymers which contain phosphorus as predominant atom i.e. as central atom.

Their general structure is



Where,

R = -Cl in poly phosphonitrile chlorides

R = -OCH₃ in polydimethoxy phosphazines

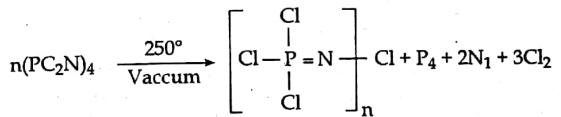
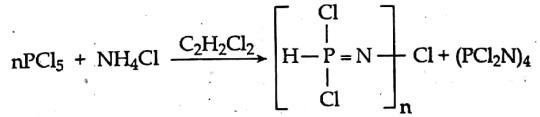
R = -OC₂H₅ in polydiethoxy phosphazines

Engineering application

- (i) Due to high flexibility used in elastic uses.
- (ii) Visible and transparent so used as glass still.
- (iii) Used in elastomers.

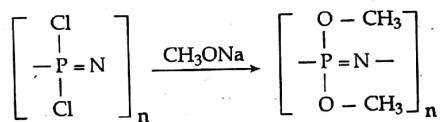
Polyphosphonitrile chloride (-R = -Cl)

They are prepared by heating cyclic tetramer in vacuum about 250° C.

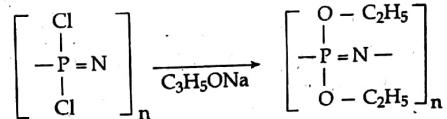


Polydimethoxy phosphazines and polydiethoxy phosphazines

They are prepared by the reaction of phosphonitride chloride with sodium methoxide and sodiummethoxide respectively.



CH₃ONa : Sodium methoxide



CH₃-CH₂-ONa : Sodium ethoxide

Uses: (i) They are used in thermopolymers.

(ii) They are used as electrical insulator.

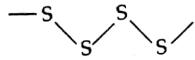
(2) Sulphur based inorganic polymers

They can be of two types

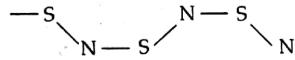
- (a) Linear chain polymers (b) Chalcogenide glass
- (a) Linear chain polymers: They are of two types

(i) Polymeric sulphur

They are polymer of pure sulphur which is prepared by the heating of rhombic sulphur above 165°C and plunging it in ice.

**(ii) Polymeric sulphur nitride (S.N.)**

The structure have bond angle 120° and bond length of 16 mm as shown in figure.

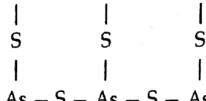
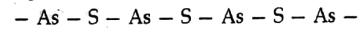


Uses: They are used for making super conductors.

(b) Chalcogenide glasses

These are the compound having cross linked structure with polyvalent elements like As, Ge, In etc. obtained from quenching of chalcogenite compound.

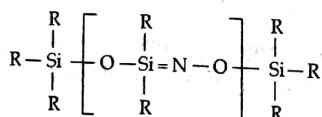
e.g. As_2S_3 .

**Engineering Application**

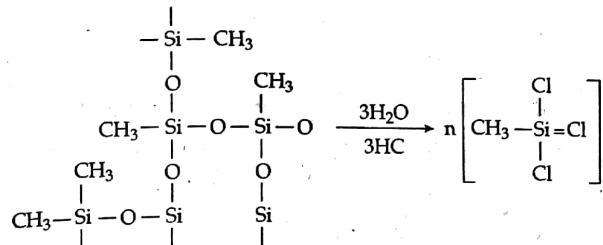
- (i) Construction of electronic devices like memory chip IC, microprocessor etc.
- (ii) Electronic display
- (iii) High energy particle detector multipliers
- (iv) Ultrasonic delay systems etc.

(3) Silicone Polymers

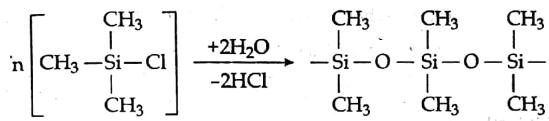
They have structure



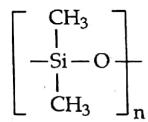
Preparation: They are prepared by reaction of $\text{R}-\text{x}$ or silicone halide with grignard reagents.

(a) Monomethyl Silicon trichloride**(b) Dymethyl silicones dichloride**

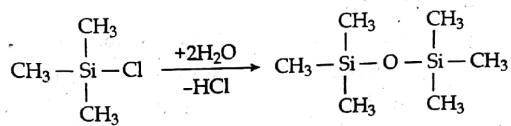
They are linear chain polymers.



Or

**(c) Trimethyl silicon choride:**

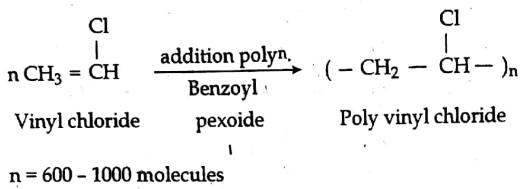
They stop the chains only. They are used as chain stopper.

**Uses:**

- (i) As electric insulators
- (ii) As adhesive in electric devices
- (iii) For plastic survery
- (iv) for making artificial heat value.

Preparation and Use of:**Poly vinyl chloride (PVC):**

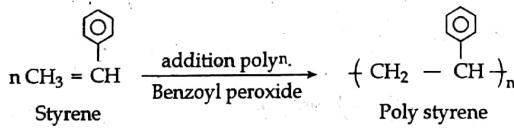
It is prepared by addition polymerization of vinylchloride in presence of benzoyl peroxide as catalyst.

**Uses:**

- (i) It can be used for insulating electronic and electrical goods. E.g. wire lamination
- (ii) Imitating leather goods. e.g. sole of shoes.
- (iii) PVC pipes, doors, tiles, toys etc.

2. Poly styrene

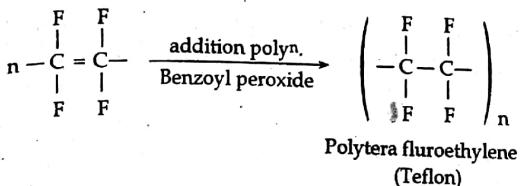
It is prepared by addition polymerization of styrene in presence of benzoyl peroxide as catalyst.

**Uses:**

- (i) Insulating agent
- (ii) Casing of TV, radio and other electronics devices.
- (iii) Manufacture of Kitchen wares e.g. glasses, plates, cups, food packing material, cosmetic bottles.

3. Poly Tetra Fluro Ethylene (PTFE or TEFLON)

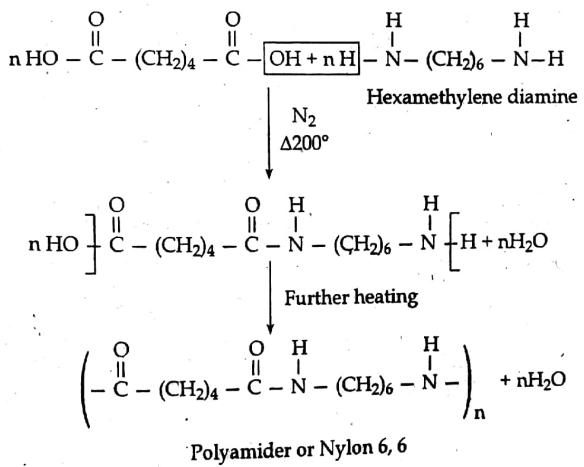
It is prepared by addition polymerization of tetrafluro ethylene in the presence of benzoyl peroxide as catalyst.

**Uses:**

- (i) Insulating agent.
- (ii) It is very though resistance to wear and tear and have low specific gravity so the mainly used for manufacture of gears, values of aircraft, gaskets etc.
- (iii) It has a self lubricating property so it is used for coating cooking utensils e.g. non-stick pans, pressure cooker, bowls etc.

4. Nylon 6, 6 (Poly amider)

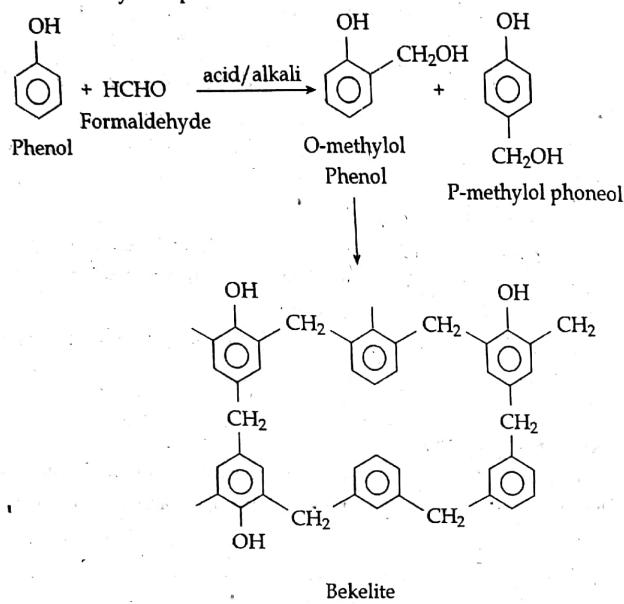
It is prepared by condensation polymerization of adipic acid and hexamethylenediamine in presence of nitrogen as catalyst heated to 200°C .

**Uses:**

- (i) Insulating material.
- (ii) Manufacture of ropes, fibers-textile, socks, stokings, bristles of brushes, tyres etc.

5. Bekelite

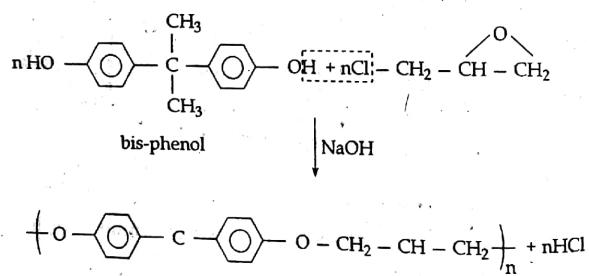
Bekelite is prepared by condensation polymerization of phenol and formaldehyde in presence of acid or alkali.

**Uses:**

- (i) Electrical insulator, switch, hoders.
- (ii) Handles of cooking utensils.

6. Epoxy Resin

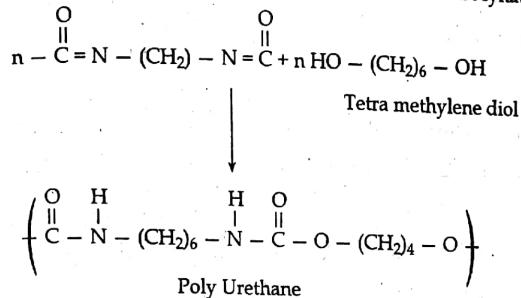
Epoxy resin is prepared by condensation polymerization of bis-phenol & epichlorohydrine in presence of alkali (NaOH) as catalyst heated to 60° .

**Uses:**

- (i) Used for surfacing road junction and highways to make skid resistant.
- (ii) It is used for lamination.
- (iii) Due to its polar nature it is used for joining metals and glasses.
- (iv) Insulating agent, encapsulation of electrical appliances.

7. Poly Urethane (PU)

It is prepared by rearrangement polymerization of di-isocyanate.

**Uses:**

- (i) Insulation, encapsulation.
- (ii) It acts as an elastomers so it is used for spander fiber for the manufacture of sports shoes, dress etc.
- (iii) It is used in biomedicals like vascular tubings, blood filters.
- (iv) It is also sued in coating, surfacing etc.

Conducting polymers

Conducting polymers or more precisely, intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conducting polymers is their procesability, mainly by dispersion conducting polymers are not generally thermoplastics.

Uses:

- (i) They can be used in rechargeable cell.
- (ii) They are used in LED which is energy saving
- (iii) They are also used in electro luminance displays like in mobile phone etc.
- (iv) They are also used in photo voltaic devices.

Bio-degradeable polymers

Bio-degradeable polymers are those polymers which undergoes degradation by biological process like enzymatic, balteriological or microbiological process. And all the natural polymers are biodegradable whereas most of the synthetic polymers are non-biodegradable so cause pollution. But synthetic polymers which are biodegradable are e.g. Poly caprolatone, polyaminotriazole, polyester polyglcoid.

Uses:

These polymers are used in medical works like sutures, orthopedic fixation, tissue cultures etc.

Fibre reinforced polymers (FRP)

Fibre reinforced polymers, also Fibre reinforced plastic, is a composite material made of a polymer matrix reinforced with fibre. The fibres are usually glass, carbon, or aramid, although other fibre such as paper or wood or asbestos has been sometimes used. The polymer is usually an epoxy, vinyl ester or polyester thermosetting plastic, and phenol formaldehyde resins are still in use. FRPs are commonly used in the aerospace, automotive, marine, and construction industry.

Uses:

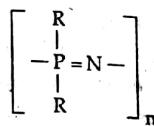
- (i) Used in aerospace, aircrafts, marine, automotive etc.
- (ii) Used in civil infrastructures such as bridges and buildings.
- (iii) Used in high performance resin system. Such as carbon nanotubes and nanoparticles.
- (iv) Used in concrete reinforcement and jacketing.

Exam Questions Solutions

1. Describe the preparation and uses of poly phosphazines and polymeric sulphur (Ps)_n. [TU 2067 Ashadh]

Ans: Polyphosphazines

these are the inorganic polymers which contain phosphorus as predominate atom. Their general structure is



Where,

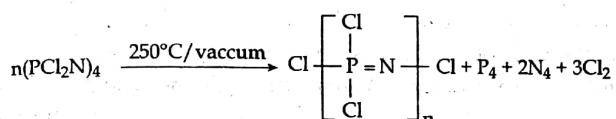
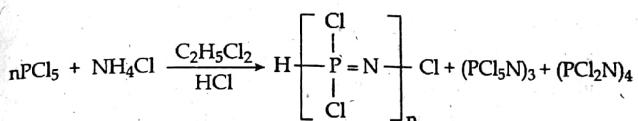
R = -Cl in poly phosphonitrile chlorides

R = -OCH₃ in polydimethoxy phosphazines

R = -OC₂H₅ in polydiethoxy phosphazines

Poly phosphonitrile chlorides

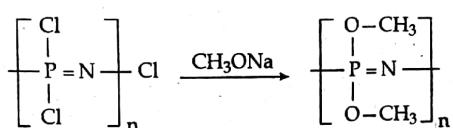
They are prepared by heating of cyclic teramer in vaccum about 250°C.



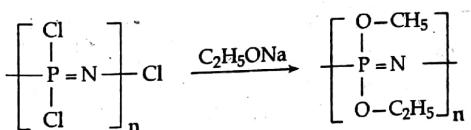
Chain polymer

Polydimethoxy phosphazines (R = -O - CH₃)

It is prepared by the reaction of phosphonitrile chloride with sodium methoxide (CH₃ONa).

Polydiethoxy phosphazines (R = -O - C₂H₅)

It is prepared by phosphonitrile chloride with sodium ethoxide.

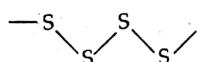


Use of polyphosphazines

- (i) Due to high flexibility used in elastic works.
- (ii) Visible and transparent so used as glass seal.
- (iii) Used in elastometers.
- (iv) Used for preparation of thermopolymers.

Polymeric sulphur

It is prepared by heating rhombic sulphur above 165°C followed by pouring molten mass so obtained in an ice bath. Then the solid mass is wash with CS_2 .



Uses:

- (i) Used in memory devices
- (ii) Used in ultrasonic delay lines
- (iii) High energy particle detectors multipliers

2. (a) What is chalcogenide glasses? Give their uses.

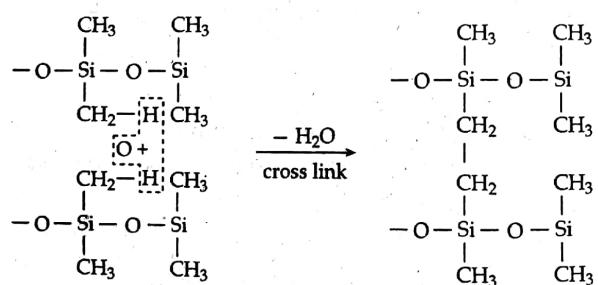
(b) Give the preparation and application of silicone rubbers.

[TU 2069 Chaitra]

Ans: (a) See theory portion

(b) Preparation of silicon rubbers

They are prepared by mixing high molecular weight of linear dimethyl / silicon polymer with filler like silica, carbon black etc. and peroxide containing curing agents oxygen of peroxide causes the formation of dimethyl bridge between methyl groups of adjacent chain.



Application

- (i) Manufacture of tyres
- (ii) Insulators of electric wires
- (iii) Forming artificial valves transfusion tubing and padding for plastic surgery.

3. Give the preparation and application of Bakelite and polyurethanes.

[TU 2068 Bhadra]

Ans: See theory part

4. What are the advantages of conducting polymers? [TU 2069 Chaitra]

Ans: See theory part

5. Write short note on:

- (a) Sulphur based polymers
- (b) Polyphosphazines

[TU 2069 Bhadra]

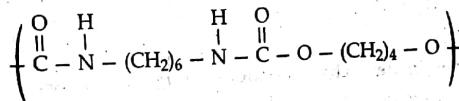
Ans: Refer to theory part.

6. What are monomers of:

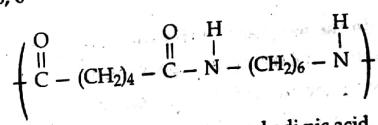
- (i) Polyurethane
- (ii) Nylon 6,6
- (iii) Bakelite
- (iv) Epoxyresin

[TU 2069 Bhadra]

Ans: (i) Polyurethane

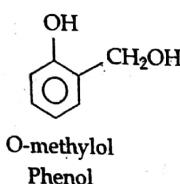


(ii) Nylon 6,6

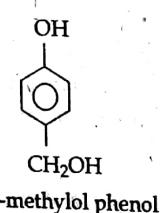


Hexamethylene diamine and adipic acid

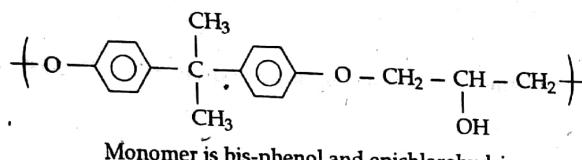
(iii) Bakelite



and



(iv) Epoxy resin



7. What are the engineering applications:

- (i) Polyvinyl chloride
- (ii) Conducting polymers

[TU 2069 Bhadra]

Ans: See theory portion

8. Write short note on

- (a) Chalcogenide glasses
- (b) Silicones

Ans: See theory part.

9. What are biodegradable polymers? Give the preparation and uses of epoxy resin and polystyrene.

[TU 2070 Bhadra]

Ans: See theory part

10. What are general characteristics of inorganic polymers? Describe the preparation and uses of polyphazines.

Ans: See theory part.

11. How do thermo plastic differ from thermo setting polymers. Give application of Bakelite and epoxy resin.

[TU 2070 Magh]

Ans: Following are the differences between thermo plastic and thermo setting polymers.

Thermo plastic polymers	Thermosetting plastic polymers
1. Formed by addition	1. Formed by condensation polymerization.
2. They have long chain structure.	2. They have three dimension.
3. They can be soften by heating.	3. They can't be soften by heating.
4. They dissolve in organic solvent.	4. They do not dissolve in solvents.
5. They can be reshaped.	5. They can't be reshaped.

Use of Bakelite

- Electrical insulator, switch, holders etc.
- Used in handles of cooking utensils
- Used in paint and varnishes.
- Uses of epoxy resin
- Used for surfacing road junction and highways to make skid resistant.
- It is used for lamination.
- Due to its polar nature it is used for coating metals and glasses.
- Insulating agent, in encapsulation of electrical appliances.

12. Give an account on chalcogenide glasses and polysulphur nitride.

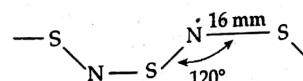
[2070 Chaitra]

Ans: Chalcogenide glasses

See theory part.

Polysulphur nitride

Polysulphur nitride $(SN)_n$ is nearly a planar chain of $(S-N)$ bond having 16 mm bond length



Its electrical conductivity at the room temperature is about 1200 to 3700 $\Omega^{-1} \text{ cm}^{-1}$ which increases 50 to 200 times on lowering the temperature to 4.2 K to 0.26 K it becomes a super conductor. This polymer is considered as the first inorganic super conductor polymer.

13. Explain about the biodegradable and non-biodegradable polymers with suitable examples. [TU 2070 Chaitra]

Ans: Biodegradable polymers are those polymers which undergo degradation by biological process like enzymatic, bacteriological or microbiological process. And all the natural polymers are biodegradable. e.g. Starch, cellulose, natural rubber protein, sutures, tissue cultures etc.

Whereas polymers which do not undergo bio-degradation by various biological process are non-biodegradable polymers. Most of the synthetic polymers are non biodegradable so cause pollution. But synthetic polymers which are biodegradable are:

Polycaprolactone

Polyaminotriajole

Polyester polyglycolid

14. What are conducting polymers? Point out their applications in engineering field. [2071 Shrawan]

Ans: See theory part.

15. Write down the main characteristics of inorganic polymers. [TU 2071 Shrawan]

Ans: Main characteristics of inorganic polymers

- (i) They generally melt but don't burn except polymer containing sulphur.
- (ii) They are cross linked so that makes them hard and brittle.
- (iii) They dissolve in polar solvent.

16. What are biodegradable polymers? Write down the preparation and uses of Nylon and Telcon. [TU 2073 Magh]

Ans: See theory portion.

17. What do you mean by crosslinked polymer? What are the general characteristics of inorganic polymer? What are the engineering application of chalcogenide polymer? [TU 2072 Ashwin]

Ans: Cross linked polymers are those polymers which are obtained by condensation polymerization of different monomers they formed by two step reactions.

e.g. Nylon 6,6, Bekelite etc.

Remaining part : See previous answers.

18. What are fibre reinforced polymers? Write their application in field of engineering. [TU 2072 Ashwin]

Ans: Fibre reinforced polymers, also Fibre reinforced plastic, is a composite material made of a polymer matrix reinforced with fibre. The fibres are usually glass, carbon, or aramid, although other fibre such as paper or wood or asbestos has been sometimes used. The polymer is usually an epoxy, vinyl ester or polyester thermosetting plastic, and phenol formaldehyde resins are still in use. FRPs are commonly used in the aerospace, automotive, marine, and construction industry.

Uses:

- (i) Used in aerospace, aircrafts, marine, automotive etc.
- (ii) Used in civil infrastructures such as bridges and buildings.
- (iii) Used in high performance resin system. Such as carbon nanotubes and nanoparticles.
- (iv) Used in concrete reinforcement and jacketing.

Chapter 5

3-d Transition Element and Their Application

Introduction

Transition elements are those elements in which two outermost shells are incomplete. In these elements the last electron is also known as differentiating electron. The last or differentiating electron enters into $(n-1)d$ orbital of the $(n-1)^{th}$ main shell. Hence these also known as d-block element.

General properties of transition elements

- They are all metals. They are very hard, highly malleable and ductile except mercury.
- They have high melting point and boiling point except mercury.
- They have high specific gravity i.e. they have heavy density.
- They are generally soluble in dilute mineral acids (HCl , HNO_3 , H_2SO_4) with few exceptions.
- They form complex compound.
- They exhibit variable oxidation states.
- They form coloured compounds.
- Their compounds are generally paramagnetic.
- They form alloy.
- Their compounds have good catalytic properties.

Detail Properties of 3d elements

The elements belong to 3d-series are known as 3d element, there are 10 elements in 3d-series: $_{21}Sc$ to $_{30}Zn$. The detail properties of 3d-series are follows:

1. Electronic configuration

Some of the elements of 3d-series have anomalous electronic configuration. The electronic configuration of 3d-series are as follows:

Gr. No.	Elements	Expected electronic conf ⁿ .	Observed elec. conf ⁿ .
III B	$_{21}Sc$ (Scandium)	$[Ar] 3d^2 4s^2$	same

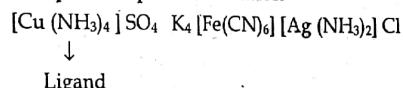
3-d Transition Element and Their Application ... 73

IV B	$_{21}Ti$ (Titanium)	$[Ar] 3d^2 4s^2$	same
V B	$_{23}V$ (Vanadium)	$[Ar] 3d^3 4s^2$	same
VI B	$_{24}Cr$ (Chromium)	$[Ar] 3d^4 4s^2$	$[Ar] 3d^5 4s^1$
VII B	$_{25}Mn$ (Manganese)	$[Ar] 3d^5 4s^2$	
	$_{26}Fe$ (Iron)	$[Ar] 3d^6 4s^2$	same
VIII	$_{27}Co$ (Cobalt)	$[Ar] 3d^7 4s^2$	same
	$_{28}Ni$ (Nickel)	$[Ar] 3d^8 4s^2$	same
I B	$_{29}Cu$ (copper)	$[Ar] 3d^9 4s^2$	$[Ar] 3d^{10} 4s^1$
II B	$_{30}Zn$ (zinc)	$[Ar] 3d^{10} 4s^2$	same

If we look at the electronic configuration of 3d-series we observe the following facts:

- The cores of the transition metals have inert gas configuration. In 3d series the core has Ar configuration.
- The two elements $_{24}Cr$ and $_{29}Cu$ have anomalous electronic configuration. The anomalous configuration are explained on the basis of extra stability of half filled d-orbital (d^5) and completely filled d-orbital (d^{10}).

2. Complex compound formation



Transition metals have great tendency to form the complex compound with several ligands such as negative ligands like CN^- , F^- , Cl^- , Br^- , I^- , OH^- , NO_3^- etc. and neutral ligands such as NH_3 , H_2O , CO , NO . The ligands must have at least one pair of electron which donates to the metal atom ion forming co-ordinate covalent bond which is shown as $L \rightarrow M$.

L = ligand M = metals

The tendency of forming the complex is due to the following reasons:

- The cations of the transition metals are vary in size and have positive charge density in the nucleus which makes them carry to accept the lone pairs of electrons donated by ligands.
- The transition metal cations can provide a number of vacant or empty atomic orbitals (s, p, d) in which the lone pairs of electrons can be accommodated.

- (iii) The transition metal exhibit variable oxidation state hence, they can form stable compound at variable oxidation state.

3. Variable oxidation states

Most of the transition metal exhibit variable oxidation state i.e. they have more than 1 valency except zinc. This is quite contrast to 'S' block and 'P' block elements. The variable oxidation state of transition elements is due to the following reasons.

- (a) The cations of the transition metal can not achieve the inert gas configuration or stable con figuration in any common oxidation state. Such inert gas configuration which is less stable. hence one or more 1s^2 e's are lost from this configuration to aquire stable configuration atom.
- $$\text{2sSc} \rightarrow [\text{Ar}]3\text{d}^1 4\text{s}^2$$
- $$\text{Sc}^{+2} \rightarrow [\text{Ar}]3\text{d}^1 \text{less stable}$$
- $$\text{Sc}^{+3} \rightarrow [\text{Ar}]3\text{d}^0 \text{more stable}$$
- (b) The energies of '3d' and '4s' orbitals are fairly close to each other. Hence, electrons are lost from both orbitals during cation formation.

4. Coloured compound formation

Transition elements are usually characterised by having d orbitals. Now when the metal is not bonded to anything else, these d orbitals are degenerate, meaning that they all have the same energy level. However when the metal starts bonding with other ligands, this changes. Due to the different symmetries of the d orbitals and the inductive effects of the ligands on the electrons, the d-orbitals split apart and become non-degerate (have different energy levels).

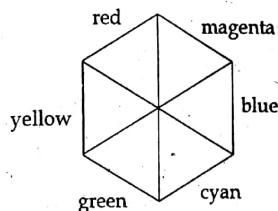
This is forms the basis of crystal field theory. How these d orbitals split depend on the geometry of the compound that is formed.

Well, electrons are able to absorb certain frequencies of electromagnetic radiation to get promoted to higher energy orbitals. These frequencies have a certain energy which correspond to the energy difference between different orbitals. Now most of the substances are only able to absorb frequencies of radiation which are outside the visible light spectrum. This means that it reflects all other type of radiation, including the full spectrum of visible light. So our eyes see a mixture of all the colors; red, green, blue, violet etc.

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However transition metals are special in that energy difference between the non-degenerated d orbitals correspond to the energy of radiation of the visible light spectrum. This means that when we look at the metal complex, we don't see the entire visible light spectrum, but only part of it.

So for example, if the electrons in an octahedral metal complex are able to absorb green light and get promoted from the d_{yz} orbital to the d_{z^2} orbital, the compound will reflect all other colors except for green. Therefore, by using the colour wheel, we can find the complementary color of green will be the color of the compound, which is magenta.



This explains why not all transmetal complex are colourful. For example copper sulphate is a bright blue compound however zinc sulphate on the hand is a white compound despite being transition metal. The reason behind this is because zinc's d orbitals are completely filled up with electrons, meaning that it is not possible for any electrons to make d to d transition as they are filled up.

5. Alloy formation

Most of the transition metals have a tendency of forming alloys. Many of the transition metals have similar at sizes due to this, atoms of non-metal can be easily replaced by the atoms of another metal. This replacement forms the alloys. when two or more metals are mixed in molten state, stirred and cooled, the alloys are formed. The alloys are generally high MP and BP and corrosion resistant. E.g. brass, stainless steel etc.

6. Magnetic properties

Most of the transition metals and their compounds are paramagnetic. When the transition metal compounds are placed

between both the magnetic field, they show different behaviour. On the basis of their behaviour, they are classified as diamagnetic substances and paramagnetic substances.

The para magnetic character or paramagnetism is due to the presence of unpaired electrons. The paramagnetic character increases, as the no. of unpaired electrons increases. The paramagnetism is expressed in magnetic moment μ . The value of μ increases as the number of unpaired electron increases. Consequently the paramagnetic character also increases.

In general if some value of $\mu = 1 \dots, 2 \dots, 3 \dots, BM$ then the substance is paramagnetic. If there is no value of μ i.e. $\mu = 0$ then substance is diamagnetic the magnetic moment μ is calculated by using the formula,

$$\mu = \sqrt{n(n+2)} \cdot BM$$

where, n = number of unpaired e⁻s.

This formula is known as spin only formula.

Application of 3d-series elements

- (1) Scandium (Sc^{++}) has greater tendency to form complexes due to its smaller ion size. e.g. $[ScF_4]^{2-}$, $[ScFs]^{-}$ etc.
- (2) Titanium is used in high speed air vehicles due to its low thermal expansion.
- (3) V_2O_5 is for manufacture of H_2SO_4 and purification of HNO_3 as catalyst.
- (4) Chromium is used manufacture of chromestee.
- (5) Iron is mostly used manufacture of steel, truss, machine parts and tools.
- (6) The solution of cobalt (Cobalt nitrate) is used in metal detection works.
- (7) Oxides of manganese is used as strong oxidising agent. e.g. $KounO_4$, MnO_2 etc.
- (8) Copper is used in making electric wire, electroplating kitchen utensils etc.
- (9) It used for making crucible, disuses and also used in electrical industries.
- (10) Zinc is used galvanization work ands sheradising etc.

Exam Question Solutions

Explain the followings:

1. (a) Transition elements are good in forming complexes.
(b) Show your acquaintance with application of 3d transition elements.

Ans: (a) See theory part.
(b) See theory part.

2. (a) What are transition elements? List the industrial application of 3d transition elements.
(b) Why do transition element show variable oxidation state?

Ans: (a) Transition elements are those elements in which two outer most shells are incomplete. E.g. $_{21}Sc$ to $_{30}Zn$. The last or differentiating electron enters into $(n-1)d$ orbital of the $(n-1)^{th}$ main shell. Hence, these are also known as d-block elements.

Following are the industrial application of 3d transition elements:

- Iron is widely used in manufacture of steel, reinforcement bars and machines.
- Chromium is used in making of stainless steel.
- Vanadium is as catalyst for manufacturing H_2SO_4 as V_2O_5 .
- Copper is widely used as electric wire & coil making.

(b) See theory part.

3. What are transition elements? Explain the following features of transition elements.

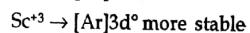
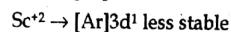
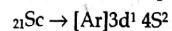
- (a) Variable oxidation states
(b) Magnetic properties.

Ans: Transition elements are those elements in which two outer most shells are incomplete. E.g. $_{21}Sc$ to $_{30}Zn$. The last or differentiating electron enters into $(n-1)d$ orbital of the $(n-1)^{th}$ main shell. Hence, these are also known as d-block elements.

- (a) Variable oxidation states

Most of the transition metal exhibit variable oxidation state i.e. they have more than 1 valency except zinc. This is quite contrast to 'S' block and 'P' block elements. The variable oxidation state of transition elements is due to the following reasons.

- (i) The cations of the transition metal can not achieve the inert gas configuration or stable configuration in any common oxidation state. Such inert gas configuration which is less stable, hence one or more electrons are lost from this configuration to acquire stable configuration atom.



- (ii) The energies of '3d' and '4s' orbitals are fairly close to each other. Hence, electrons are lost from both orbitals during cation formation.

(b) Magnetic properties

Most of the transition metals and their compounds are paramagnetic. When the transition metal compounds are placed between both the magnetic field, they show different behaviour. On the basis of their behaviour, they are classified as diamagnetic substances and paramagnetic substances.

The para magnetic character or paramagnetism is due to the presence of unpaired electrons. The paramagnetic character increases as the no. of unpaired electrons increases. The paramagnetism is expressed in magnetic moment μ . The value of μ increases as the number of unpaired electron increases. Consequently the paramagnetic character also increases.

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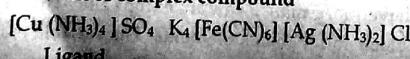
This formula is known as spin only formula.

4. Explain the following features of transition elements with reference to 3-d transition series.

- (a) Formation of complex compound.
(b) Formation of coloured compound.

[TU 2069 Bhadra]

Ans: (a) Formation of complex compound



Transition metals have great tendency to form the complex compound with several ligands such as negative ligands like CN⁻, F⁻, Cl⁻, Br⁻, I⁻, OH⁻, NO₃⁻ etc. and neutral ligands such as NH₃, H₂O, CO, NO. The ligands must have at least one pair of electron which donates to the metal atom ion forming co-ordinate covalent bond which is shown as L → M.

L = ligand M = metals

The tendency of forming the complex is due to the following reasons:

- (i) The cations of the transition metals are vary in size and have positive charge density in the nucleus which makes them carry to accept the lone pairs of electrons donated by ligands.
- (ii) The transition metal cations can provide a number of vacant or empty atomic orbitals (s, p, d) in which the lone pairs of electrons can be accommodated.
- (iii) The transition metal exhibit variable oxidation state hence, they can form stable compound at variable oxidation state.

(b) Formation of coloured compound

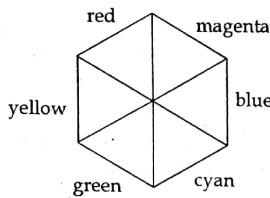
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Well, electrons are able to absorb certain frequencies of electromagnetic radiation to get promoted to higher energy orbitals. These frequencies have a certain energy which correspond to the energy difference between different orbitals. Now most of the substances are only able to absorb frequencies of radiation which are outside the visible light spectrum. This means that it reflects all other type of radiation, including the full spectrum of visible light. So our eyes see a mixture of all the colors; red, green, blue, violet etc.

However transition metals are special in that energy difference between the non-degenerated d orbitals correspond to the energy of radiation of the visible light spectrum. This means that when we look at the metal complex, we don't see the entire visible light spectrum, but only part of it.

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5. Why do transition elements form complex compounds? List the industrial application of 3-d transition elements in engineering.

Ans: See theory part.

6. Explain the following features of transition elements with reference to 3-d transition series.

(a) Variable oxidation state

(b) Formation of coloured compound

Ans: (a) See the answer of Q.N.3 (2067 Ashad)
(b) See the answer of Q.N.4 (TU 2068 Bhadra)

Why do transition metals.

7. (a) Forms complex compound
(b) Exhibit variable oxidation states.

[TU 2069 Bhadra]

Ans: Same as before questions answer

8. Why are 3-d series called transition element? Give their characteristic on the basis of valency.

[TU 2069 Bhadra]

Ans: The elements of sub group III B to VII B, VIII, I B & II B are transition elements. These are so called as their position in periodic table lie between S-block and P-block elements.

The properties of these elements are also between highly electropositive elements of S-block which form ionic compounds and electropositive element of p-block which largely form covalent compounds.

2nd part: See theory part.

9. (a) Write the general outer electronic configuration of transition elements.

- (b) Give reason why transition elements are coloured and paramagnetic.

[TU 2070 Bhadra]

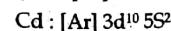
Ans: (a) The general outer electronic configuration of transition elements is: $(n-1)d^{(1-9)} 4s^2$.

(b) See answer of Q.No. 18(b) (TU 2073 Magh)

10. Give reason why Zn and Cd are not considered as typical transition metals.

[TU 2070 Bhadra]

Ans: The elements in atomic form or in any common oxidation state if they should have partially filled $(n-1)d$ orbitals of the $(n-1)^{th}$ main shell are known as typical transition metals. Due to this they are paramagnetic & form coloured compound.



Since the d-orbital of Zn and Cd is completely filled therefore they are not considered as typical transition metals.

11. Explain the main characteristics of 3-d transition element.

[TU 2070 Bhadra]

Ans: See theory part.

12. What are transition elements? Why do transition metal

- (a) form complex compound?
- (b) exhibit variable oxidation state?

[TU 2070 Magh]

Ans: See answer of Q.No.7 (TU 2069 Bhadra).

13. Explain the following:

- (a) Transition metals are coloured
- (b) Transition metal compound paramagnetic.

Ans: See previous answer.

14. A transition metal form alloy with other transition metals easily, why? Which divalent metal has maximum paramagnetic character among the first transition metals. [TU 2071 Shrawan]

Ans: Transition elements have atomic and ionic size and non metal like carbon, oxygen, nitrogen etc. can easily accommodated in the interstitial space to make alloys. E.g. in steel and cast iron, carbon atoms are present in such spaces.

They can also form alloys with 'S' and 'P' block metals. And such alloys formation is used to modify the properties of metal. E.g. stainless steel is resistant the corrosion.

Mn^{++} has maximum paramagnetic character among the first transition metals because of the maximum number of unpaired electrons i.e. S.

15. Explain the following:

- (i) 3d-transition series show variable oxidation state.
- (ii) Completely filled 3-d transition series are unable to form coloured compound. [TU 2071 Shrawan]

Ans: (i) See the answer of Q.No.3 (TU 2067 Ashad)
(ii) See theory part

16. (a) Are all d-block elements called transition elements? Justify your answer with reason. Why do transition elements called so?

- (b) Why do transition element show variable oidaion state? Point out the industrial application of 3-dseries elements?

[TU 2072 Ashwin]

Ans: (a) No all d-block elements are transition elements because the elements of sub group III B to VII B, VIII, IB & II B are transition elements. These are so called as their position in periodic table lie

between S-block and P-block elements. The properties of these elements are also between highly electro positive elements of S-block which form ionic compounds and less electropositive elements of P-block which largely form covalent bond.

(b) See the ans of Q.No.3 (TU 2067 Ashadh) and (TU 2069 Chaitra.)

17. (a) Why do transition elements form complex?

- (b) Why are most of the compounds of transition elements are coloured? [TU 2073 Magh]

Ans: See previous answers & theory part.

18. (a) Why do the transition metal show paramagnetism?

- (b) Why do transition metals exhibit variable oxidation state?

[TU 2073 Magh]

Ans: (a) The paramagnetic character or paramagnetism is due to the presence of unpaired electrons. The paramagnetic character increases as the number of unpaired electrons increases. The paramagnetism is expressed in magnetic moment μ .

$$\therefore \mu = \sqrt{n(n+2)} BM$$

Where,

n = no. of unpaired e's

(b) See previous ans.

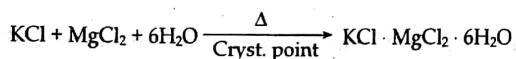
Chapter 6

Co-ordination Complexes

6.1 Additional Compound

When two normal salt solutions are mixed in equimolar quantities and the solution is heated to crystallization point, we get the crystals of new compound, known as additional compound.

Example



Types of additional compound

- (a) Double salt (b) Complex salt or co-ordination compound

6.1.1 Double Salt

These are additional compound which exist only in solid state when they dissolve in water, they ionize in the same way as the constituent component salt. So they give the test of all the ions present in the constituent component salt.

Example:- $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (carnalite)

6.1.2 Complex Salt

These are also additional compound which exists in solid as well as aqueous state. When they dissolve in water, they do not ionize in the same way as the constituent component salt. So, they do not give the test of all the ions present in the constituents component salt.

Example:

$4\text{KCNFe}(\text{CN})_2$ or $\text{K}_4[\text{Fe}(\text{CN})_6]$

pot. Ferro cyanide

6.2 Difference between Double salt and complex salt

Double salt	Complex salt
(i) The two salts content must be in equimolar ratios.	(i) The two salts contents may or may not be in equimolar ratios.
(ii) They ionize to give simple or compound ions.	(ii) They ionize to give the complex ion.

(iii) They lost their properties as double salt when dissolved in water but individual properties of ions are not lost.	(iii) They show properties of additional compound even after dissolved in water but properties of individual ions are lost.
(iv) It exists in crystalline state only.	(iv) It can also exist in solution state.
(v) They shows single valency.	(v) They show primary as well as secondary valency.
(vi) They have ionic bond.	(vi) They have co-ordinate bond.
(vii) Example: $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	(vii) Example: $\text{Ku}[\text{Fe}(\text{CN})_6]$

6.3 Complex compounds

The additional compound which gives complex ions in the solution are called complex compounds.

Technical terms

- (i) **Complex ions:** These are +vely or -vely charged ions containing metal and the definite number of attached species, the ligand.
e.g. $[\text{Cu}(\text{NH}_3)_4]^{2+}$ $[\text{Fe}(\text{CN})_6]^{4-}$
- (ii) **Ligands:** The ions or molecules which are attached with the central metal atoms/ion to form a complex compound are called ligands.

The ligands must have at least one lone pair of electron.

Example, $[\text{Fe}(\text{CN})_6]^{3-}$

CN^- is ligand.

Types of ligands

- (a) monodentate ligands → having one lone pair of electron.
- (b) Bidentate ligands → having two lone pair of electrons.
- (c) Polydentate Ligands → having three or more lone pair of electrons.
- (iii) **Central metal atom/ion**
When the ligands are attached to the metal atom/ion, then the metal atom/ion is said to be central metal atom/ion.
- (iv) **Co-ordinate number (CN) or ligancy:**
Generally, the number of ligand attach to the metal atom/ion is the coordination numbers of metal atom/ion.

(v) **Co-ordination sphere:**

The central metal atom and ligands which are attached to central metal atom are enclosed in bracket known as co-ordinate sphere which are non-ionisable in nature.

(vi) **Outer - sphere**

The species which are outside the brackets in the complex compound is known as outer sphere. It is ionizable in nature.

Example,



Here,

$(Fe(CN)_6)$ is co-ordinate sphere and K is outer sphere.

6.4 Werner's theory

This theory was first theory to explain co-ordinate complex. He explained structure and properties of complex compounds.

Postulates:

1. **The central metal atom/ions show two types of valencies in co-ordinate compounds.**

- (i) Primary valency
- (ii) Secondary valency

2. **Characteristics of secondary valency**

- (i) The secondary valency of the central atom is equal to co-ordination number of that metal.
 - (ii) The secondary valency is either satisfied by anions or neutral ion only or both combines.
- Example, $K_u[Fe(CN)_6]$
- Here, 6 numbers of CN ion is attached as ligands so secondary valency of Fe is 6.
- (iii) The species which satisfies the secondary valency can't be obtain in free state in solutions.
 - (iv) Every metal has fixed number of secondary valency.
 - (v) The secondary valency determines the sphere of compounds.

3. **Characteristics of primary valency**

- (i) It is equal to oxidation number of metal ion.
- (ii) Primary valency is always satisfied by anions.

- (iii) The ion which satisfies the primary valency can have free states in solution.
- (iv) They do not show geometric characteristic.

6.5 **Nomenclature of co-ordinate compounds
Rules**

- 1. If the complex contain positive ion and negative ion, the positive ion is named first followed by the negative ion.

Ex. $K_u[Fe(CN)_6]$

$K \rightarrow$ cation, so K named first

- 2. For naming inside complex ion i.e. within bracket the metal ion is named first and ligands are named according to alphabetical order.

- 3. The -ve, ligand which end at 'ate' or 'ite', 'e' is changed into 'o' for example,

sulphate (SO_4) into sulphato

The -ve ligand which and with 'ide' is changed into 'O'.

Floride = Flouro

Positive ligand end in 'm'

NO^+ \longrightarrow Nitro sonium

In case of neutral ligands

$H_2O \longrightarrow$ Aqua

$NH_3 \longrightarrow$ Carbonyl

Nitrosyl (NO) \longrightarrow Nitroso.

- 4. If same kinds of ligands are present in compound, then we use di, tri, tetra etc.

- 5. If ligands contain number indication like dimethyl we use bis, tris, tetrakis etc.

- 6. The oxidation number of central metal atom is shown by Roman number in bracket immediately following its name.

Example,

$[Fe(H_2O)_5(NO)]^{2+}$

IUPAC name:- Pento aquanitrogyl iron (III) ion

6.6 **Sidwick's Atomic Number Rules (EAN rule)**

EAN = Effective atomic number the total number of electrons around central atom of ion donated by the ligands through co-ordinate bond is EAN of the central atom. It can be calculated by the formula.

$$EAN = (z - x) + ny$$

Where,

z = atomic number of central metal atoms

x = Oxidation number of central metal ion.

n = number of ligands

y = number of electron donated by one ligand.

The EAN number has much significant, if the EAN number is equal to inert gas atomic number then the complex is stable and diamagnetic. Else the complex is paramagnetic and unstable.

Valency Bond Theory

Postulates

- (i) The central atom provides orbitals to form co-ordinate bond.
- (ii) Hybridization of vacant orbital happens with equivalent energy and definite geometry which gives bond formation.
- (iii) Ligands must have at least one lone pair of electron. They can also donate more than one lone pair.
- (iv) The geometry of the complex is given by geometry of the hybrid orbitals.
- (v) If the complex contains unpaired electrons, it shows paramagnetic characteristics. If there is no unpaired electron then it shows diamagnetic properties.
- (vi) If the ligands are strong present $(n-1)d$ orbit is used for hybridization and pair up is against Hund's rule.
- (vii) $SP^3 \rightarrow$ Give Tetrahedral complex
 $dSp^2 \rightarrow$ Gives square planar complex
 $d^2Sp^3 \rightarrow$ Give octahedral structure complex.

Some Examples

1. Write IUPAC name of following compounds.

- (a) $[CrCl_3(NH_3)_3]$
Triaminetrichloro chromium (III)
- (b) $K_3[Fe(CN)_6]$
Potassium hexacyanoferrate (IV)
- (c) $[PtCl_6(NH_3)_2]Cl_3$
Pentaammine Chloroplatinum (III) Chloride
- (d) $[CO(NH_3)_6]Br_3$
Hexaammine cobalt (III) bromide

- (e) $[ZnCl_4]^{2-}$
Tetrachlorozincate (II) ion
- (f) $[Au(CN)_4]^{-3}$
Tetracyanoaurate (III) ion
- (g) $[CrCl_2(H_2O)_6]Cl$
Dichlorotetraqua chromium (III) chloride
- (h) $bis(\text{ethylenediamine})\text{copper (II)}\text{ ion}$
 $[Cu(en)_2]^{2+}$
- (i) $[CO(ONO)(NH_3)_5]SO_4$
Petaammine nitroso cobalt (II) Sulphate
- (j) $Na[CO(CO)_4]$
Sodiumtetrocarbonyl cobaltate (I)
- (k) $[Cr(en)_3]Cl_3$
Tris (diethyldiammine) chromium (III) chloride
- (l) $[Fe(H_2O)_5(NO)]^{2+}$
pentoaqua nitrosyl iron (III) ion
- (m) $[pt(py)_3]Cl_3$
Tetrapyridine (II) tetrachloroplatinate (II)
- (n) $K_3[Fe(CN)_5NO]$
Potassium pentacyanonitrosyl ferrate (III)
- (o) $Na_2[ZnCl_4]$
Sodium Tetrachloro zincate (II)

2. Predict the stability and magnetic properties of following compounds.

- (i) $[Fe(CN)_6]^{4-}$

Soln: EAN of $Fe^{+3} = (z - x) + ny$

$$= (26 - 3) + 6 \times 2 = 23 + 12 = 35$$

Which is not equals to any inert gas atomic number so, it is unstable and paramagnetic.

- (ii) $[CO(NH_3)_4]^{2-}$

Soln: EAN = $(z - x) + ny$

$$= (27 - 3) + 6 \times 2 = 36$$

Equals to inert gas stable and diamagnetic.

- (iii) $[Ni(CN)_4]^{2-}$

Soln: EAN of $Ni^{2+} = (28 - 2) + 4 \times 2 = 34$

The EAN is not equal to 36 i.e. inert gas Kr atomic number. This ion is unstable and paramagnetic.

3. Predict the geometry and magnetic properties of following complex

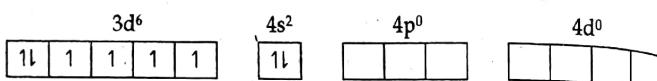
(i) $[\text{Fe}(\text{Cl})_4]^{2-}$

Soln: Oxidation number of Fe = +2

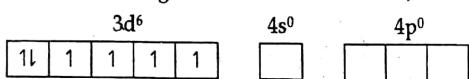
Co-ordination number of Fe^{2+} = 4

Electronic configuration of Fe

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

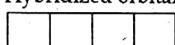


Electronic configuration of Fe^{2+}



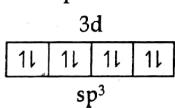
Since Cl is weak ligand back pairing doesn't occur i.e. 3d⁶ orbitals are remain unchanged. Therefor one 'S' and 3-p orbital takes part in hybridization i.e. sp^3 hybridization.

Hybridized orbital

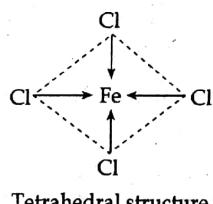


4sp^3 hybridized orbitals

For Cl ligands donate 4-lone pair of electron is sp^3 hybridized orbitals.



Since the 3-d orbitals has unpaired electron it is paramagnetic geometrical shape.



Exam Question Solutions

1. Give IOPAC name of followings.

(i) $\text{K}_4[\text{Fe}(\text{CN})_6]$

Potassium hexacyanoferrate (III)

(ii) $\text{Tgrioxialatoaluminate (III)}$ ion

$[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$

(iii) $[\text{Cr}(\text{en})_3]\text{Cl}_3$

Tris (ethylenediamine) Chromium (III) chloride

(iv) Bis (benzenen) chromium (0)

$[\text{Cr}(\text{bn})_2]^0$

(v) $\text{K}[\text{PtCl}_5(\text{NH}_3)]$

Potassium ammine penta chloroplatinate (IV).

(vi) $[\text{CO}(\text{NH}_3)_5\text{SO}_4]\text{Br}$

Sulphate pentaammine cobalt (III) bromide

[2068 Bhadra]

[TU 2069 Bhadra]

2. Name the IUPAC names. [2070 Bhadra]

(i) $\text{Na}[\text{au}(\text{CN})_2]$

Sodiumdicyano Aurate (III)

(ii) $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$

Potassium trioxalato ferrate (III)

(iii) $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}$

Dichlorotetraammine platinum (III) Bromide

(iv) $[\text{CO}(\text{NH}_3)_6]\text{Cl}_3$

Hexaammine cobalt (III) chloride

(v) $\text{Na}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$

Sodium trioxalato alumunate (III)

3. Why do the presence of unpaired electrons make a substance paramagnetic in nature? Show geometry and magnetic properties of $[\text{Ni}(\text{Cl})_4]^{2-}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$. [2068 Magh]

Ans: Paramagnetic compounds contain one or more unpaired electrons and are attracted to the poles of a magnet.

Elemental iron and iron (III) are paramagnetic because of the necessity of unpaired electrons in their orbital's. Iron (II) is also in this same position most of the time. When iron (II) is bonded to certain ligands,

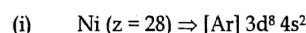
however, the resulting compound may be diamagnetic because of the creation of a low -spin situation.

If the ligands attached to the Fe(II) metal are strong field ligands in an octahedral configuration, a low spin situation is created in the d-orbitals. All of the electrons are paired and as a result, the complex is diamagnetic.

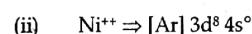


In the complex ion, central atom is nickel (Ni) which has O.N. is +2 & co-ordination no. is +4. Hence, the geometry is tetrahedral or square planar.

Using the VBT theory,



$1\downarrow$	$1\downarrow$	$1\downarrow$	1	1	$1\downarrow$	\square	\square	\square	\square	\square	$n=2$
3d ⁸	4s ²	4p ⁰		4d ⁰							

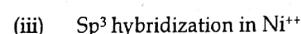


1↓	1↓	1↓	1	1
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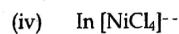
$n=2$

sp³ hybridization

Cl^- is the weak ligand, hence no back pairing in 3d-orbitals. One 4s orbital and three 3p-orbitals hybridize to give 4sp^3 hybrid orbitals.



11	11	11	1	1			
					n=2		



$1\downarrow$	$1\downarrow$	$1\downarrow$	1	1	$\times x$	$\times x$	$\times x$	$\times x$	$n=2$
					↑	↑	↑	↑	

Cl^- Cl^- Cl^- Cl^-

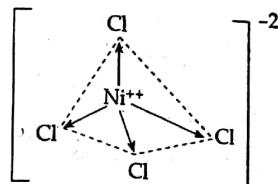


Fig: Tetrahedral geometry of $[\text{NiCl}_4]^{2-}$ complex.

This complex is formed by Sp^3 hybridization, the geometry of complex is tetrahedral. Due to the presence of two unpaired electrons ($n = 2$), it is paramagnetic in nature.

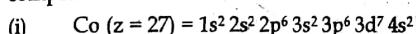


Central atom is Co.

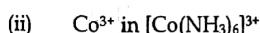
Oxidation no. = +3

Co-ordination no. = 6

Now, using the VBT to explain the geometry and magnetic property of complex.

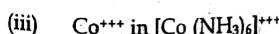


				
3d ⁷	4s ²	4p ⁰	4d ⁰	n=3



1↓	1	1	1	1					n=4
					3d ⁶	4s ⁰	4p ⁰	4d ⁰	

In this complex, NH_3 is present so the back pairing of the electrons in 3d orbitals take place.



11	11	11					
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$d^3 sp^3$

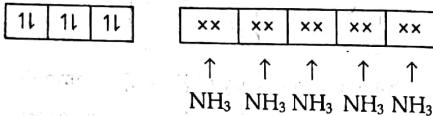
94 ... A Refresher Solution of Eng. Chemistry (B.E. I Yr I Part)

- (iv) Formation of hybrid orbitals in $[\text{Co}(\text{NH}_3)_6]^{+++}$



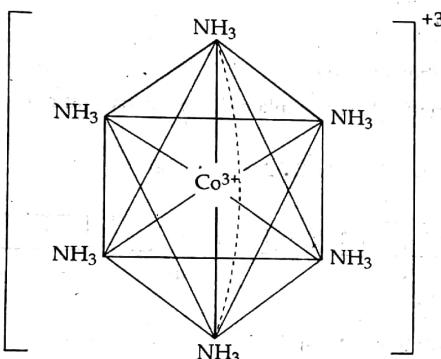
$n=0$

- (v) Formation of $[\text{Co}(\text{NH}_3)_6]^{+++}$



$\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$
 $\text{NH}_3 \text{ NH}_3 \text{ NH}_3 \text{ NH}_3 \text{ NH}_3 \text{ NH}_3$

The given complex ion is formed by d^2sp^3 hybridization and contains no unpaired electrons i.e. $n = 0$. Hence, the complex ion has octahedral ion geometry and is diamagnetic in nature.



4. Write the formula of the following co-ordination compounds.

[2071 Bhadra, 2069 Magh]

- Ans: (a) Sodium hexacyanoferrate (II)
 $[\text{C}_6\text{FeN}_6\text{Na}_4]$ Or $[\text{Na}_4\text{Fe}(\text{CN})_6]$
(b) Hexaamminecobalt (III) chloride
 $[\text{Co}(\text{NH}_3)_6\text{Cl}_3]$
(c) Bromochloro tetraamminecobalt (III) sulphate
 $[\text{CoBrCl}(\text{NH}_3)_4]\text{SO}_4$
(d) Hexafluoro aluminate (III) ion
 $[\text{AlF}_6]^{3-}$
(e) Potassium tetrachlorozincate (II)
 $\text{K}_2[\text{ZnCl}_4]$

Co-ordination Complexes ... 95

5. Differentiate between low spin and high spin complexes.

[2069 Bhadra]

Ans:

Low spin complexes	High spin complexes
(i) Ligands cause a large splitting D of the d-orbitals.	(i) Ligands cause a small splitting D of the d-orbitals.
(ii) They are diamagnetic.	(ii) They are paramagnetic.
(iii) They obey Aufbau rule.	(iii) They obey Hund's rule.
(iv) The energy difference between the two d-orbital level is relatively large.	(iv) The energy difference between the two d-orbital levels is relatively small.
(v) 2 nd and 3 rd row transition metal are usually low spin.	(v) 1 st row transition metals are often high spin.

6. Write down the IUPAC names of the following co-ordination compounds.

[2070 Chaitra]

- Soln: (a) $[\text{Cr}(\text{NH}_3)_6]^{3+}$
Hexa-amminechromium (III)
(b) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
Diammine dichloro platinum (IV)
(c) $\text{Na}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$
Sodium trioxalatochromate (III)
(d) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
Tetraammine dichlorocobalt (III) Chloride

7. What is EAN? How would you explain the stability and magnetic behaviour of a complex compound by EAN rule.

[2070 Chaitra]

Ans: See the theory portion 6.6

8. Write down the IUPAC names of the following compounds.

[2071 Shrawan]

- Soln: (i) $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$
Petaamminenitrisocobalt (II) chloride
(ii) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$
Trioxalato ferrate (III)
(iii) $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$
Bis (ethylenediamine) dichlorochromium (III)

9. What is complex compound? What do you understand by principle and auxiliary valency of the central ion in complex compound?

[2071 Shrawan]

Ans: See the theory portion.

10. Explain how the two complexes of Ni, $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{CO})_4]^0$ have different structures but do not differ in their magnetic behaviour. ($\text{Ni} = 28$). [TU 2071 Shrawan, 2074 Bhadra]

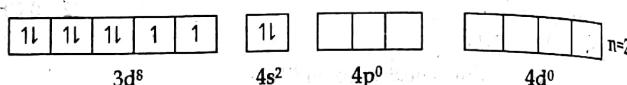
Ans: To explain about the two complexes of Ni, $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{CO})_4]^0$, we have to draw their structure first.

In $[\text{Ni}(\text{CN})_4]^{2-}$, the central metal atom is Ni whose oxidation number = 2.

Co-ordination number = 4.

Now using VBT, theory.

(i) $\text{Ni} (z = 28) \Rightarrow [\text{Ar}] 3d^8 4s^2$



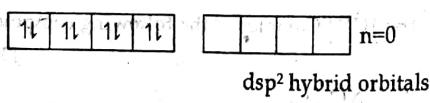
Here, strong ligand CN^- is present in this complex, so back pairing of electrons in 3d orbitals takes place.

(ii)



ds²p hybridization

(iii) Formation of hybrid orbitals in Ni^{2+}



ds²p hybrid orbitals

(iv) Formation of $[\text{Ni}(\text{CN})_4]^{2-}$

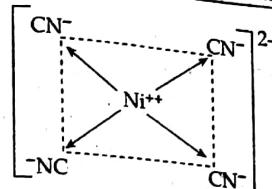
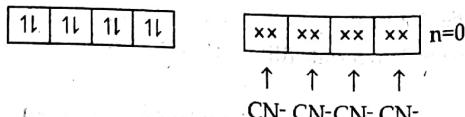


Fig: Square planer geometry of $[\text{Ni}(\text{CN})_4]^{2-}$

Since, the complex ion is formed by $d\text{sp}^2$ hybridization so, it has square planer geometry. The electronic configuration of this ion contains no unpaired electrons ($n = 0$). So, it is diamagnetic in nature.

Now, $[\text{Ni}(\text{CO})_4]^0$ contains no unpaired electrons ($n = 0$). So, it is paramagnetic in nature.

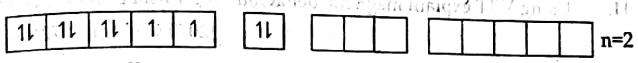
Central metal atom is Ni.

Oxidation no. = 0

Co-ordination number = 4

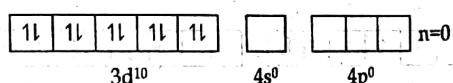
Using VBT, we can draw its structure and predict its nature.

(i) $\text{Ni} (z = 28) \rightarrow [\text{Ar}] 3d^8 4s^2$



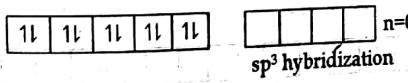
In this complexon, strong ligand i.e. Co is present so back pairing of electrons in 3d-orbitals take place.

(ii) Now, Ni in $[\text{Ni}(\text{Co})_4]^0$



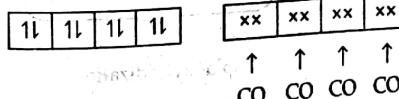
sp³ hybridization

(iii) Formation of hybrid orbitals in Ni



sp³ hybridization

(iv) Formation of $[\text{Ni}(\text{Co})_4]^0$



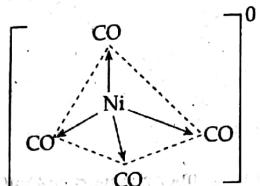


Fig: Tetrahedral geometry of $[\text{Ni}(\text{Co})_4]^0$

Since, the complex ion is formed by sp^3 hybridization so, it has tetrahedral geometry. The electronic configuration of this ion contains no unpaired electrons ($n = 0$), so it is diamagnetic in nature.

Hence from the formation of both complexes i.e. $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]^0$, it can be concluded that the geometries of both complexes are different but they have same magnetic properties.

11. Using VBT explain magnetic behaviour and formation of $[\text{FeF}_6]^{4-}$.

[2070 Chaitra, 2072 Ashwin]

Solution:

Here, the central metal atom is 'Fe', whose oxidation number = + 2

Co-ordination number = 6

Now, using VBT:

(i) Fe ($z = 26$) \Rightarrow [Ar] $3d^6 4s^2$

In this complex ion, weak ligand i.e. F⁻ is present, so no back earring of electron in 3d orbitals takes place.

(ii) $\text{Fe}^{3+} = [\text{Ar}] 3\text{d}^5 4\text{s}^0$

The diagram illustrates the atomic orbital configuration for sp^3d^2 hybridization. It shows the filling of orbitals starting from the innermost shell. The first shell contains five 1s orbitals. The second shell contains two 2s orbitals and five 2p orbitals. The third shell contains one 3s orbital, three 3p orbitals, and five 3d orbitals. The fourth shell contains one 4s orbital, five 4p orbitals, and seven 4d orbitals. The fifth shell contains five 5s orbitals and seven 5p orbitals. A bracket groups the 3s, 3p, and 3d orbitals as the sp^3 hybrid set, and another bracket groups the 4s, 4p, and 4d orbitals as the d^2 set.

(iii) Formation of hybrid orbitals in F

1. legodllogog, legodllogog n=5

sp²d² hybrid orbitals

(iv)

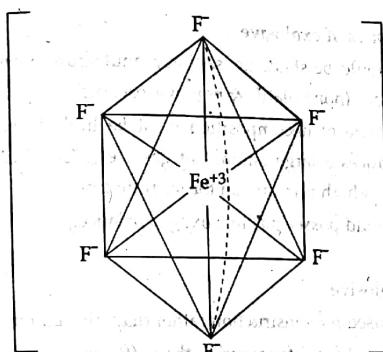


Fig: Octahedral geometry of $[\text{FeF}_6]^{3-}$

Since, the complex ion is formed by sp^3d^2 hybridization. So, it has octahedral geometry. The electronic configuration of this ion contains 5 unpaired electrons. So, it is highly paramagnetic in nature.

Chapter 7 & 8

Explosive, Paint and Lubricants

Explosive

It is a substance of a mixture which on detonation a very rapid chemical reaction takes and explodes which produces a large amount of gases, heat, light, sound and generates a high pressure on the surrounding.

Characteristics of explosive

1. It should be stable i.e. safe in manufacture, transportation and storage (non volatile & non hygroscopic).
2. The rate of decomposition must be high & exothermic so, it produces a large amount of gases e.g. CO, CO₂, NO₂, H₂O & exert a high pressure on the surrounding.
3. It should possess positive oxygen balance.

Uses of explosive

1. It is used for construction rather than destruction.
2. It is used for defence rather than offence.
3. Blasting rocks, mountains for the construction of roads, tunnels, excavation of earth for dams, seismic purpose, blasting mines, salts etc.

Types of explosive

There are two types of explosive

1. Primary explosive
2. Secondary explosive

1. Primary explosive or initiating (detonators) explosive

These explosive explodes on receiving small detonation but the reaction that not occur violently so this explosive in small amount is kept in contact with stable explosive for its detonation.

E.g.: Lead azide (PbN₆), Diazodinitrophenol (DDNP) etc.

Explosive, Paints and Lubricants ... 101

2. Low explosive (propellant)

These explosives simply burn and they do not explode violently. This explosive if used under control condition can be used as propellant. E.g. gun cotton i.e. trinitro cellulose

3. High explosive (Distructant)

These explosives are highly destructive in nature. These explosive detonates with high amount of heat, light, sound and high pressure on surrounding.

E.g. TNT (Stable)

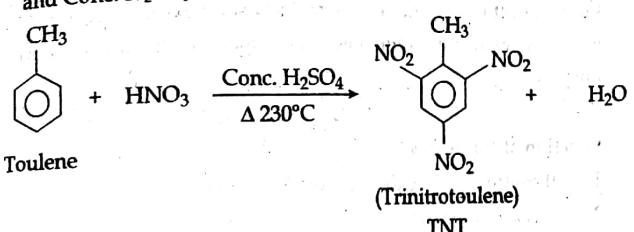
GTN (unstable)

Dynamite

ROX etc.

Preparation of TNT (Trinitrotoulene)

It is prepared by nitration of toluene in the presence of conc. HNO₃ and Conc. H₂SO₄ at 230°C.



Uses:

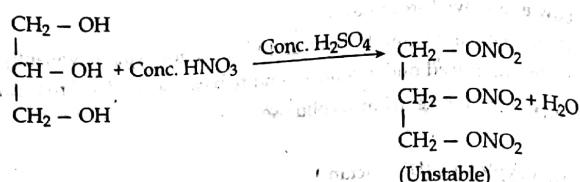
1. It is used as safe military explosive because it is safe in transportation and storage.
2. Used in excavation works like tunneling, earth excavation etc.

Properties:

1. It is violent destructive explosive.
2. Non reactive with metal.
3. Non hygroscopic.

Trinitroglycerol (TNG or GTN)

It is prepared by treating glycerol with a mixture of conc. nitric acid and conc. Sulphuric acid. (60% of H₂SO₄ & 40% of conc. HNO₃).



It is pale yellow oily liquid, which explodes small detonation.

Uses

1. It is used for preparing dynamite. (by absorbing GTN in inert absorbent) e.g. rice husk, sawdust etc.

Lubricants & Paints

Lubricant: It is a liquid or semi solid or solid ex-product of petroleum which is mainly used in mechanical tool for cooling & lubricating purpose.

Function of lubricants

1. It controls surface deformation.
2. It act as coolant.
3. Provide control use of energy & fuel.
4. Reduces the maintenance cost of machine.
5. Control the ceasing of engines.
6. Prevent the corrosion of surface.
7. It can act as seal for IC engines.

Types of lubricants

1. Liquid lubricant
e.g. Vegetable oil/animal origin oil, petroleum lubricants, mix oil lubricants.
2. Semi-solid lubricant
e.g. greases (soap + lubricating oil)
3. Solid lubricants
e.g. graphite, molydenum disulphide

Paints

- Paint is a surface coating material which is mechanical dispersion mixture of one or more pigments in a vehicle.
- Pigments provide color to paint.
- Vehicle is a solvent with film forming property.

Property of good paint

1. It should have high fluidity.
2. It should cover large surface area.
3. It should not corrosive to applied surface.
4. It should not have asthetic appreance.
5. It should not be skinning. (anti-skinning)
6. It should not crack after drying.

Types of the paints

1. Varnishes

It is homogeneous colloidal dispersion of natural or synthetic resins in vehicle. It is protective & decorative in nature.

2. Enamels

It is similar to varnishes only pigments are used with varnish for coloring. On drying gives shiny, hard and glossy finish.

3. Liquers

It is a mixture of cellulose acetate with vehicle.

4. Emulsions

It is a mixture of resin in water with drying oil. They have fewer odour, non-inflammable.

Exam Question Solutions (Explosive)

1. Define explosive. Give the preparation, properties and uses of TNT. What are the plas. explosive? [TU 2067 Ashadh]

Ans: First part : See theory part

Plastic explosive

They are combination of explosive in polymer state and they can be hand moulded, pressed and cut to make various shape without risk of explosion.

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2. What are low explosive? Write their uses. Give the preparation and application of glycerol trinitrate. [TU 2068 Bhadra]

Ans: Low explosive

These explosive simply burn and they do not explode violently. This explosive if used under control condition can be used as propellant.
e.g. gun cotton (trinitro cellulose)

gun powder (75% KNO_3 + 15% charcoal + 10% sulphur)

Use:

They are used as propellant such as gunpowder.

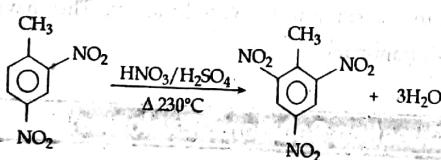
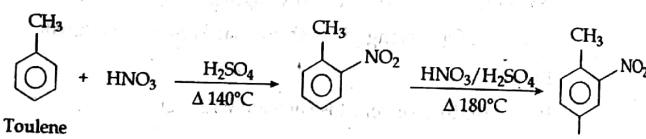
For preparation of TNT: See theory part.

3. What are primary explosive, low explosive and plastic explosive? Give the preparation and application of 2, 4, 6 trinitrotoluene (TNT). [TU 2069 Chaitra]

Ans: For primary explosive, low explosive & plastic explosive : Refer theory part.

Preparation of 2, 4, 6 trinitrotoluene

It prepared by nitration of toluene in a specific tank at specific condition with conc. HNO_3 & conc. H_2SO_4 .



Application

- It is used as safe military explosive because it is safe in transportation and storage.
- Used in excavation works like tunneling and various engineering works.

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4. Mention the importance of primary and low explosive. Give the preparation and uses of TNT and TNG. [TU 2069 Bhadra]
Ans: Primary and low explosives are the initiating (or detonators) and propellant respectively so they useful in preparation of high explosive. For detonation of high explosive we have to use primary and low explosive as a safety detonators by increasing the time of detonation.
2nd part: For the preparation and use of TNT & TNG See theory part.

5. List the important characteristics of explosives. Give the preparation and uses of trinitrotoluene (TNT). [TU 2070 Bhadra]

Ans: See theory part

6. Give an account of low and high explosive. Write the preparation & used of TNT. [TU 2070 Magh]

Ans: See theory part & previous questions solution.

7. What are plastic explosive? Write down the characteristic of explosive. Give the preparation and uses of explosive obtained from toluene. [TU 2070 Chaitra]

Ans: See theory part.

8. Differentiate between high explosive and low explosives. Write preparation and application of TNT. [TU 2072 Chaitra]

Ans: Following are differences between low explosive and high explosives:

Low explosive	High explosive
1. They do not explode violently.	1. They explode violently.
2. They do not produce large amount of energy and gases on explosion.	2. They produce large amount of energy and gases on explosion.
3. They are used as propellant.	3. They are used as distractant.
4. They simply burn.	4. They burn with high energy and producing high pressure on surrounding.
5. E.g. gun cotton (trinitrocellulose), gun powder etc.	5. E.g.: TNT, GTN, Dynamite, BOX etc.

For preparation and use of TNT refer theory part.

9. What is plastic explosive? Write preparation and use of following:
 (a) TNT (b) Dynamite [TU 2072 Chaitra]

Ans: Plastic explosive

They are combination of explosive in polymer state and they can be land moulded, pressed and art to make various shape without risk of explosion. Within the field of engineering, plastic explosive are also known as putty explosive.

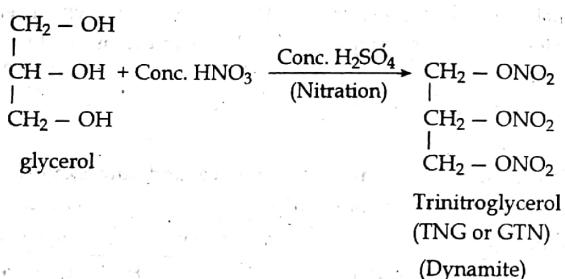
Plastic explosives are especially suited for explosive demolition. Common plastic explosive includes semiters and C-4.

(a) Preparation of TNT

See theory part.

(b) Dynamite

Dynamite is an explosive made of nitro glycerin, Sorbents (such as powdered shell or clay) and stabilizers. It is prepared from TNG by absorbing GTN in inert absorbent (e.g. ricehusk, saw dust etc).



Uses:

1. It is mainly used in mining, quarrying, construction and demolition industries.

Exam Question Solutions (Lubricants & Paints)

1. Define lubricants and mention their functions. Name the different types of liquid lubricant with example. Show your familiarity with type of paint. [TU 2067 Ashad]

Ans: Lubricants:

These are the liquid or semi-solid or solid exproduct of petroleum which is mainly used in machines and tools for cooling and lubricating purpose.

Functions of lubricant

- (1) It controls surface deformation.
- (2) It acts as coolant.
- (3) Provides control use of energy & fuel.
- (4) Reduces the maintenance cost of machines.
- (5) Controls the ceasing of engines.
- (6) Prevents the corrosion of surface.
- (7) It can act as seal for I.C. engines.

Types of liquid lubricants

- Vegetable oil
- Animal origin oil
- Petroleum lubricants
- Mixed oil lubricants: e.g. esters, castor oil
- Synthetic oil: polypropylene

Types of paints

- (1) Varnishes
- (2) Enamel
- (3) Lacquers
- (4) Emulsion paint
- (5) Special paints

(1) **Varnishes:** It is homogeneous colloidal dispersion of natural or synthetic resins in a vehicle. It is protective & decorative in nature.

(2) **Enamel:** It is similar to varnishes only pigments are used with vehicle for coloring. On drying gives shiny, hard and glossy finish.

(3) **Lacquers:** It is a mixture of cellulose acetate with vehicle.

(4) **Emulsion paint:** It is a mixture of resin in water with drying oil. They have sweet odour, non inflammable.

(5) **Special paints:** These paints like luminescent paint that fluoresces in UV rays, fire resistance, acid proof etc.

2. What are paints? Discuss any two kinds of paints indicating their application in engineering work. [TU 2068 Bhadra]

Ans: Paints:

Paints are the surface coating materials which is mechanical dispersion mixture of one or more pigments in a vehicle.

Types of paint**• Varnish:**

It is homogeneous colloidal mixture of natural or synthetic resin in a vehicle. It is protective and decorative in nature.

In engineering works like binding of coil, transparent painting of woods metals, it is used.

• Enamels

These are the paints which is mixture of pigment and vehicle. After evaporation of oil and thinner, it gives shiny & glossy surface finish.

It is used painting of wood, metal & walls.

3. What are lubricating oils? Indicate their importance in engineering.

Ans: Lubricating oils:

These are the lubricant having liquid or viscous form which are bi-product of petroleum used as coolant and sealing agent in engines.

Importance

- (1) It reduces the friction.
- (2) It reduces the surface deformation of machine parts.
- (3) It acts as coolant.
- (4) It provides anti corrosive film on surfaces.

4. Discuss any two types of paints showing their application in engineering works. [TU 2069 Chaitra]

Ans: See solution of TU 2068 Bhadra above.

5. Show your acquaintance with type of paints. [TU 2069 Chaitra]

Ans: See theory part.

6. Mention the requisites of good paints and write about varnish.

[PU 2070]

Ans: Requisites of good paint

- (1) It should have high fluidity.
- (2) It should cover large surface area.
- (3) It should not corrosive to surface.
- (4) It should be aesthetic in nature.
- (5) It should not crack on drying.
- (6) It should not be skinning. (anti-skinning)

Varnish:

It is homogeneous colloidal mixture of natural or synthetic resin in a vehicle. It is protective and decorative in nature. In engineering works like binding of coil, transparent painting of woods metals, it is used.

7. Describe liquid lubricants with emphasis on their classification.

Ans: Liquid lubricants are film forming lubricants which reduces the friction between two surface in contact. [2070 Back]

Liquid lubricants are of following type:

(1) Animal and vegetable oil:

These are the lubricating oils obtained from animal fat and plants.

Various animal origin oils are fats from animal like goat, buffalow, whales etc. Vegetable origin such as mustard oil, olive oil, palm oil, castor oil etc.

(2) Mineral or petroleum lubricants

These lubricants are obtained by fraction distillation of crude petroleum oil as bi-product. These lubricants are refined for its purity. These mostly used lubricants because they are high specific heat capacity, cheap & easily available.

(3) Mixed oil lubricants

These are the petroleum lubricants which are prepared by adding special additive to it. e.g. esters, ester oil etc.

8. What is paint? Write three important constituents of paint.

[2068 Magh]

Ans: paint is the surface coating materials which is mechanical dispersion mixture of one or more pigments in a vehicle.

Three important constituents of paint

(1) Pigments

These are the solid coloring substance mixed in vehicle to provide color to the paint.

White pigment: Zinc oxide, titanium oxide etc.

Red pigment: red lead, ferric oxide etc.

(2) Vehicle

It is mixture of thinner (volatile oil) and drying oils (vegetable oils) which provides base to the paint.

(3) Thinner

It is a solvent which is used to increase fluidity of paint. E.g.: Turpentine oil.

9. What are lubricating greases? Give their functions. [2069 Bhadra]

Ans: Lubricating greases are the mixture of soap and lubricating oil. The lubricating oil may petroleum or may be synthetic oil.

Function of grease:

- (1) It should be in contact with lubricate moving surface without leaking out under the force of gravity, centrifugal action or being squeezed out under pressure.
- (2) It retain its property under shear force at out temperature.
- (3) It reduces friction and wear in the machine.
- (4) Protect against rust & corrosion.
- (5) Maintain its structure and consistency during long periods of use.

10. Explain the method of application of paint in galvanised iron. [2070 Chaitra]

Ans: Galvanized metal is difficult to paint because it's coated with a layer of oil to prevent white rust. Alkyd and oil-based paints may seem to stick at first, but the oily layer eventually "sheds" the paint. Beside this, zinc content of galvanised coating reacts with paint's binder to create a film that causes the paint to peel. Therefore, it is important to follow the correct procedure when painting galvanised iron sheet.

Procedure

- (1) Wash the metal thoroughly with hot soapy water.
- (2) Rinse the metal and let it dry completely for several hours.
- (3) Rinse the metal with weak solution of water and ammonia and allow it to dry.
- (4) Sand the entire metal surface thoroughly, including crevices and dents.
- (5) Wipe the entire surface with the tack cloths.
- (6) Apply the primer as directed, covering the entire surface of the metal.
- (7) Let the primer dry according to the directions.
- (8) Apply the metal paint which should be same brand as the primer.
- (9) Let the paint dry according to the directions.

11. Write the function of lubricant. Show your acquaintance with fluid film lubrication and its role in engineering. Give an example each of (a) semi-solid lubricant (b) emulsion. [TU 2072 Chaitra, 2071 Back]

Functions of lubricant

- Ans:
- (1) Controls surface deformation
 - (2) It is a good coolant.
 - (3) Provides control use of energy & fuel.
 - (4) Reduces the maintenance cost of machine.
 - (5) Prevents the corrosion of surface
 - (6) Controls the ceasing of engines.
 - (7) It can act as seal for I.C. engines.

Fluid film lubricants are most used lubricant in engineering field. It must possess high boiling point or low pressure. It should help in cooling, sealing and decreasing friction in engine. Lubricants forming fluid film makes the machine long lasting and good working condition.

- (a) Semi-solid lubricant: grease, tar etc.
- (b) Emulsion: vinaigrettes, homogenized milk, mayonnaise etc.

Chapter 9

Stereo-Chemistry

9.1 Introduction

The branch of organic chemistry which deals with structure of the compounds in three dimensional spaces is known as stereo-chemistry.

9.2 Stereo-isomerism

The compounds having the same molecular formula but differs in the arrangement of atoms or group of atoms in space is known as stereoisomer and the phenomenon is called the stereoisomerism.

Types:

- (i) Geometrical isomerism
- (ii) Optical isomerism

9.2.1 Geometrical isomerism

The compounds having the same molecular formula but with different arrangement of atoms or group of atoms across single bond or C=C double bond (in alkene) is known as geometrical isomers and the phenomenon is called geometrical isomerism.

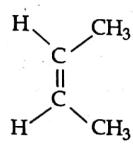
For the molecules exhibit the geometrical isomerism, each double bonded carbon must be linked with different atoms or group.

If the same atoms or group of atoms are on the same side in C=C double bond is represented by 'Cis' isomers.

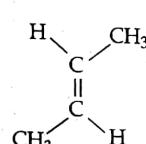
While similar group are attached to different side of molecules is called 'trans' isomers.

Examples: $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$

2-butene



Cis -2- butene



trans -2- butene

Note:

Trans compounds are more stable because in Cis - compound repulsion of bulky group on same side make it unstable.

Stereo-Chemistry ... 113
If the geometrical isomers can not be differentiated by Cis & trans then it is differentiated by Z and E notation.

Where,

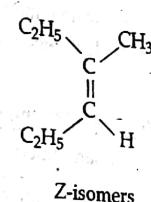
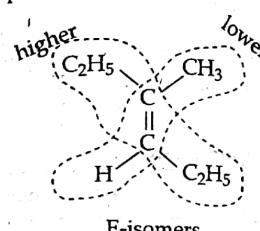
Z (Zusammen) → same side → together

E (Entgegen) → opposite side

E represents the atoms or group of higher precedence are on opposite side.

Z represents the atoms of higher precedence on same side.

Example:



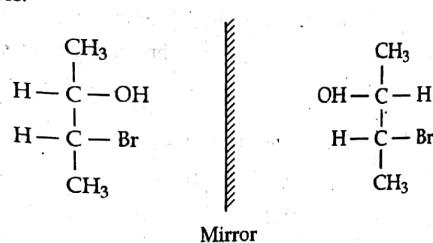
9.2.2 Optical isomerism

Those compounds which have same molecular and structural formula but are different in the rotation of plane polarized light are called optical isomers and phenomenon is known as optical isomerism.

Enantiomers

Enantiomerism is the phenomenon of isomerism of isomers that are not superimposable mirror image of each others.

Example:

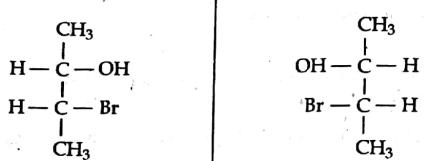


In this example, they are image of each other but are not superimposable, so they are enantiomers.

9.4 Diastereomers

They have same chemical and physical properties but differs in rotation of plane polarized light.

Example; 3-bromo -2- butanol shows diastereomerism.



Here, they are not mirror image of each other and they are same compound. That's why they are known as diastereomers.

9.5 Difference between enantiomers and diastereomers.

Enantiomers	Diastereomers
(i) Optical isomers which are non-superimposable mirror images of each other are known as enantiomers.	(i) Stereoisomers which are not mirror images of each other are known as diastereomers.
(ii) They have identical physical properties.	(ii) They have different physical properties
(iii) They can not be separated by physical technique like fractional distillation.	(iii) They can be separated by physical techniques like fractional distillation etc.
(iv) Examples: Enantiomers of 3-bromo-2-butanol	(iv) Example: Diastereomers of 3-bromo-2-butanol
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{H} - \text{C} - \text{Br} \\ \\ \text{CH}_3 \end{array}$  $\begin{array}{c} \text{CH}_3 \\ \\ \text{OH} - \text{C} - \text{H} \\ \\ \text{Br} - \text{C} - \text{H} \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{H} - \text{C} - \text{Br} \\ \\ \text{CH}_3 \end{array}$ $\begin{array}{c} \text{CH}_3 \\ \\ \text{OH} - \text{C} - \text{H} \\ \\ \text{Br} - \text{C} - \text{H} \\ \\ \text{CH}_3 \end{array}$

Exam Questions Solutions

1. What are geometrical isomers? Draw the structure of 2-chloro -3-methylpent -2-ene and specify z and E configuration.

[TU 2067 'R'/2069 'Back']

Ans: Geometricaal isomers

The compounds having the same molecular formula but with different arrangement of atoms or group of atoms across single bond or C = C double bond (in alkene) is known as geometrical isomers and the phenomenon is called geometrical isomerism.

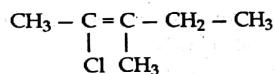
For the molecules exhibit the geometrical isomerism, each double bonded carbon must be linked with different atoms or group.

If the same atoms or group of atoms are on the same side in C = C double bond is represented by 'Cis' isomers.

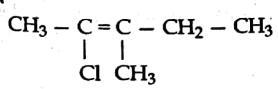
While similar group are attached to different side of molecules is called 'trans' isomers.

Now,

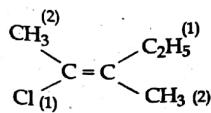
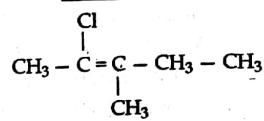
2 - chloro - 3- methylpent - 2 - ene



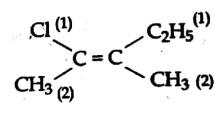
Structure 1



Structure 2



E-configuration

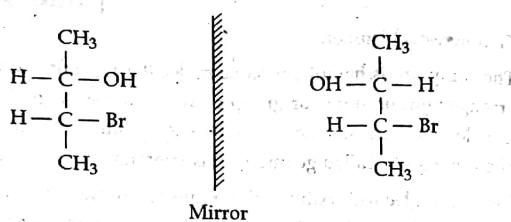


Z-configuration

2. Illustrate enantiomerism with an example. Mention a typical organic molecule which exhibits diastereomerism. [TU 2067 Ashadhy]

Ans: Enantiomerism is the phenomenon of isomerism of isomers that are not superimposable mirror image of each others.

Example:



In this example, they are image of each other but are not superimposable, so they are enantiomers.

3. What are geometrical isomers? Give an example specifying Z and E configuration. [TU 2068/2073 Bhadra]

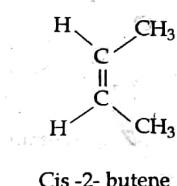
Ans: The compounds having the same molecular formula but with different arrangement of atoms or group of atoms across single bond or C = C double bond (in alkene) is known as geometrical isomers and the phenomenon is called geometrical isomerism.

For the molecules exhibit the geometrical isomerism, each double bonded carbon must be linked with different atoms or group.

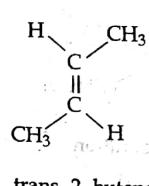
If the same atoms or group of atoms are on the same side in C = C double bond is represented by 'Cis' isomers.

While similar group are attached to different side of molecules is called 'trans' isomers.

Examples: $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$
2-butene



Cis -2- butene



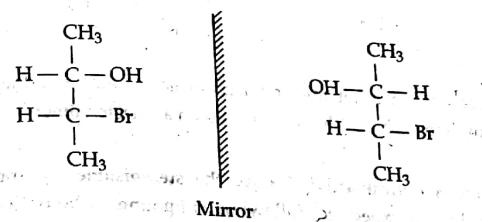
trans -2- butene

4. Show your familiarity with enantiomerism and diastereomers. [2068 Bhadra/2073 Back]

Ans: Enantiomers

Enantiomerism is the phenomenon of isomerism of isomers that are not superimposable mirror image of each others.

Example:

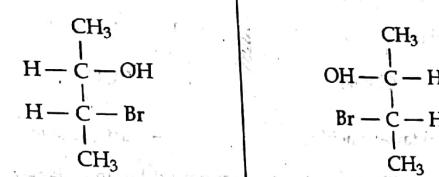


In this example, they are image of each other but are not superimposable, so they are enantiomers.

Diastereomers

They have same chemical and physical properties but differs in rotation of plane polarized light.

Example; 3-bromo-2-butanol shows diastereomerism.



Here, they are not mirror image of each other and they are same compound. That's why they are known as diastereomers.

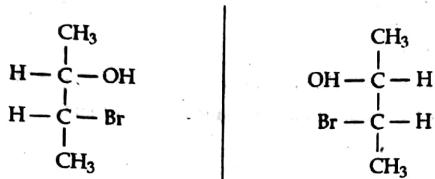
5. What are geometrical isomers? Give an example. [2069 Chaitra]

Ans: See the theory parts of geometrical isomerism

6. Show your familiarity with diastereomerism. [TU 2069 Chaitra/2074 Back]

Ans: They have same chemical and physical properties but differs in rotation of plane polarized light.

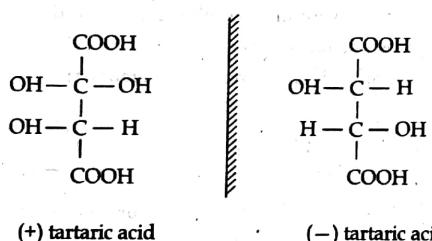
Example: 3-bromo-2-butanol shows diastereomerism.



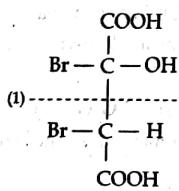
Here, they are not mirror image of each other and they are same compound. That's why they are known as diastereomers.

7. What is optical activity? Give the stereoisomers of tartaric acid. Would you expect the following compound to be optically active? Explain. [TU 2069/2072]

Ans: When plane polarized light is passed through the solution of some compound the plane polarized light is deviated through some angle from its original plane. This phenomenon is known as optical activity.



The given compound is a meso compound having plane of symmetry as shown below.



(1) - (1) is plane of symmetry. The rotation in plane polarized light done by upper half is cancel by lower half. So, there will be no optical activity.

8. Define the geometrical isomerism and write an example with 2 and E notation. [TU 2070 Bhadra]

Geometrical isomerism

The compounds having the same molecular formula but with different arrangement of atoms or group of atoms across single bond or C = C double bond (in alkene) is known as geometrical isomers and the phenomenon is called geometrical isomerism.

For the molecules exhibit the geometrical isomerism, each double bonded carbon must be linked with different atoms or group.

If the same atoms or group of atoms are on the same side in C = C double bond is represented by 'Cis' isomers.

While similar group are attached to different side of molecules is called 'trans' isomers.

If the geometrical isomers can not be differentiated by Cis & trans then it is differentiated by Z and E notation.

Where,

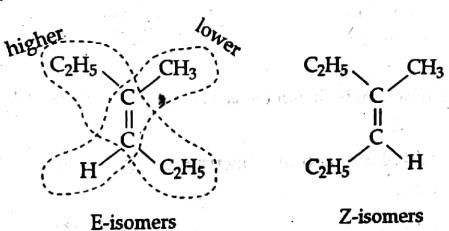
Z (Zusammen) → same side → together

E (Entgegen) → opposite side

E represents the atoms or group of higher precedence are on opposite side.

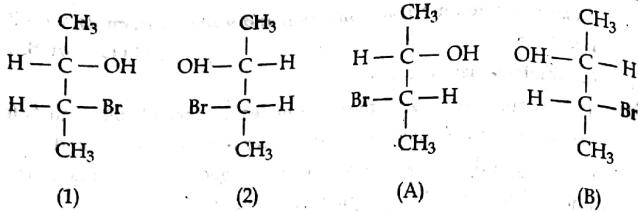
Z represents the atoms of higher precedence on same side.

Example:



9. Write the possible isomers of 3-bromo-2-butanol and specify enantiomers, resemination and resolution of racemic mixture [2070 Bhadra]

Ans: The given compound is 3-bromo-2-butanol their possible structures are as:



We can say that

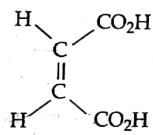
The structures (1) - (2) and (A) - (B) are enantiomers.

Recemicization: It is the process of making equimolar solution of enantiomers which makes the solution optically inactive.

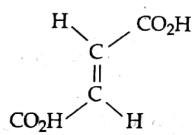
Resolution of recemic mixture: The process of the separation of the recemic mixture into optical active isomers is known as resolution of recemic mixture.

10. Specify Z and E configuration of maleic acid and fumaric acid. [2068 Magh]

Ans: The structures of maleic and fumaric acid are shown as



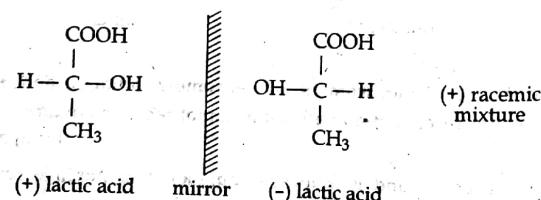
Maleic acid
(Z-isomer)



Fumaric acid
(E-isomers)

11. What isomerism is shown by lactic acid? Write its possible isomers. [2070 Chaitra]

Ans: Lactic acid shows optical isomerism. Lactic acid exists in following three forms.



Hence, lactic acid shows enantiomerism.

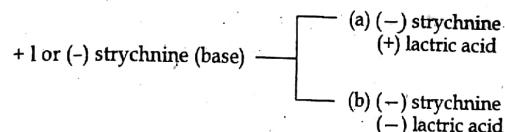
12. What do you mean by recemic mixture? Explain chemical resolution of a racemic mixture. [2070 Chaitra, 2072 Back]

Ans: A mixture having an equal amount of d or l isomer is called racemic mixture or dl mixture. It is optically inactive because the rotation caused by one molecule of isomer is cancelled by equal and opposite rotation called by another molecule which is the enantiomer of the first. It is denoted by (+).

Recemic mixture + another optically active compound \longrightarrow Different compounds are formed and then separated

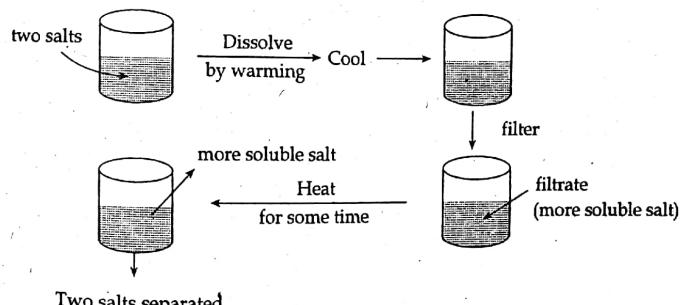
Example:

Racemic mixture of lactic acid



Chemical resolution

The two salts a and b have different solubility (one soluble in water easily) and separated by fractional crystallization.



Treated the salt separately with dil. HCl to remove base \rightarrow d or l lactic acid is separated.

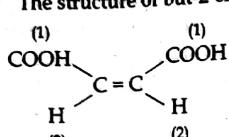
13. Write the differences between enantiomers and diastereomerism giving appropriate examples. [2071 Regular/2074 Bhadra]

Ans: See theory part on 9.5

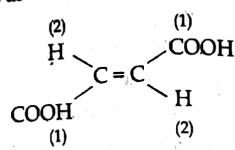
122 ... A Refresher Solution of Eng. Chemistry (B.E. I Yr I Part)

14. Write Cis, Trans and Z, E notations for the possible isomers of but-2-enedioic acid. [2071 Shrawan]

Ans: The structure of but-2-enedioic acid is as



(Z) But-2-enedioic acid
or
Cis - But - 2 - endioic acid



(E) But-2-enedioic acid
or
trans - But - 2 - endioic acid

15. What are Cis and trans - isomers? Which of these two isomers is more stable and why? [2072 Magh]

Ans: See theory part.

Reaction Mechanism in Organic Reaction ... 123

Chapter 10

Reaction Mechanism in Organic Reaction

INTRODUCTION

The process which describe how the chemical reaction takes place by breaking and formation of bond is known as reaction mechanism. Reactants generally consist of two species (i.e. substrate and reagents) combine together to give product.

i.e.,



Substrate:- It is an active part of reactants which is attacked by the reagents to form the products.

Reagents:- It is an active part of reactants that attacks substrate to form product.

Substitution Reaction:-

Substitution reactions are those reaction in which an atom or group of atom attached to a carbon atom in a substrate molecule is replaced by another atom or a group of atom depending upon the mechanism, the substitution reaction are further classified into three types.

- (i) free radical substitution reaction
- (ii) electrophilic substitution reaction
- (iii) nucleophilic substitution reaction

Nucleophilic Substitution Reaction :-

The substitution reaction in which attacking reagents are nucleophiles are known as nucleophilic substitution reactions. The nucleophilic substitution reactions are divided into two classes.

- (a) unimolecular nucleophilic substitution reaction.
- (b) bimolecular nucleophilic substitution reaction.

Bimolecular Nucleophilic Substitution Reaction ($\text{S}_{\text{N}}2$ Reaction)

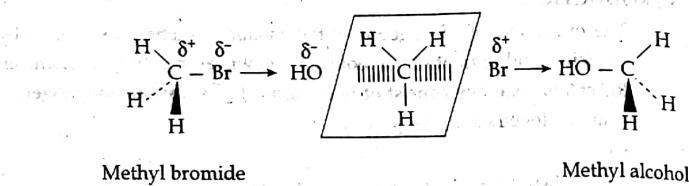
The Nucleophilic Substitution Reaction in which the rate of reaction depends on the concentration of both substrate and the nucleophilic are known as bimolecular nucleophilic substitution reaction. ($\text{S}_{\text{N}}2$)

reaction) the rate of reaction is proportional to the concentration of the substrate multiplied by concentration of nucleophile.

i.e.,

$$\text{Rate} \propto [\text{substrate}] [\text{nucleophile}]$$

Mechanism:-



Methyl bromide

Methyl alcohol

In the SN^2 reaction mechanism the nucleophile (OH^-) attacks the substrate carbon from the opposite side of the leaving group halide (Br) because both are electron negative as well as the density of electrons will be higher towards the leaving group or halide.

In the transition state the nucleophile starts to shear its electron pair with the substrate carbon by the formation of the partial bond simultaneously partial breakage of bond takes place between the substrate carbon and the leaving group. So the substrate carbon in P.S is in SP^2 hybridized state and will have trigonal planar geometry.

The partial bonds $\text{C} \equiv \text{O} \text{H}$ and $\text{C} \equiv \text{Br}$ lie perpendicular to the plane of the three $\text{C}-\text{H}^-$ bonds.

Here the charge of the nucleophile decrease is represented by δ^- and the charge of halide also decreases and shown by δ^- .

Finally the product (1° alcohol) is obtained with inversion at conjunction known as warden inversion.

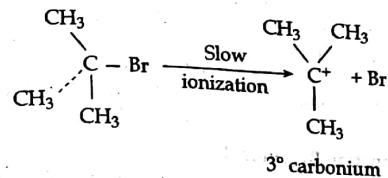
Unimolecular Nucleophilic Substitution Reaction ($\text{S}^{\text{N}}\text{I}$ Reaction)

The Nucleophilic substitution reaction in which rate of reaction depends only on the concentration of substrate molecule is known as ($\text{S}^{\text{N}}\text{I}$) unimolecular nucleophilic substitution reaction. The rate of reaction is proportional to concentration of the substrate only.

i.e., Rate \propto [substrate]

Mechanism:-

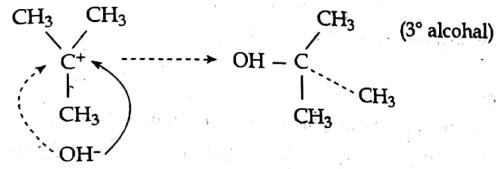
Step - I:



3° carbonium

In this step ionization of alkyl halide to produce carbonium ion takes place.

Step - II



Intermediate

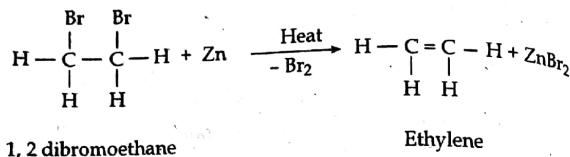
The tertiary carbonium ion undergoes slow ionization with the formation of tertiary carbonium ion as an intermediate. In this case the nucleophile can not directly attack the substrate carbon because of the presence of the three alkyl group which are electron releasing group or due to steric hindrance.

As the tertiary carbonium ion is formed immediately the nucleophile attacks it get the nucleophile attacks from the backside, the product is obtained with inversion of configuration but if the nucleophile attacks from the front side, the product is obtained with retention of configuration.

Elimination Reaction:-

In elimination reaction generally atoms or groups from two adjacent carbon atoms in the substrate molecule are removed and multiple bond is formed. In this process two sigma bonds are lost and a new bond is formed.

Example:-



Bimolecular Elimination Reaction: (E₂)

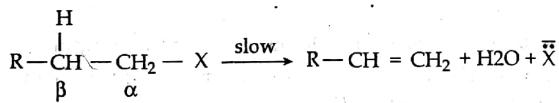
The elimination reaction in which rate of reaction depends on the concentration of both substrate and nucleophile is known as bimolecular elimination reaction. The rate of reaction is proportional to concentration of substrate multiplied by concentration of nucleophile.

i.e.

Rate \propto [Substrate] [Nucleophile]

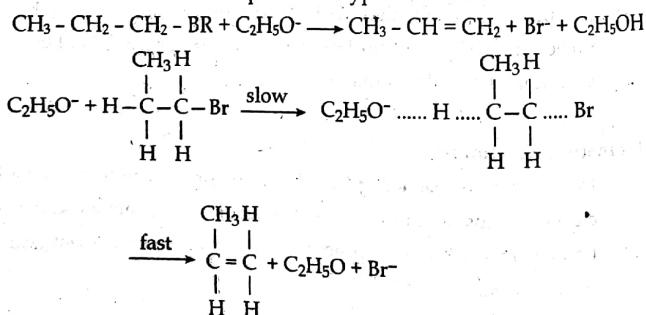
Mechanism:-

It is one step process in which the abstraction of the proton from the B-carbon and expulsion of the leaving group i.e. halide ion etc. from the L-carbon occur simultaneously.



In these reaction, two groups to be eliminated i.e. H atom and X are forms to each other and hence ER reactions generally trans elimination reactions.

The dehydratation of the alkyl halides with alcoholic alkali halides with alcoholic alkali is an example of E^{m} 's type of reaction.



Unimolecular Elimination Reaction (E_1)

The elimination reaction in which rate of reaction depends on the concentration of substrate only. The rate of reaction is proportional to the concentration of substrate.

i.e. *et cetera* etc. &c. &c.

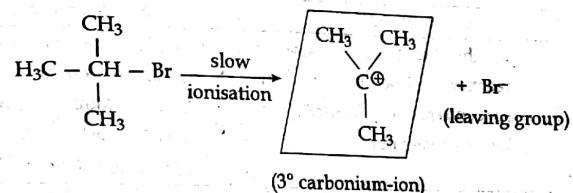
Rate α [substrate]

Mechanism:-

Step-I:

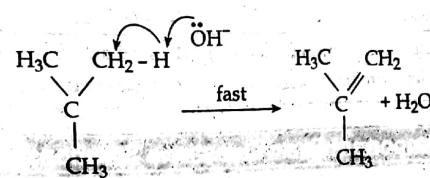
The first step involves the slow ionization of the alkyl halide to give the carboxium ion and leaving group.

i.e.



Step-II:

The fast abstraction of a proton by the base from the adjacent β -carbon atom leading to the formation of an alkenes.



2-Methyl Propene

Difference between E₁ and E₂ reaction.

E ₁ reaction	E ₂ reaction
i) The rate of reaction depends upon concentration of substrate.	i) Rate of reaction depends upon concentration of both substrate and base.
ii) It does not require strong base, attacking group.	ii) It requires strong base nucleophiles.
iii) Tertiary alkyl halide favors E ₁ reaction mostly.	iii) Primary alkyl halide favors E ₂ mostly.
iv) It is two-step process of elimination, ionization and deprotonation.	iv) It is one-step process of elimination with a single transition state.

Difference between S_N1 and S_N2 reaction.

S _N 1 reaction	S _N 2 reaction
i) In this reaction, the rate of reaction depends on the concentration of substrate. i.e. Rate \propto [substrate]	i) In this reaction, the rate of reaction depends upon the concentration of substrate and nucleophile i.e. Rate \propto [substrate][nucleophile]
ii) Two types of products are formed by retention of configuration and inversion of configuration.	ii) The product is formed by inversion of configuration.
iii) It is two step reaction.	iii) It is only one step reaction.
iv) Solvents of high polarity favors this reaction.	iv) Solvents of low polarity favors this reaction.
v) Carbonium ion attacked by nucleophiles from both sides.	v) It is attacked by nucleophile from backside only.

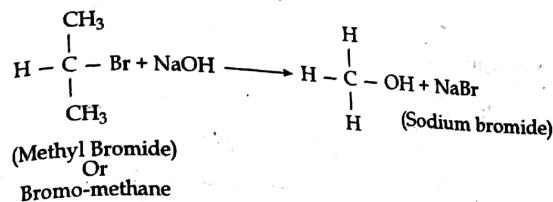
Important Exam Questions Solutions

1. Explain the mechanism involved in the reaction between bromo-methane and aq. NaOH. [2071 Shrawan]

Or

- Explain the mechanism of S_N2 reaction [2074 Bhadra]

Ans:- The reaction between bromo-methane or methyl bromide and aqueous NaOH is given by the following reaction:

**Mechanism (S_N2 reaction)**

See the theory portion

2. Why does nucleophile attack the substrate molecule from backside in S_N2 reaction mechanism? Discuss E₁ reaction with reference to the dehydrohalogenation of alkyl halide. How does E₁ differs from E₂ reaction.

[TU 2070 Chaitra, TU 2073 back]

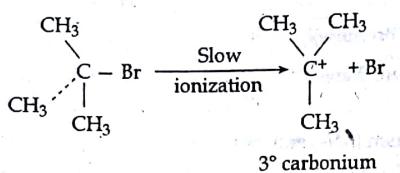
Ans: See the theory portion.

Difference between E₁ and E₂ reaction.

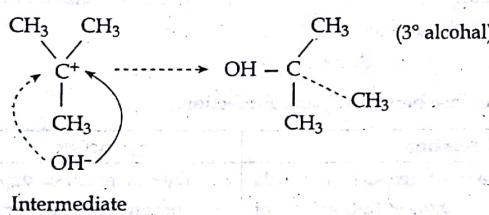
E ₁ reaction	E ₂ reaction
i) The rate of reaction depends upon concentration of substrate.	i) Rate of reaction depends upon concentration of both substrate and base.
ii) It does not require strong base, attacking group.	ii) It requires strong base nucleophiles.
iii) Tertiary alkyl halide favors E ₁ reaction mostly.	iii) Primary alkyl halide favors E ₂ mostly.
iv) It is two-step process of elimination, ionization and deprotonation.	iv) It is one-step process of elimination with a single transition state.

3. Describe S_N1 reaction mechanism in haloalkane shown stereochemistry. [2070 Chaitra]

Ans: The Nucleophilic substitution reaction in which rate of reaction depends only on the concentration of substrate molecule is known as (S_N1) unimolecular nucleophilic substitution reaction. The rate of reaction is proportional to concentration of the substrate only.
i.e. Rate \propto [substrate]

Mechanism:-**Step - I:**

In this step ionization of alkyl halide to produce carbonium ion takes place.

Step - II

The tertiary carbonium ion undergoes slow ionization with the formation of tertiary carbonium ion as an intermediate. In this case the nucleophile can not directly attacks the substrate carbon because of the presence of the three alkyl group which are electron releasing group or due to steric hindrance.

As the tertiary carbonium ion is formed immediately the nucleophile attacks it get the nucleophile attacks from the backside, the product is obtained with inversion of configuration but if the nucleophile attacks from the front side, the product is obtained with retention of configuration.

4. Explain the reaction mechanism involved in E₂ and S_N₂ reactions mention the one factor governing S_N₂ reaction.[2068 Magh, 2071 Back]

Ans: Mechanism of E₂ and S_N₂

See theory parts.

One factor governing S_N₂ reaction(i) **Nature of solvent**

Solvent polarity has slight effect on S_N₂ reaction. The rate decreases slightly with the increasing polarity of the solvent, hence, it is favoured by low polarity of solvent.

5. Give an account of S.N. relation. Explain the reaction mechanism for the reaction between alkyl halide and aqueous NaOH.

[TU 2070 Bhadra]

Soln: Same as Q.No. 1.

6. Explain the reaction mechanism for the dehydrohalogenation of tertiary butyl-bromide. Differentiate between E₁ and E₂ mechanism.

[T.U. 2069/2072]

Soln: **Reaction mechanism:**

See theory portion

Difference between E₁ and E₂ reaction.

E ₁ reaction	E ₂ reaction
i) The rate of reaction depends upon concentration of substrate.	i) Rate of reaction depends upon concentration of both substrate and base.
ii) It does not require strong base, attacking group.	ii) It requires strong base nucleophiles.
iii) Tertiary alkyl halide favors E ₁ reaction mostly.	iii) Primary alkyl halide favors E ₂ mostly.
iv) It is two-step process of elimination, ionization and deprotonation.	iv) It is one-step process of elimination with a single transition state.

7. What do you mean by elimination reaction? Explain the reaction mechanism for the dehydrohalogenation of tertiary alkyl halide.

[T U 2069 Bhadra]

Ans: **Elimination reaction:**

In elimination reaction generally atoms or groups from two adjacent carbon atoms in the substrate molecule are removed and multiple bond is formed. In this process two sigma bonds are lost and a new bond is formed.

Second part: See theory portion.

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8. How SN_1 and SN_2 reaction differ in halo alkane? Mention the factors which regulate the reactions. [T U 2069 Bhadra]

Ans: Difference between SN_1 and SN_2 reaction.

SN_1 reaction	SN_2 reaction
i) In this reaction, the rate of reaction depends on the concentration of substrate. i.e. Rate \propto [substrate]	i) In this reaction, the rate of reaction depends upon the concentration of substrate and nucleophile i.e. Rate and [substrate][nucleophile]
ii) Two types of products are formed by retention of configuration and inversion of configuration.	ii) The product is formed by inversion of configuration.
iii) It is two step reaction.	iii) It is only one step reaction.
iv) Solvents of high polarity favors this reaction.	iv) Solvents of low polarity favors this reaction.
v) Carbonium ion attacked by nucleophiles from both sides.	v) It is attacked by nucleophile from backside only.

Factors which regulates the reaction

- (i) Concentration of substrate
- (ii) Polarity
- (iii) Nature of Solvent

9. What is meant by elimination reaction? Discuss E_1 and E_2 reaction. [T U 2069 Chaitra]

Ans: Elimination reaction:

In elimination reaction generally atoms or groups from two adjacent carbon atoms in the substrate molecule are removed and multiple bond is formed. In this process two sigma bonds are lost and a new bond is formed.

Second part: See theory portion.

10. Discuss the unimolecular nucleophilic substitution reaction mechanism in alkyl halide showing the stereochemistry. [2069 Chaitra PU]

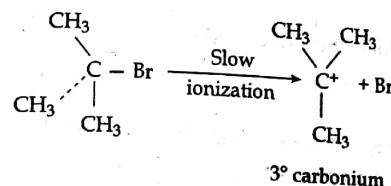
Ans: The Nucleophilic substitution reaction in which rate of reaction depends only on the concentration of substrate molecule is known as

Reaction Mechanism in Organic Reaction ... 133

(SN_2) unimolecular nucleophilic substitution reaction. The rate of reaction is proportional to concentration of the substrate only.
i.e. Rate \propto [substrate]

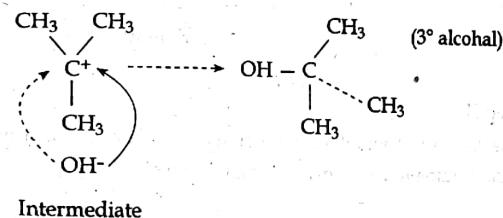
Mechanism:-

Step - I:



In this step ionization of alkyl halide to produce carbonium ion takes place.

Step - II



The tertiary carbonium ion undergoes slow ionization with the formation of tertiary carbonium ion as an intermediate. In this case the nucleophile can not directly attacks the substrate carbon because of the presence of the three alkyl group which are electron releasing group or due to steric hindrance.

As the tertiary carbonium ion is formed immediately the nucleophile attacks it get the nucleophile attacks from the backside, the product is obtained with inversion of configuration but if the nucleophile attacks from the front side, the product is obtained with retention of configuration.

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11. What is meant by elimination reaction? Discuss E₁ and E₂ reaction mechanism. [TU 2068 Chaitra]

Soln: Elimination reaction:

In elimination reaction generally atoms or groups from two adjacent carbon atoms in the substrate molecule are removed and multiple bond is formed. In this process two sigma bonds are lost and a new bond is formed.

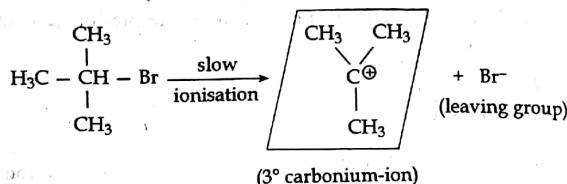
Unimolecular Elimination Reaction (E₁)

Mechanism:-

Step-I:

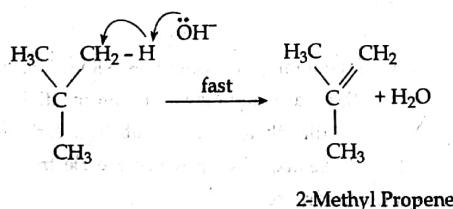
The first step involves the slow ionization of the alkyl halide to give the carbocation and leaving group.

i.e.



Step-II:

The fast abstraction of a proton by the base from the adjacent β-carbon atom leading to the formation of an alkenes.

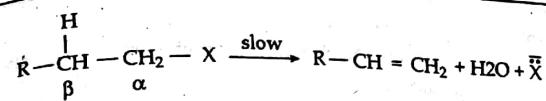


Bimolecular Elimination Reaction: (E₂)

Mechanism:-

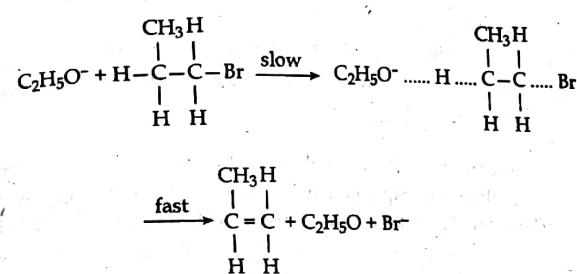
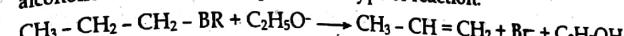
It is one step process in which the abstraction of the proton from the β-carbon and expulsion of the leaving group i.e. halide ion etc. from the α-carbon occur simultaneously.

Reaction Mechanism in Organic Reaction ... 135



In these reactions, two groups tend to be eliminated i.e. H atom and X are forms to each other and hence E₁ reactions generally trans elimination reactions.

The dehydration of the alkyl halides with alcoholic alkali halides with alcoholic alkali is an example of E₁'s type of reaction.



12. Discuss the unimolecular nucleophilic substitution reaction mechanism in alkyl halide showing the stereochemistry. What types of solvent favours this type of mechanism? [TU 2068 Bhadra]

Ans: See theory portion

13. a. Write mechanism of bimolecular elimination rxn.
b. Mention the effect of nucleophile substrate and solvent on nucleophilic substitution reaction mechanism.

[TU 2067][PU 2069]

Ans: (a) Bimolecular elimination rxn

The elimination reaction in which rate of reaction depends on the concentration of both substrate and nucleophile is known as bimolecular elimination reaction. The rate of reaction is proportional to concentration of substrate multiplied by concentration of nucleophile.

i.e.

$$\text{Rate} \propto [\text{Substrate}] [\text{Nucleophile}]$$

(b) Effect of nucleophile

SN₁ reaction:- Nucleophile concentration doesn't affect the reaction rate.

SN₂ reaction:- Nucleophile concentration affects the rate of reaction.

i.e. rate \propto [Nucleophile]

Effect of substrate

Both reactions are depended upon the concentration of substrate. Bulky substrate means reaction is **SN₁** reaction and vice versa. Bulky substrate has **SN₁** mechanism with two steps and open kind of substrate means **SN₂** mechanism with one step.

Effect of solvent

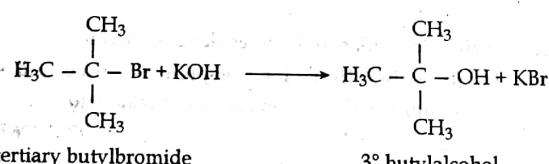
SN₁ reaction:- High polarity in solvent favors **SN₁** reaction.

SN₂ reaction:- Low polarity in solvent favors **SN₂** reaction. i.e. rate \propto [nucleophile]

14. Describe the mechanism involved in the reaction between a tertiary alkyl halide and aqueous caustic potash. How **SN₂** reactions do differ from **SN₁** in its stereochemistry? [TU 2067 Ashadh, 2070 Back]

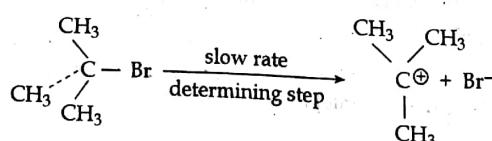
Ans:- Tertiary halide has three alkyl group which acts as bulky group which prevents direct attack of nucleophile to centre carbon. Therefore the reaction rate is dependent of concentration of alkyl halide but not nucleophile. This is **SN₁** i.e. unimolecular nucleophilic substitution reaction which has two steps.

Hydrolysis of tertiary alkyl halide by aq. KOH (caustic potash)



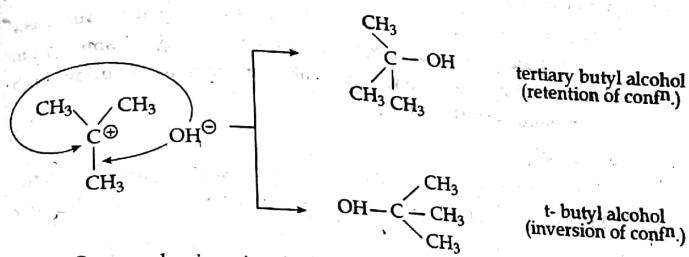
Mechanism steps:-

Step I: Heterolysis of substrate slowly to form carbocation.



The step I is slower and determines the rate of reaction. Hence, it is known rate determining step. The carbonium ion is planar as the central positively charged carbon atom is SP^2 hybridised. The required bonds between ions produced and the solvent.

Step II:-



Once carbonium ion is formed nucleophilic attack takes place from front side as well back side, so there is formation of mixture of inversion and retention products.

Exam 2072 Chaitra

(Regular /Back)

Attempt all the questions.

1. What is buffer solution? Derive Henderson's equation for basic buffer. Calculate p^H of a mixture of 10 ml of 0.1 M ammonium chloride solution and same volume of 0.2 M ammonia solution. (pK_b for ammonia solution = 4.74)

Ans: Buffer solⁿ

The solution which can maintain its p^H value almost constant even the addition of small amount of strong acid or base is called buffer solution.

Henderson's equation for basic buffer

Let us take basic buffer of BOH (weak base) and its salt BCl.

- (a) $BOH \rightleftharpoons B^+ + OH^-$ (feebly ionized)
 (b) $BCL \longrightarrow B^+ + Cl^-$ (completely ionized)

Now,

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \quad \dots \dots \dots (1)$$

Where, K_b is ionization of base.

Ionization of weak electrolyte is great if decreases due to common ion effect. Therefore, the concentration remains same. Accordingly it is assumed that the concentration of common ion is same as the concentration of salt it is because the concentration from base is negligible.

So, $[BOH] = [Base]$ & $[B^+] = [Salt]$

Then eqn. (1) becomes,

$$K_b = \frac{[OH^+][salt]}{[Base]} \quad \dots \dots \dots (2)$$

$$\text{or, } [OH^-] = K_b \frac{[Base]}{[Salt]}$$

Taking log on both side, we get

$$\text{or, } \log_{10} [OH^-] = \log_{10} \left\{ K_b \frac{[Base]}{[Salt]} \right\}$$

$$\text{or, } \log_{10} [OH^-] = \log_{10} K_b + \log_{10} \frac{[Base]}{[Salt]}$$

$$\text{or, } -\log_{10} [OH^-] = -\log_{10} K_b - \log_{10} \frac{[Base]}{[Salt]}$$

$$\text{or, } p^{OH} = p^{Kb} + \log_{10} \frac{[Salt]}{[Base]}$$

$$\therefore p^{OH} = -\log [OH]$$

$$\therefore p^{Kb} = -\log K_b$$

Which is required equation.

$$\therefore p^H = 14 - p^{OH}$$

Numerical part:

Solution:

Volume of NH_4Cl = 10 ml

concentration of NH_4Cl = 0.1 M

Concentration of ammonia solution = 0.2 M

Total volume of mixture = 20 mL

$$p^{Kb} = 4.74$$

Here,

$$[Salt] = \frac{0.1 \times 10}{20} = 0.05 \text{ M}$$

$$[base] = \frac{0.2 \times 10}{20} = 0.1 \text{ M}$$

Now,

From Henderson's eqn. we have

$$p^{OH} = p^{Kb} + \log_{10} \frac{[Salt]}{[Base]}$$

$$= 4.74 + \log_{10} \frac{0.05}{0.1}$$

$$= 4.74 + (-0.301)$$

$$\therefore p^{OH} = 4.389$$

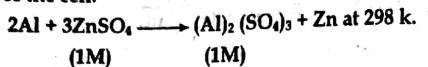
Here,

$$p^H = 14 - p^{OH}$$

$$= 14 - 4.389$$

$$= 9.611$$

2. How does galvanic cell generate electricity? Construct a cell with the following cell reaction. Write cell notation and calculate standard emf of the cell.



Given, standard reduction potential of Al and Zn are -1.66 V and 0.76 V respectively.

Ans: 1st part:

It is a voltaic cell based on electric effect of chemical reaction. It generates electricity by spontaneous redox reactions. Let's see the simple example of Daniell cell.

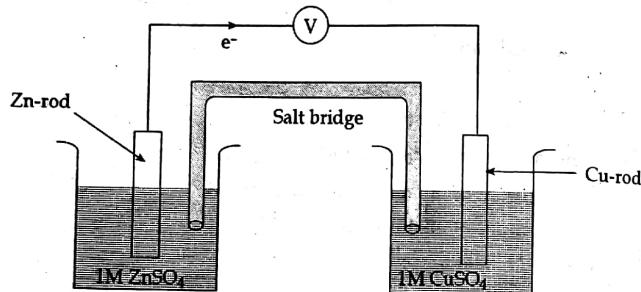
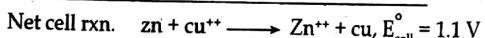
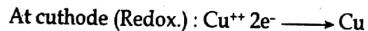
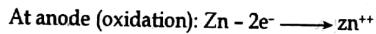


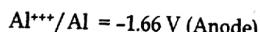
Fig: Galvanic cell



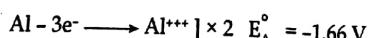
As the reaction occurs, the electrons are transferred from $\text{Zn}^{+} + e^- \text{ Cu}^{++}$ through wire which produces the electrical energy. In this way electrical energy is generated in galvanic cell.

Numerical

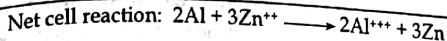
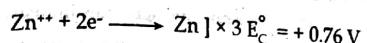
Given that,



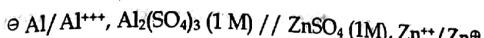
At anode (oxidation)



At cathode (Reduction)



Cell notation



Now,

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_C^{\circ} - E_A^{\circ} \\ &= 0.76 - (-1.66) \\ &= 2.42 \text{ V} \end{aligned}$$

Using Nernst eqn. we get,

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Al}^{+++}]}{[\text{Zn}^{++}]} \\ &= 2.42 - \frac{0.0591}{2} \log \frac{[1]}{[1]} \\ &= 2.42 - \frac{0.0591}{2} \times 0 = 2.42 \text{ V.} \end{aligned}$$

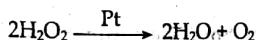
The standard emf. of cell is 2.42 V.

3. What is catalyst? Explain intermediate compound formation theory and in industrial application of catalyst.

Ans: The substances which alters the rate of chemical reaction without undergoing any change in mass and composition at the end of the reaction is known as catalyst and the phenomenon is called catalysis.

For example,

platinum increases the rate of decomposition of hydrogen peroxide as



Here,

pt = catalyst

Second part: Refer to theory part.

4. What are the parameters of water pollution? Explain its causes and adverse effects.

Ans: Following are the parameter of water pollution:

- (i) Natural source

Water gets polluted from natural wastes like decomposed animals and degraded/weathered products of agriculture.

(ii) Human activities

This parameter includes domestic activities industrial activities.

- Domestic activities: Includes the waste water which contains human faces, kitchen wastes, organic water solution that helps in breeding of bacteria and fungi.
- Industrial activities: Includes the waste from factory and refineries. These waste contains several chemical that drained into streams which cause water pollution. These type of waste decrease the BOD & COD of water.

- (iii) In metropolitan city the surface run off rain water also get into rivers and cause it's pollution.

Cause of water pollution

- (i) Mixing of organic decomposed waste into river.
- (ii) Use of insecticides and pesticides in agriculture.
- (iii) Untreated sewer water draining into rivers.
- (iv) Untreated industrial waste.
- (v) Improper management or surface runoff water in urban areas.

Effects of water pollution

1. It cause various water based disease like typhoid, cholera, dysentery, etc.
2. Use of pesticides and insecticides although it's increase the crop production but it effect on human health and cause malaria, Kalahari and typhoid.
3. The eco-system get disturbed.
4. Aquatic life get disturbed.

5. Write the functions of lubricant. Show your acquaintance with fluid film lubricant and its role in engineering. Give an example each of (a) Semi-solid lubricant and (b) emulsion.

Ans:- Function of lubricant

1. Control surface deformation.
2. It is a good coolant.
3. Control use of fuel and energy.
4. Decrease the maintenance cost of machine.
5. Control the ceasing of engine.
6. Prevents the corrosion of surface.
7. It can act as seal for I.C. engine.

Fluid film lubricants are most used lubricant in engineering field. It must posses high boiling point or low pressure. It helps the cooling, sealing and decreasing frictions in engine. Lubricants forming fluid makes the machine long lasting and good working condition.

- (a) Semi solid lubricant example grease, tar
- (b) Emulsion: example Vinaigrettes, homogenized mayonnaise, etc.

6. Write short notes on: (any two)

Global warming

Ans: Global warming, also referred to as climate change, is the observed century scale rise in the average temperature of the earth's climate system and it's related effects. Multiple lines of scientific evidence show that the climate system is warming.

Many of the observed changes since 1950s are an precedent in the instrumental temperature record which extends back to the mid-19th century, and in paleoclimate proxy records covering thousands of year.

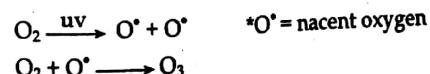
The largest human influence has been the emission green house gases such as carbon dioxide, methane and nitrous oxide. Future climate change and associated impacts will differ from region to region around the globe. Anticipated effects includes increase global temperature, rising sea levels, changing precipitation and expansion of deserts in the sub tropics. Other likely changes include more frequent extreme weather events such as heat waves, droughts, heavy rainfall with floods and heavy snowfall, ocean acidification and species extinctions due to shifting temperature regem.

Formation and depletion of ozone layer

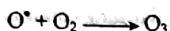
Ans: Ozone layer is the layer of pale blue gas which is mainly found in stratosphere. This gas is a allotrope of oxygen.

Formation of ozone layer

It is a photo chemical reaction in which O_2 molecule gets split into two nascent oxygen by UV ray then it again combines with O_2 which cause formation O_3 molecule i.e. ozone.

Reaction:

It is also formed in lower atmosphere due to decomposition of NO_2 gas by sunlight.

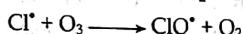
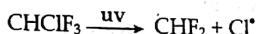


Depletion of ozone layer

It is also a photochemical reaction in which ozone layer gets destroyed by following gases CO, NO, NO_2 , CH_4 . The main gases that causes depletion of ozone layer are CFC like CFCl_3 , CHC_2F_3 , CF_2Cl , etc.

Process: CFC are chlorine containing compounds which absorbs UV rays from the sun and decomposes to give C_2 atom which destroys ozone.

Reactions:



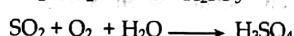
Acid rain and its effect

Ans: As the name refers acid rain that is the rain water which contains small amount of acid. It happens due to presence of CO_2 in atmosphere which gets dissolve into rain water during raining thus formation acidic rain. Its pH value is 5.6.



The acid rain mainly cause due to polluted environment which contains oxides of sulphur SO_x and nitrogen NO_x . During raining these oxides are dissolved in rain droplets resulting in the formation of sulphuric and nitric acid and the mixture of these acid and water is called acid rain. Its pH value is lower than 5.7.

Reactions:



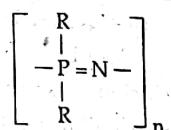
7. What is conducting polymer? Give an account of photosynthesis and field.

Conducting polymer

Conducting polymers or more precisely, intrinsically conducting polymers (ICP) are organic polymers. That conduct electricity such compounds may have metallic conductivity or can be semi conductors. The biggest advantage of conductive polymers is their process ability, mainly by dispersion. Conductive polymers are not generally thermoplastics.

Polyphosphazines

These are the inorganic polymers which contain phosphorus as predominant atom. Their general structure is



Where,

$\text{R} \Rightarrow -\text{Cl}$ in polyphosphonitrile chlorides

$\text{R} \Rightarrow -\text{OCH}_3$ in polydimethoxy phosphazines

$\text{R} \Rightarrow -\text{OC}_2\text{H}_5$ in polydiethoxy phosphazines

Engineering application

- Due to high flexibility used in elastic uses.
- Visible and transparent so used as glass sills.
- Used in elastometers.

Chalcogenide glasses

These are the compound having cross linked structure with polyvalent elements like As, Ge, In etc. obtained from quenching of chalcogenite compound.

E.g. AS_2S_3

Engineering application field

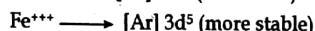
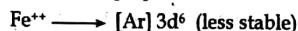
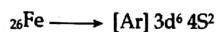
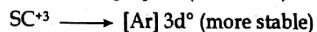
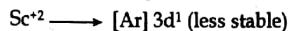
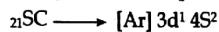
- Construction of electronic devices like memory chip, IC, microprocessor etc.
- Electronic display
- High energy particle detector multipliers.
- Ultrasonic delay systems etc.

8. Explain the following.

- (i) 3d-transition series show variable oxidation states
- (ii) Completely filled 3-d transition series are unable to form coloured compounds.

Ans: (i) 3- transition series show variable oxidation states most of the transition metal exhibit variable oxidation state i.e. they have more than one valency except zinc. This is quite contrast to 'S' block and 'p' block elements. The variable oxidation states of transition elements is due to the following reasons:

(a) The cations of the transition metal can not achieve the inert gas configuration or stable configuration in any common oxidation state. Such inert gas configuration which is less stable. Hence one or more e⁻s are lost from this configuration to acquire stable configuration atom.



(b) The energy of '3d' and '4s' orbitals are fairly close to each other. Hence, electrons are lost from both the orbitals during cation formation.

- (ii) Completely filled 3-d transition series unable to form coloured compounds.

→ See theory portion.

9. What is a complex ion? Give example of a (i) complex ion and (ii) complex anion with their IUPAC name.

Also calculate EAN of central metal of these ions.

Ans: Complex ion

These are positively or negatively charged ions containing metal and the definite number of attached species, the ligands.

e.g. (i) Complex cation

Remaining parts

See theory part.

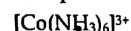
10. Show your acquaintance on the basis of hybridisation with inner orbital and outer orbital complexes with example.

Ans: The geometry of 6-coordinated complex ions is octahedral complexes. This complex arises due to d²sp³ or sp³d² hybridization of the central metal atom or ion.

These are two types

- (i) Inner orbital complexes
- (ii) Outer orbital complexes
- (iii) Inner orbital complexes

It is formed due to d²sp³ hybridization in the central metal atom/ion. It is formed by strong ligands.
for example:



For the formation of $[\text{Co}(\text{NH}_3)_6]^{3+}$:

See on the Q.No.3 of 2068 (Magh soln).

(ii) Outer orbital complexes

They are formed due to sp³d² hybridization in the central metal atom/ion. They are formed by weak ligands.

example:



For the formation of $[\text{FeF}_6]^{4-}$:

See on the Q.No. 11 of 2070 Chaitra Soln.

11. Differentiate between high explosive and low explosive. Write the preparation and applications of TNT.

Soln: See previous question soln. of this chapter.

12. Write the method of preparation and uses of (a) polystyrene (b) bakelite.

Soln: See theory parts of this chapter.

13. Distinguish between enantiomers and diastereomers. Show all optical isomers of (a) 3-Bromo 2-butanol and (b) Tartaric acid. Also show optically inactive meso form of tartaric acid. Explain why 3-Bromo 2-butanol doesn't exist in meso form.

Soln: See theory parts and their soln. of this chapter.

14. Explain E_2 and E_1 reactions with reference to dehydrohalogenation of haloalkane and point out the factors affecting these mechanism.

Soln: See previous exam solution and respective theory.

15. Why does haloalkane favour SN reaction? Explain why there is only inversion product in SN_2 and both inversion and retention products in SN_1 path.

Soln: See theory parts.

15. What is plastic explosive? Write preparation and uses of following
(a) TNT (b) Dynamites

Soln: See theory portion and previous exam solution.