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Unit - 1

Metallurgy

1. **What are the differences between minerals and ores?**

Ore :

i) Materials which contains sufficient quantity of minerals so that metals can be extracted profitably.

ii) Ore contains a good percentage of metal.

iii) All ores are minerals.

Example : ZnS (Zinc blende) , $Al_2O_3.nH_2O$ (Bauxite),

Minerals :

i) Minerals are natural materials in which the metals or their compounds are found in earth.

ii) Minerals contains small percentage of metals.

iii) All minerals are not all minerals are not ores.

Example: Gypsum is a mineral from which calcium is extracted.

2. **What are the various steps involved in extraction of pure metals from their ores?**

Steps involved in extraction of metals

A) concentration of the ore

1 Gravity separation or Hydraulic wash

2 Froth flotation

3 Leaching **i) Cyanide leaching** **ii) Ammonia leaching** **iii) Alkali leaching** **iv) Acid leaching**

4. Magnetic separation

B) extraction of crude metal

i) Conversion of ores into oxides **a)Roasting** **b)Calcination**

ii) Reduction of metal oxides

a) Smelting **b) Reduction by carbon** **c) Reduction by hydrogen**

d) Reduction by metal **e) Auto-reduction:**

C) refining of crude metal

a) Distillation b) Liquation c) Electrolytic refining d) Zone Refining

e) Vapour phase method

i) Mond process for refining nickel: **ii) Van-Arkel method for refining zirconium / titanium:**

3. **What is the role of Limestone in the extraction of Iron from its oxide Fe_2O_3?**

It acts as a basic flux to remove impurities like silica, sulphur and phosphorus in the form of slag.e.g.,

i) $CaCO_3 \rightarrow CaO + CO_2$ ii) $CaO + SiO_2 \rightarrow CaSiO_3$

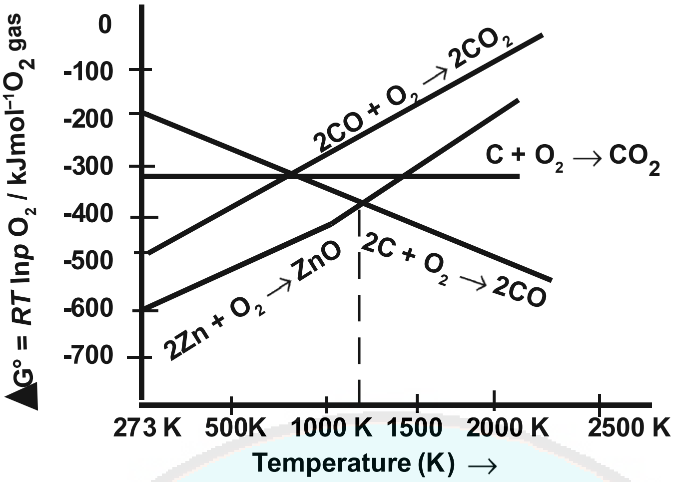
Here silica has been removed in the form of slag (calcium silicate).

4. **Which type of ores can be concentrated by froth floatation method? Give two examples for such ores.**

Sulphide ores can be concentrated by froth floatation method.

For example- PbS (galena), HgS (cinnabar) , ZnS (zinc blende)

5. Out of coke and CO, which is better reducing agent for the reduction of ZnO? Why?



From Ellingham diagram:

Coke is definitely the better reducing agent for the reduction of zinc oxide (ZnO) than (CO).

The Gibbs free energy of formation becomes lower at temperatures above 1273 K, for CO_2 from C.

In case of CO_2 from CO, the Gibbs free energy of formation is always higher than ZnO.

6. Describe a method for refining nickel.

Mond process for refining nickel:

The impure nickel is heated in a stream of carbon monoxide at around 350 K. The nickel reacts with the CO to form a highly volatile nickel tetracarbonyl. The solid impurities are left behind.

$$\text{Ni (s)} + 4\text{CO} \xrightarrow{350K} \text{(g) Ni(CO)}_4\text{ (g)}$$

On heating the nickel tetracarbonyl around 460 K, the complex decomposes to give pure metal.

$$\text{Ni (s)} + 4\text{CO} \xrightarrow{460K} \text{(g) Ni(CO)}$$

7. Explain zone refining process with an example .

Principle - The impurities in the molten state are more soluble than in the solid state of the metal .

Method - In this method , a circular mobile heater is fixed at one end of a rod of the impure metal .

The molten zone moves along with the heater which is moved forward .As the heater moves forward , pure metal crystallizes out of the melt and the impurities pass on into the adjacent molten zone.

The process is repeated several times and heater is moved in the same direction. At one end ,impurities gets concentrated .This end is cut off.This method is very useful for producing semi-conductors and other metals of very high purity.

eg- B, Si ,Ge,In,Ga ,etc

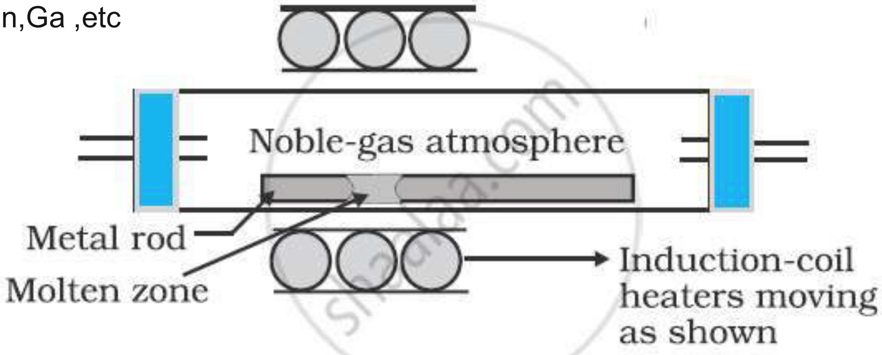
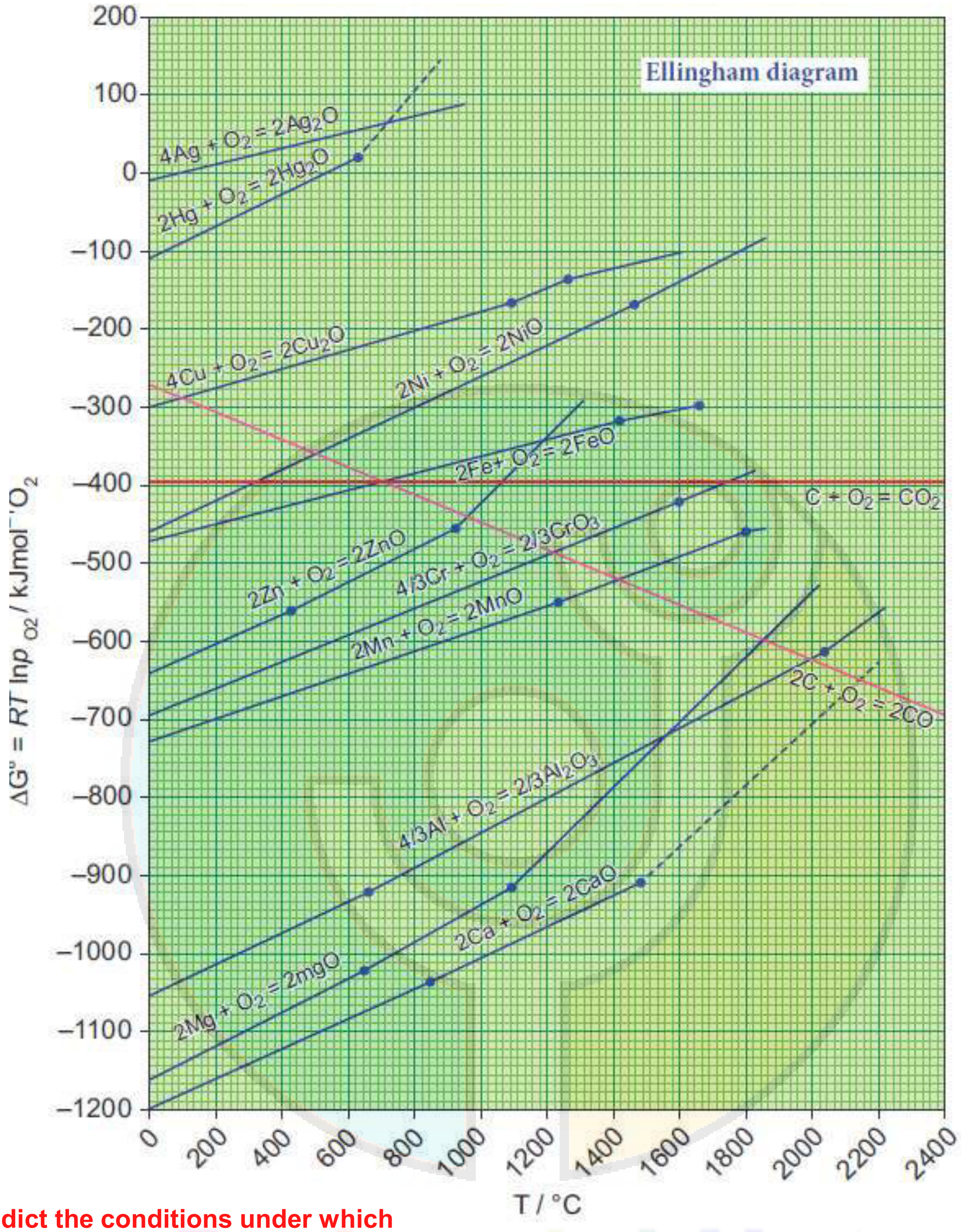


Fig. Zone refining process

8. Using the Ellingham diagram given below.



(A) Predict the conditions under which

(i) Aluminium might be expected to reduce magnesia.

Aluminium can reduce magnesium oxide at a temperature of about 2000 K because in this temperature range the line of ΔG° (Mg, MgO) lies above the line of ΔG° (Al, Al_2O_3) in the Ellingham diagram. Therefore, under these condition $\Delta_r G^\circ$ for reduction of MgO with Al will be negative and hence the reaction would be feasible.

$$3\,MgO + 2Al \rightarrow 3Mg + Al_2O_3$$

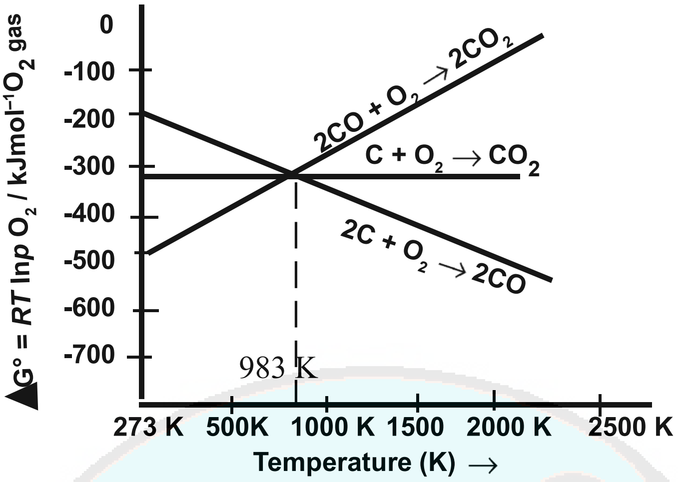
(ii) Magnesium could reduce alumina.

1. The reaction: $3\,Mg + Al_2O_3 \rightarrow 2\,Al + 3\,MgO$

2. On studying the Ellingham diagram we see that point of intersection, below which ΔG for the above reaction is negative is above 2000 K.

3. Thus, this reaction is feasible at a very high temperature.

(B) Carbon monoxide is more effective reducing agent than carbon below 983K but, above this temperature, the reverse is true –Explain.



From Ellingham diagram , we find that 983 K, the curves intersect. The value of ΔG° for change of C to CO_2 is less than the value of ΔG° for change of CO to CO_2. Therefore, coke (Carban) is better reducing agent than CO at 983 K (or) above temperature, However below this temperature (eg 673 K) , CO is more effective reducing agent than C

(C) it is possible to reduce Fe_2O_3 by coke at a temperature around 1200K

Yes , it is possible for reduction

Coke is a better reducing agent for than CO above 1000K.

Explanation:

Iron(III) oxide gets converted to iron by the process of reduction. The reducing agent used for reducing iron(III) oxide to iron is carbon monoxide and coke.

The equation for the reduction of iron oxide by coke, the reaction follows:

$$FeO(s) + C(s) \rightarrow Fe(s/l) + CO(g) \ ......(1)$$

The two half reactions for thew above reaction is given by the equations:

Reduction : $FeO(s) + C(s) \rightarrow Fe(s) + \frac{1}{2}O_2(g)\ . \quad \Delta G^\circ_{(FeO,\ Fe)}$

Oxidation : $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)\ . \quad \Delta G^\circ_{(C,\ CO)}$

The net free energy change of the above reactions is:

Below 1000 K, ΔG° formation of Fe_2O_3 is more than the formation of CO_2 from CO. So, CO is the reducing agent for Fe_2O_3 below 1000 K.

$$\text{As, } \Delta G^\circ_{(FeO,\ Fe)} > \Delta G^\circ_{(C,\ CO)}, \text{ above 1000 K.}$$

So, $\Delta_r G^\circ$ becomes negative and the reaction 1 becomes favourable. Hence, C is a better reducing agent than CO above 1000 K.

9. Give the uses of zinc.

i) Metallic zinc is used in galvanising metals such as iron and steel structures to protect them from rusting and corrosion.

ii) Zinc is also used to produce die-castings in the automobile, electrical and hardware industries

10. Explain the electrometallurgy of aluminium.

Hall–Héroult process

Cathode : iron tank lined with carbon

Anode : carbon blocks

Electrolyte : 20% solution of Al_2O_3 + molten cyrolite + 10% $CaCl_2$

Temperature : above 1270 K.

Ionisaiton of alumina $Al_2O_3 \rightarrow 2Al^{3+} + 3O_2^{-}$

Electrolysis in chamber process :

Cathode reaction : $4Al^{3+}_{(melt)} + 12e^{-} \rightarrow 4Al$

Anode reaction : $6O_2^{-} \rightarrow 2O_2 + 12\,e^{-}$

Carbon act as anode ; $(C_{(s)} + O^{2-}_{(melt)} \rightarrow CO + 2e^{-}) \times 2$

$C_{(s)} + 2O^{2-}_{(melt)} \rightarrow CO_2 + 4e^{-}$

Overall reaction $4Al^{3+}_{(melt)} + 6O^{2-}_{(melt)} + 3C\,(s) \rightarrow 4Al\,(l) + 3CO_2\,(g)$

11. Explain the following terms with suitable examples.

(i) Gangue **(ii) slag**

Gangue :- The ores are associated with nonmetallic impurities, rocky materials and siliceous matter which are collectively known as gangue. **Ex.** $CaCO_3$, SiO_2

Slag: The light fusible substance which is made my the combination of gangue and flux, is called slag.

$CaO + SiO_2 \rightarrow CaSiO_3$

gangue + Flux → slag

12. Give the basic requirement for vapour phase refining.

Two requirements for vapour phase refining are

(i) The metal should form a volatile compound with an available reagent.

(ii) The volatile compound should be easily recovered by decomposition.

13. Describe the role of the following in the process mentioned.

(i) Silica in the extraction of copper.

The role of silica in the metallurgy of copper is to remove the iron oxide obtained during the process of roasting. If the sulphide ore of copper contains iron, then silica (SiO_2) is added as flux before roasting. Then, FeO combines with silica to form iron silicate, $FeSiO_3$(slag).

(ii) Cryolite in the extraction of aluminium.

Cryolite (Na_3AlF_6) is a flux (or solvent) that allows alumina to melt at a lower temperature and feed the igneous electrolytic cells that operate at 900 to 1000°C. Without it, alumina will melt at 2050°C' which is quite challenging.

(iii) Iodine in the refining of Zirconium.

Zirconium Crude metal is heated with iodine in an evacuated vapour to separate from impurities and this decomposes at 1800K to give a pure Zirconium metal and iodine. Iodine is heated with Zirconium to form a volatile compound which on further heating decompose to give pure zirconium

(iv) Sodium cyanide in froth floatation.

In froth floatation process,depressants helps to separate two sulphide ores by selective prevention of froth formation by one ore and allowing the other to come into froth **floatation**.

For example, in order to separate two sulphide ores (ZnS and Pbs), NaCN is used as a depressant. It selectively allows PbS form froth, but prevents ZnS from coming to froth. This happens due to the fact that NaCN reacts with ZnS to form $Na_2[Zn(CN)_4]$.

$$4NaCN + ZnS \rightarrow Na_2[Zn(CN)_4] + Na_2S$$

14. Explain the principle of electrolytic refining with an example.

Cathode : Pure silver

Anode : Impure silver rods

Electrolyte : Acidified aqueous solution of silver nitrate.

When a current is passed through the electrodes the following reactions will take place

Reaction at anode : $Ag^+ (aq) + 1e^- \rightarrow Ag (s)$

Reaction at Cathode : $Ag (s) \rightarrow Ag+ (aq) + 1e^-$

During electrolysis, at the anode the silver atoms lose electrons and enter the solution The positively charged silver cations migrate towards the cathode and get discharged by gaining electrons and deposited on the cathode.

Other metals such as copper, zinc etc.,can also be refined by this process in a similar manner.

15. The selection of reducing agent depends on the thermodynamic factor: Explain with an example.

I absolutely agree with the statement that choice of reducing agent depends on thermodynamic factors most importantly free energy change.$\Delta G°$ of the reducing agent must be more than the oxide it has to reduce. i.e. oxide with more negative $\Delta G°$ reduces oxides with less negative ΔG°

Examples

(1) C (more negative ΔG°) can be used as reducing agent to reduce ZnO (less negative ΔG°).

$$ZnO + C \rightarrow Zn + CO$$

(2) Mg (more negative ΔG°) can be used as reducing agent to reduce Cu_2O (less negative $\Delta G°$).

$$Cu_2O + Mg \rightarrow MgO + 2Cu$$

16. Give the limitations of Ellingham diagram.

1. Ellingham diagram is constructed based only on thermodynamic considerations. It gives information about the thermodynamic feasibility of a reaction. It does not tell anything about the rate of the reaction. More over, it does not give any idea about the possibility of other reactions that might be taking place.

2. The interpretation of ΔG is based on the assumption that the reactants are in equilibrium with the products which is not always true.

17. Write a short note on electrochemical principles of metallurgy.

Gibbs free energy change for the electrolysis process is given by the following expression

$$\Delta G^\circ = -nFE^\circ$$ **Where**

n - number of electrons involved in the reduction process,

F - Faraday

E^0 - is the electrode potential of the redox couple.

E^0 - is positive then the ΔG— is negative and the reduction is spontaneous and hence a redox reaction is planned in such a way that the e.m.f of the net redox reaction is positive.

When a more reactive metal is added to the solution containing the relatively less reactive metal ions, the more reactive metal will go into the solution. For example,

$$Cu_{(s)} + 2Ag^+_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$$

$$Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

P-BLOCK ELEMENTS - I

1. **Write a short note on anamolous properties of the first element of p-block.**

The following factors are responsible for this anomalous behaviour.

1. Small size of the first member
2. High ionisation enthalpy and high electronegativity
3. Absence of d orbitals in their valance shell

2. **Describe briefly allotropism in p- block elements with specific reference to carbon.**

Allotropism (or) allotropy is the property of some chemical elements to exist in two or more different forms, in the same physical state, known as allotropes of the elements.

Allotropic forms of Carbon are

i) Graphite ii) Diamond iii) fullerenes

iv) carbon nanotubes v) graphene,

3. **Boron does not react directly with hydrogen. Suggest one method to prepare diborane from BF_3.**

Boron does not react directly with hydrogen. However, it forms a variety of hydrides called boranes. The simplest borane is diborane - B_2H_6.

$$2BF_3 + 6NaH \xrightarrow{450\text{ K}} B_2H_6 + 6NaF$$

To prevent subsequent pyrolysis, the product diborane is trapped immediately.

4. **Give the uses of Borax.**

1. Borax is used for the identification of coloured metal ions
2. In the manufacture optical and borosilicate glass, enamels and glazes for pottery
3. It is also used as a flux in metallurgy and also acts as a preservative

5. **What is catenation ? describe briefly the catenation property of carbon.**

Catenation is an ability of an element to form chain of atoms.

Catenation property of carbon.

(i) the valency of element is greater than or equal to two,

(ii) element should have an ability to bond with itself

(iii) the self bond must be as strong as its bond with other elements

(iv) kinetic inertness of catenated compound towards other molecules. Carbon possesses all the above properties and forms a wide range of compounds with itself and with other elements such as H, O, N, S and halogens.

6. **Write a note on Fisher tropsch synthesis.**

The reaction of carbon monoxide with hydrogen at a pressure of less than 50 atm using metal catalysts at 500 - 700 K yields saturated and unsaturated hydrocarbons.

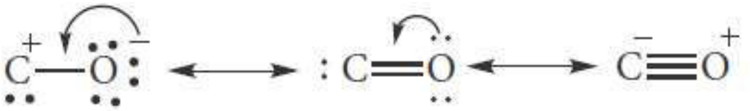
$$nCO + (2n+1)H_2 \longrightarrow C_nH_{(2n+2)} + nH_2O$$

$$nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$$

Eg. Nickel tetracarbonyl $[Ni(CO)_4]$, Iron pentacarbonyl $[Fe(CO)_5]$, Chromium hexacarbonyl $Cr(CO)_6]$.

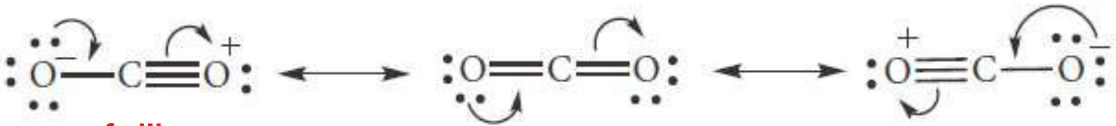
7. Give the structure of CO and CO_2.

i) **CO - linear structure.** ii) The C-O bond distance is 1.128Å. iii) Two canonical forms.



i) **CO2 liner structure** ii) equalbond distance for the both C-O bonds

iii) Addition there is 3c-4e bond covering all the three atoms.

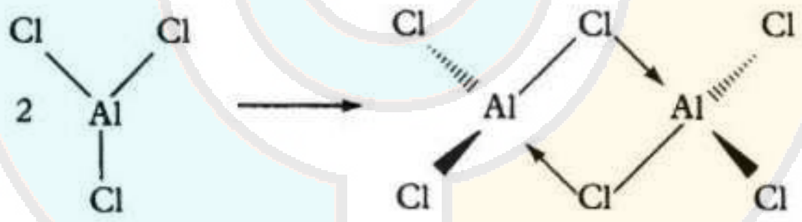


8. Give the uses of silicones.

1. Silicones are used for low temperature lubrication and in vacuum pumps, high temperature oil baths etc...
2. They are used for making water proofing clothes
3. They are used as insulting material in electrical motor and other appliances
4. They are mixed with paints and enamels to make them resistant towards high temperature, sunlight, dampness and chemicals.

9. $AlCl_3$ behaves like a lewis acid. Substantiate this statement.

In $AlCl_3$, it forms three bonds and hence outer shell has 6 electrons. In $AlCl_3$, Al needs two electron to complete its octet so it needs electron from outside and it exist in **dimer form** and form bond with Cl atom and complete its octet so its accept non bonding electron pair from Cl so we called it lewis acid.



10. Describe the structure of diborane.

i) In diborane two BH_2 units are linked by two bridged hydrogens.

ii) It has eight B-H bonds.

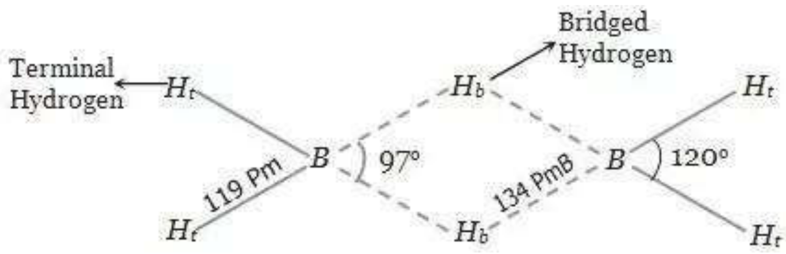
iii) Diborane has only 12 valance electrons

iv) The four terminal B-H bonds is 2c-2e bond (two centre - two electron bond.)

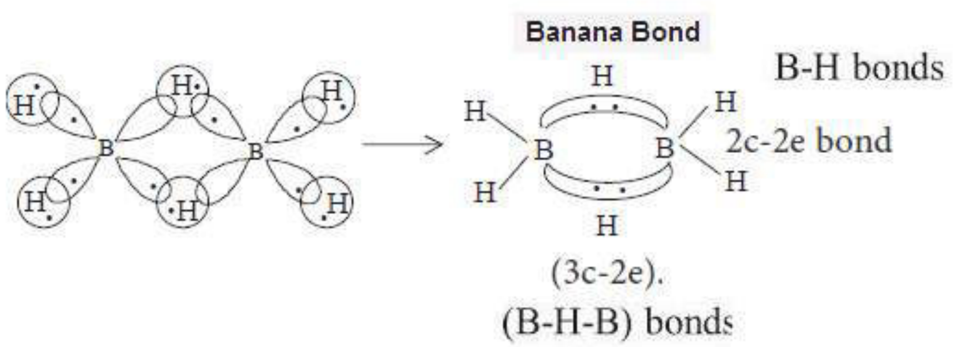
v) Two three centred B-H-B bonds utilise two electrons each. (3c-2e).

vi) In diborne, the boron is sp^3 hybridised

vii) Three of the four sp3 hybridised orbitals contains single electron and the fourth orbital is empty.

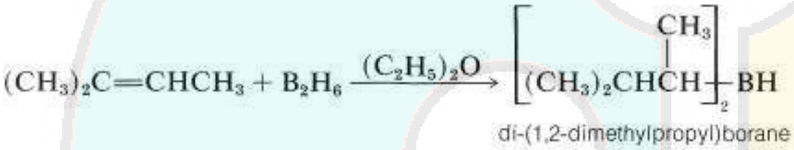


Structure of diborane



11. Write a short note on hydroboration.

Diborane adds on to **alkenes and alkynes in ether solvent at room temperature.** This reaction is called hydroboration and is highly used in synthetic organic chemistry, especially for anti Markovnikov addition



$$(CH_3)_2C{=}CHCH_3 + B_2H_6 \xrightarrow{(C_2H_5)_2O} \left[(CH_3)_2CH\overset{CH_3}{\overset{|}{C}}H\right]_2 BH$$

di-(1,2-dimethylpropyl)borane

12. Give one example for each of the following

(i) icosogens (ii) tetragen (iii) pnictogens (iv) chalcogen

i) Icosogens -- **Group No.13** - Boron family

(ii) Tetragen -- **Group No.14** - Carbon family

(iii) Pnictogens -- **Group No.15 -** Nitrogen family

(iv) Chalcogen -- **Group No.16** - Oxygen family

13. Write a note on metallic nature of p-block elements.

The tendency of an element to form a cation by loosing electrons is known as electropositive or metallic character. This character depends on the ionisation energy. Generally on descending a group the ionisation energy decreases and hence the metallic character increases.

14. Complete the following reactions

a) $B(OH)_3 + NH_3 \rightarrow BN + 3H_2O$

b) $Na_2B_4O_7 + 5\,H_2SO_4 + H_2O \rightarrow 4H_3BO_3 + Na_2SO_4$

c) $B_2H_6 + 2NaOH + 2H_2O \rightarrow 2NaBO_2 + 6H_2$

d) $B_2H_6 + CH_3OH \rightarrow 2B(OCH_3)_3 + 6H_2$

e) **$BF_3 + 9\,H_2O \rightarrow H_3BO_3 + HBF_4 + 2HF$ (book back questions answer)**

$3BF_3 + 3H_2O \rightarrow H_3BO_3 + 3H^+ + 3[BF_4]^-$ (book inside questions answer)

f) $HCOOH + H_2SO_4 \rightarrow CO + H_2O + H_2SO_4$

g) $2SiCl_4 + NH_3 \xrightarrow{330K/ether} Cl_3Si\text{-}NH\text{-}SiCl_3 + 2HCl$

h) $SiCl_4 + 4C_2H_5OH \rightarrow Si(C_2H_5O)_4 + 4HCl$

i) $2B + NaOH \rightarrow 2Na_3BO_3 + 3H_2$

j) $H_2B_4O_7 \xrightarrow{\text{red hot}} 2B_2O_3 + H_2O$

15. How will you identify borate radical?

When boric acid or borate salt is heated with ethyl alcohol in presence of conc. sulphuric acid, an ester, trialkylborate is formed. The vapour of this ester burns with a **green edged flame** and this reaction is used to identify the presence of borate.

$$H_3BO_3 + 3C_2H_5OH \xrightarrow{\text{Conc } H_2SO_4} B(OC_2H_5)_3 + 3H_2O$$

16. Write a note on zeolites.

Zeolites are three-dimensional crystalline solids containing aluminium, silicon, and oxygen in their regular three dimensional framework. They are hydrated sodium alumino silicates with general formula

$NaO.(Al_2O_3).x(SiO_2).y\ H_2O$ (x=2 to 10; y=2 to 6).

The Si and Al atoms are **tetrahedrally** coordinated with each other through shared oxygen atoms. Zeolites are **similar to clay** minerals but they **differ in their crystalline structure.**

17. How will you convert boric acid to boron nitride?

Fusion of urea with $B(OH)_3$, in an atmosphere of ammonia at 800 - 1200 K gives boron nitride

$$B(OH)_3 + NH_3 \xrightarrow{\Delta} BN + 3H_2O$$

18. A hydride of 2nd period alkali metal (A) on reaction with compound of Boron (B) to give a reducing agent (C). identify A , B and C.

$$4LiH + BF_3 \rightarrow LiBH_4 + 3LiF$$

A is lithium hydride (LiH) **B** is boron trifluoride (BF_3) **C** is lithium borohydride ($LiBH_4$)

Lithium borohydride is used in organic synthesis as a reducing agent for esters.

19. A double salt which contains fourth period alkali metal (A) on heating at 500K gives (B). aqueous solution of (B) gives white precipitate with $BaCl_2$ and gives a red colour compound with alizarin. Identify A and B.

i) Compound A is potash alum

$$K_2SO_4.Al_2(SO_4)_3.24H_2O \xrightarrow{500\ K} K_2SO_4.Al_2(SO_4)_3 \text{ (burnt alum)} + 24H_2O$$

ii) Compound B is (**burnt alum**)

ii) Aqueous solution of (B) gives white precipitate with $BaCl_2$ and gives a red colour compound with alizarin

$$4\ BaCl_2 + K_2SO_4.Al_2(SO_4)_3.24H_2O \rightarrow 4\ BaSO_4 \text{ (White ppt) } + 2\ AlCl_3 + 24\ H_2O + 2KCl$$

But $AlCl_3$ + alizarin to gives red colour

20. CO is a reducing agent . justify with an example.

Carbon monoxide also useful as a metallurgical reducing agentbecause at high temperatures it reduces many metal oxides to the elemental metal.

For example, copper(II) oxide, CuO, and iron(III) oxide, Fe_2O_3, are both reduced to the metal by carbon monoxide.

UNIT - 3

S.SHANMUGAM *P - BLOCK ELEMENTS - II* **St.John's M.H.S.S porur Ch -116**

1. What is inert pair effect?

In heavier post-transition metals, the outer s electrons (ns) have a tendency to remain inert and show reluctance to take part in the bonding, which is known as inert pair effect. This effect is also observed in groups 14, 15 and 16.

2. Chalcogens belongs to p-block. Give reason.

i) The chalcogens are the first group in the p block to have no stable metallic elements.

ii) All isotopes of polonium (Po), the only metal in group 16, are radioactive, and only one element in the group, tellurium (Te), can even be described as a semimetal.

iii) As in groups 14 and 15, the lightest element of group 16, oxygen, is found in nature as the free element.

3. Explain why fluorine always exhibit an oxidation state of -1?

1.fluorine the most electronegative element, also behaves quiet differently compared to the rest of the members of group

2. Absence of d orbitals in their valance shell

3. The fluorine is the strongest oxidising agent and the most reactive element among the halogens.

4. Give the oxidation state of halogen in the following.

a) OF_2 **b) O_2F_2** **c) Cl_2O_3** **d) I_2O_4**

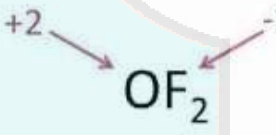
Fluorine shows only -1 oxidation state

a) OF_2

$2 + 2x = 0$

$2x = -2$

$x = -1$



b) O_2F_2

$2(1) + 2x = 0$

$2 - 2x = 0$

$2x = - 2$, $X = - 1$

c) Cl_2O_3

$2x + 3(-2) = 0$

$2x - 6 = 0$

$2x = 6$

$X = 3$

Oxidation state of Cl is +3

I) I_2O_4

$2x + 4(-2) = 0$

$2x - 8 = 0$

$2x = 8$

$X = 4$

Oxidation state of I is +4

5. What are interhalogen compounds? Give examples.

Each halogen combines with other halogens to form a series of compounds called inter halogen compounds.

A is less electronegative than B.

AB type - ClF, BrF

AB_3 type -BrF_3

AB_5 type - IF_5

AB_7 type - IF_7

6 Why fluorine is more reactive than other halogens?

Fluorine is more reactive.

Due to very small size of F there is inter electronic repulsion in F_2

This is due to the low value of F-F bond dissociation energy.

Fluorine wants to get to a stable 10 electrons to be like Neon.

This is because the valence/bonding electrons are closer to the nucleus in Fluorine than they are Chlorine and others and thus more strongly attracted

Fluorine is most electronegative, thus it is most reactive.

7. Give the uses of helium.

i). Helium is used to provide inert atmosphere in electric arc welding of metals

ii). Helium has lowest boiling point hence used in cryogenics (low temperature science).

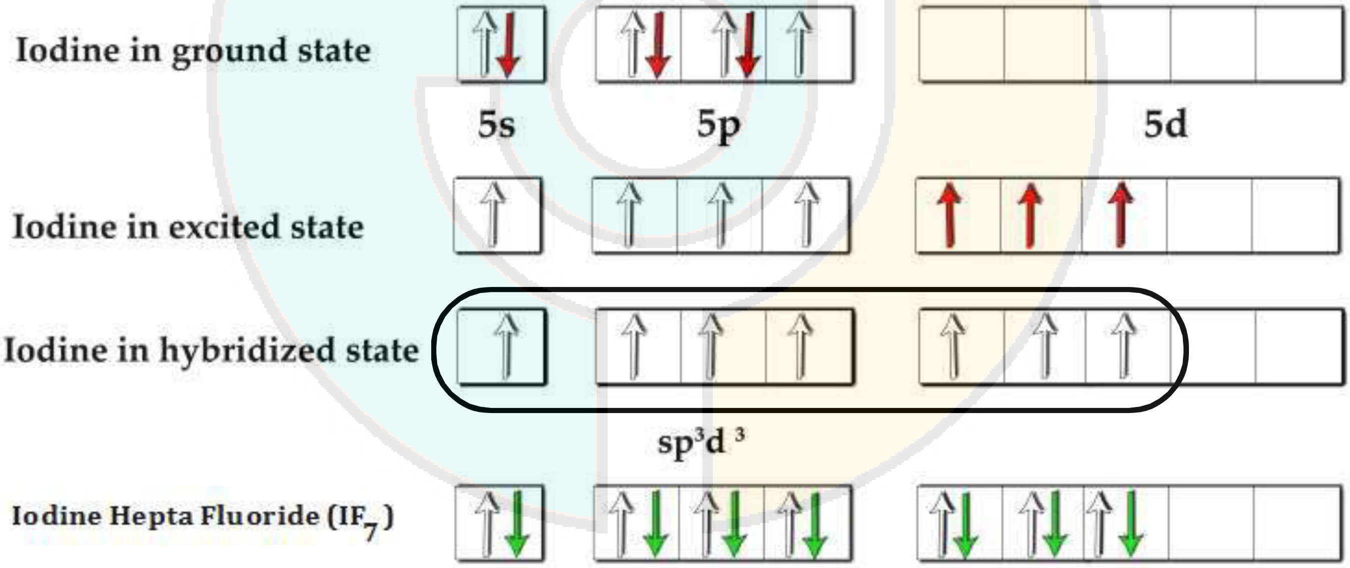
iii) It is much less denser than air and hence used for filling air balloons

8. What is the hybridisation of iodine in IF_7? Give its structure.

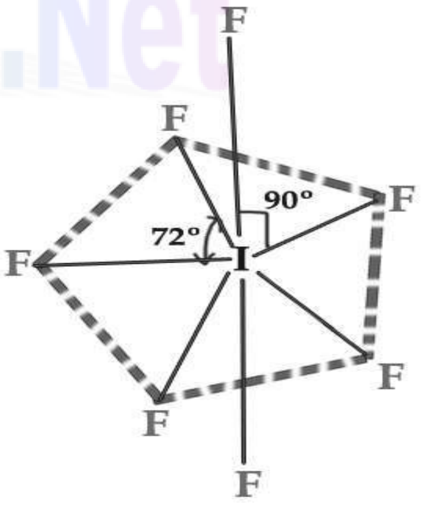
Iodine atom undergoes sp^3d^3 hybridization to give 7 half filled sp^3d^3 hybrid orbitals in

pentagonal bipyramidal symmetry. shape of IF_7 is pentagonal bipyramidal.

F - I - F bond angles in the pentagonal plane are equal to 72°



Geomentry of IF_7 is pentagonal bipyramidal.



9 Give the balanced equation for the reaction between chlorine with cold NaOH and hot NaOH.

i) Cold dilute alkali to give chloride and hypochlorite

$$2NaOH_{(aq)} + Cl_2 \rightarrow NaCl_{(aq)} + NaOCl + H_2O$$

ii) hot concentrated alkali to give chlorides and chlorates are formed.

$$6NaOH_{(aq)} + 3Cl_2 \rightarrow 5\,NaCl_{(aq)} + NaClO_3\,(aq) + 3H_2O\,(l)$$

10. How will you prepare chlorine in the laboratory?

Chlorine can also be prepared by dripping concentrated hydrochloric acid on $KMnO_4$ crystals:

$$2KMnO_4 + 16HCl \rightarrow 2\,KCl + 2\,MnCl_2 + 8H_2O + 5Cl_2$$

11. Give the uses of sulphuric acid.

1. Sulphuric acid is used in the manufacture of fertilisers, ammonium sulphate and super phosphates and other chemicals such as hydrochloric acid, nitric acid etc...
2. It is used as a drying agent and also used in the preparation of pigments, explosives etc..

12. Give a reason to support that sulphuric acid is a dehydrating agent.

i) It is highly soluble in water and has strong affinity towards water and hence it can be used as a dehydrating agent .

ii) When dissolved in water, it forms mono ($H_2SO_4.H_2O$) and dihydrates ($H_2SO_4.2H_2O$) and the reaction is exothermic

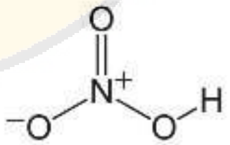
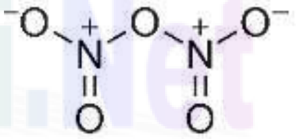
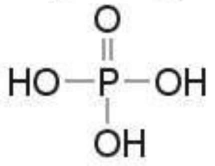
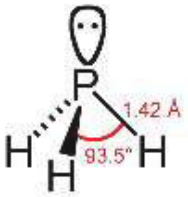
Example : $C_{12}H_{22}O11 + H_2SO_4 \rightarrow 12C + H_2SO_4.11H_2O$

13. Write the reason for the anamolous behaviour of Nitrogen.

i) Small size of N atom.
ii) High value of electronegativity of N atom and high ionization energy.
iii) Absence of d-orbitals in the valency shell.
iv) Tendency of form multipole bonds.
v) As a result the catenation tendency is weaker in nitrogen

14. Write the molecular formula and structural formula for the following molecules.

a) Nitric acid b) dinitrogen pentoxide c) phosphoric acid d) phosphine

Name	Molecular Formula	Structure
a) Nitric acid	HNO_3	
b) dinitrogen pentoxide	N_2O_5	
c) phosphoric acid	H_3PO_4	
d) phosphine	PH_3	

15. Give the uses of argon.

Argon prevents the oxidation of hot filament and prolongs the life in filament bulbs

16. Write the valence shell electronic configuration of group-15 elements.

The general valence shell electronic set up of group fifteen elements is **ns^2, np^{1-6}**

17. Give two equations to illustrate the chemical behaviour of phosphine.

Basic nature: Phosphine is weakly basic and forms phosphonium salts with halogen acids.

$$PH_3 + HI \rightarrow PH_4I$$

Reducing property : Phosphine precipitates some metal from their salt solutions.

$$3AgNO_3 + PH_3 \rightarrow Ag_3P + 3HNO_3$$

18. Give a reaction between nitric acid and a basic oxide.

Nitric acid react with zinc oxide to produce zinc nitrate and water.

$$2HNO_3 + ZnO \rightarrow Zn(NO_3)_2 + H_2O$$

Magnesium react with nitric acid to produce nitrate magnesium and water.

$$MgO + 2HNO_3 \rightarrow Mg((NO_3)_2 + H_2O$$

19. What happens when PCl_5 is heated?

$$PCl_{5(g)} \xrightarrow{\Delta} PCl_{3(g)} + Cl_{2(g)}$$

20. Suggest a reason why HF is a weak acid, whereas binary acids of the all other halogens are strong acids.

HF is the weakest acid because of it's strong H-F bond.
Fluorine being small in size overlaps better with 1s orbital of hydrogen leading to a strong bond.
Hence can not give proton easily.Here bond strength overweighs the electronegativity of F

21. Deduce the oxidation number of oxygen in hypofluorous acid – HOF.

H - O - F **+1 + x - 1= 0 , x =0**

The oxidation state of the oxygen in hypofluorites is 0.
It is also the only hypohalous acid that can be isolated as a solid.

22. What type of hybridisation occur in a) BrF_5 b) BrF_3

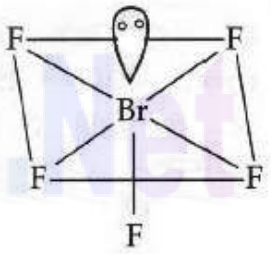
b) BrF_5

Valence electron 7+ bonding electron 5 = 12

$$X = \frac{12}{2} = 6$$

Hybridization : sp^3d^2

Geometry: Square Pyramidal



b) BrF3

Valence electron 7+ bonding electron 3 = 10

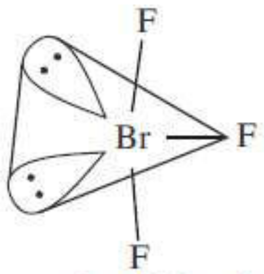
$$X = \frac{10}{2} = 5$$

Hybridization: sp^3d

Geometry: Trigonal Bipyramidal

Shape - T-shaped

lone pair - 2 **bond pair - 3**



Bent T–shaped

23. Complete the following reactions.

1. $NaCl + MnO_2 + H_2SO_4 \longrightarrow$
2. $NaNO_2 + HCl \longrightarrow$
3. $IO_3^- + I^- + H^+ \longrightarrow$
4. $I_2 + S_2O_3^{2-} \longrightarrow$
5. $P_4 + NaOH + H_2O \longrightarrow$
6. $AgNO_3 + PH_3 \longrightarrow$
7. $Mg + HNO_3 \longrightarrow$
8. $KClO_3 \xrightarrow{\Delta}$
9. $Cu + \underset{\text{Hot conc}}{H_2SO_4} \longrightarrow$
10. $Sb + Cl_2 \longrightarrow$
11. $HBr + H_2SO_4 \longrightarrow$
12. $XeF_6 + H_2O \longrightarrow$
13. $XeO_6^{4-} + Mn^{2+} + H^+ \longrightarrow$
14. $XeOF_4 + SiO_2 \longrightarrow$
15. $Xe + F_2 \xrightarrow[400^0C]{Ni / 200\ atm}$

Ans:

1. $4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow Cl_2 + MnCl_2 + 4NaHSO_4 + 2H_2O$
2. $NaNO_2 + HCl \longrightarrow NaCl + HNO_2$
3. $IO^{3-} + 5\ I^- + 6\ H^+ \longrightarrow 3\ I_2 + 3\ H_2O$
4. $I_2 + 2\ S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$
5. $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$
6. $3AgNO_3 + PH_3 \longrightarrow Ag_3P + 3HNO_3$
7. $4Mg + 10\ HNO_3 \longrightarrow 4Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$

   If the acid is diluted we get N_2O

   $4Mg + 10\ HNO_3 \longrightarrow 4Mg(NO_3)_2 + N_2O_5 + 5H_2O$
8. $2\ KClO_3 \xrightarrow{MnO_2} 2\ KCl + 3O_2$
9. $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

   (Hot Conc.)
10. $2Sb + 3Cl_2 \longrightarrow 2SbCl_3$
11. $2HBr + H_2SO_4 \longrightarrow 2H_2O + Br_2 + SO_2$
12. $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$
13. $5XeO_6^{4-} + 2\ Mn^{2+} + 14H^+ \longrightarrow 2MnO_4^- + 5XeO_3 + 7H_2O$
14. $2\ XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$
15. $Xe + F_2 \xrightarrow[400°C]{Ni /200\ atm} XeF_2$

TRANSITION AND INNER TRANSITION ELEMENTS

1. What are transition metals? Give four examples.

Transition elements that have incompletely filled d sub shell in the neutral or cationic state are called transition metals

Four examples.

First (3d) : Ti , V , Cr , Fe
Second : (4d) Mo , Ru , Rh, pd
Third (5d) : W, Os ,Ir, Pt,
Fourth : (6d) Db , Sg, Bh, Ds

2. Explain the oxidation states of 4d series elements.

al At the beginning of the series, +3 oxidation state is stable but towards the end +2 oxidation state becomes stable

b) The oxidation states of **4d series elements** vary from

+3 for Y and + 2 to +8 for Ru , Cd for +2.

c) The highest oxidation state of **4d elements** are found in their compounds with the higher electronegative elements like O, F and Cl. for example: RuO_4, .

d) Generally in going down a group, a stability of the higher oxidation state increases while that of lower oxidation state decreases.

3. What are inner transition elements?

The last electron enters into (n - 2) f - orbital which is inner to the penultimate shell,they are also called inner transition elements.

In the inner transition elements there are two series of elements.

1) Lanthanoids (previously called lanthanides (57-71))

2) Actinoids (previously called actinides (89-103))

4. Justify the position of lanthanides and actinides in the periodic table.

The actual position of Lanthanoids in the periodic table is at group number 3 and period number 6. However, in the sixth period after lanthanum,

The electrons are preferentially filled in inner 4f sub shell and these fourteen elements following lanthanum show similar chemical properties.

Therefore these elements are grouped together and placed at the bottom of the periodic table. This position can be justified as follows.

1. Lanthanoids have general electronic configuration [Xe] $4f^{1-14}\ 5d^{0-1}6s^2$

2. The common oxidation state of lanthanoides is +3

3. All these elements have similar physical and chemical properties.

5. What are actinides? Give three examples.

The fourteen elements following actinium ,i.e., from thorium (Th) to lawrentium (Lr) are called actinoids

Actinide - These are elements with atomic numbers from 90 to 103

Examples.

The 15 elements include: Actinium (Ac), Thorium (Th), Protactinium (Pa), Uranium (U),

6 Why Gd $^{3+}$ is colourless?

The At.No of Gd is 64. EC is (Xe) $4f^7\ 5d^1\ 6s^2$. In Gd $^{+3}$, they have exactly half filled f-orbitals

Hence (Xe) $4f^7 5d^0\ 6s^0$. Due to this it is colourless.

7. Explain why compounds of Cu^{2+} are coloured but those of Zn^{2+} are colourless.

1) Zn^{2+} ion has all paired electrons (configuration [Ar] $3d^{10}$)

Cu^{2+} ion has an **unpaired electron** (its configuration is [Ar] $3d^9$)

2) i) In case of Zn^{2+} ion **fully filled** d orbital is present therefore no d-d transition can be possible in this case and it is colorless.

ii) In case of Cu^{2+} ion because of d-d transition electrons emits light in the visible range and hence they are colored compounds

8. Describe the preparation of potassium dichromate.

Potassium dichromate is prepared from chromate ore. The ore is concentrated by gravity separation

i) Conversion of Chromate ore into Sodium chromate

$$4FeCr_2O_3 + 8Na_2CO_3 + 7O_2 \xrightarrow{900\text{-}1000^oC} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

ii) Conversion of Sodium chromate into Sodium di chromate

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

iii) Conversion of Sodium di chromate into Potassium dichromate

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2\,NaCl$$

9. What is lanthanide contraction and what are the effects of lanthanide contraction?

As we move across 4f series, the atomic and ionic radii of lanthanoids show gradual decrease with increse in atomic number. This decrese in ionic size is called lanthanoid contraction.

A. Basicity differences

As we from Ce^{3+} to Lu^{3+} , the basic character of Ln^{3+} ions decrease. Due to the decrease in the size of Ln^{3+} ions, the ionic character of Ln - OH bond decreases (covalent character increases) which results in the decrease in the basicity.

B. Similarities among lanthanoids:

In the complete f - series only 10 pm decrease in atomic radii and 20 pm decrease in ionic radii is observed. because of this very small change in radii of lanthanoids, their chemical properties are quite similar.

10. complete the following

a) $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

b) $C_6H_5CH_3 \xrightarrow{KMnO_4/H^+} C_6H_5\text{-}COOH$

c) $MnO_4^- + 5\,Fe^{2+} + 8\,H^+ \rightarrow Mn^{2+} + 5\,Fe^{3+} + 4H_2O$

d) $KMnO_4 \xrightarrow{\text{Red hot / }\Delta} K_2MnO_4 + MnO_2 + O_2$

e) $Cr_2O_7^{2-} + 6\,I^- + 14\,H^+ \rightarrow 2Cr^{3+} + 3\,I_2 + 7H_2O$

f) $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2\,NaCl$

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11. What are interstitial compounds?

An interstitial compound or alloy is a compound that is formed when small atoms like hydrogen carbon or nitrogen are trapped in the interstitial holes in a metal lattice .

Example :TiC, $ZrH_{1.92}$, Mn_4N etc

12. Calculate the number of unpaired electrons in Ti^{3+} , Mn^{2+} and calculate the spin only magnetic moment.

ion	configuration	n	$\mu_s = \sqrt{n(n+2)}\ \mu_B$	μ_s (observed)
Ti^{3+}	d^1	1	$\mu_s = \sqrt{1(1+2)} = \sqrt{3} = 1.73\ \mu_B$	paramagnetic
Mn^{2+}	d^5	5	$\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.91\ \mu_B$	paramagnetic

13. Write the electronic configuration of Ce^{4+} and Co^{2+}.

i) **configuration of** Ce^{4+} $[Xe_{54}]\ 4f^0\ 5d^0\ 6s^0$

ii) **configuration of** Co^{2+} $[Ar_{18}]\ 3d^7 4s^0$

14. Explain briefly how +2 states becomes more and more stable in the first half of the first row transition elements with increasing atomic number.

i) All the metals display +2 oxidation states except Sc.

ii) On moving from the Sc to the Mn, the atomic numbers increase from 21 to the 25.

iii) It means the number of electrons in the 3d-orbital also increases from 1 to 5.

Sc (+2) = d^1,

Ti (+2) = d^2,

V (+2) = d^3,

Cr (+2) = d^4

and Mn (+2) = d^5.

iv) The +2 oxidation state is achieved by loss of the two 4s electrons by the metals.Since the number of d electrons in (+2) state also increases from Ti(+2) to Mn(+2), the stability of +2 state increases (as d-orbital is becoming more and more half-filled). Mn (+2) has d^5 electrons

15. Which is more stable? Fe3+ or Fe2+ - explain.

Fe^{3+} ion is more stable due to its half-filled 3d5 electron configuration.

As half filled and completely filled shells are more stable Fe^{3+} ion is more stable.

While Fe^{2+} ion is partially filled d sub shell ($3d^6$) in not stable.Hence, Fe^{3+} is more stable than Fe^{2+}.

16. Explain the variation in $E^o_{M3+/M2+}$ /3d series.

ii) In 3d series as we move from Ti to Zn, the standard reduction potential **($E^o_{M3+/M2+}$**) value is approaching towards less negative value and copper has a positive reduction potential.ie elemental copper is more stable than Cu^{2+}.

ii) In the general trend, $(E^o_{M3+/\,M2+})$

The value for manganese and zinc are more negative than the regular trend. It is due to extra stability which arises due to the half filled d^5 configuration in $Mn^{2+}$and completely filled d^{10} configurationin Zn^{2+}.

iii) Transition metals in their high oxidation states tend to be oxidizing . For example, Fe^{3+} is moderately a strong oxidant, and it oxidises copper to Cu^{2+} ions.

The feasibility of the reaction is predicted from the following standard electrode potential values.

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+} \qquad E^0 = 0.77\ V$$

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^0 = +0.34\ V$$

iv) The standard electrode potential for the $(E^o_{M3+/\,M2+})$ half-cell gives the relative stability between M^{3+} and M^{2+}.

i) $Ti^{3+} + e^- \rightarrow Ti^{2+}$ **Standard reduction potential = - 0.37 V**

ii) $V^{3+} + e^- \rightarrow V^{2+}$ **Standard reduction potential = - 0.26 V**

iii) $Cr^{3+} + e^- \rightarrow Cr^{2+}$ **Standard reduction potential = - 0.41 V**

v) The negative values for titanium, vanadium and chromium indicate that the higher oxidation state is preferred. If we want to reduce such a stable Cr^{3+} ion, strong reducing agent which has high negative value for reduction potential like metallic zinc . (E^0= -0.76 V) is required.

eg) The high reduction potential of **M3+/ M2+** indicates Mn^{2+} is more stable than Mn^{3+}.

$$Mn^{2+} + 2e^- \rightarrow Mn \qquad E^o_{Mn^{2+}/Mn} = -1.18\ V$$

$$Mn^{3+} + e^- \rightarrow Mn^{2+} \qquad E^o_{Mn^{3+}/Mn^{2+}} = +1.51\ V$$

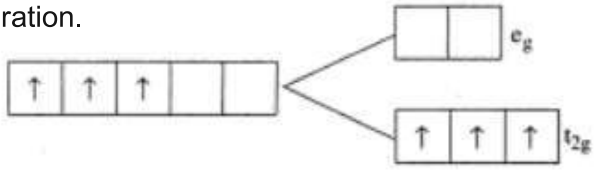
Mn^{3+} has a $3d^4$ configuration while that of Mn^{2+} is $3d^5$. The extra stability associated with a half filled d sub shell makes the reduction of Mn^{3+} very feasible (E^0 = +1.51V). .

17. Compare lanthanides and actinides.

1 Differentiating electron eneters in 4f orbital	Differentiating electron eneters in 5f orbital
2 Binding energy of 4f orbitals are higher	Binding energy of 5f orbitals are lower
3 They show less tendency to form complexes	They show greater tendency to form complexes
4 Most of the lanthanoids are colourless	Most of the actinoids are coloured. eg) U^{3+}(red),U^{4+}(green) ,UO_2^{2+} (yellow)
5 They do not form oxo cations	They do form oxo cations such as UO_2^{2+} O_2^{2+},etc

18. Explain why Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidizing.

Cr^{2+} is strongly reducing in nature. It has a d4configuration. While acting as a reducing agent, it gets oxidized to Cr^{3+} (electronic configuration, d^3). This d^3configuration can be written as t_{2g}^3 configuration, which is a more stable configuration.



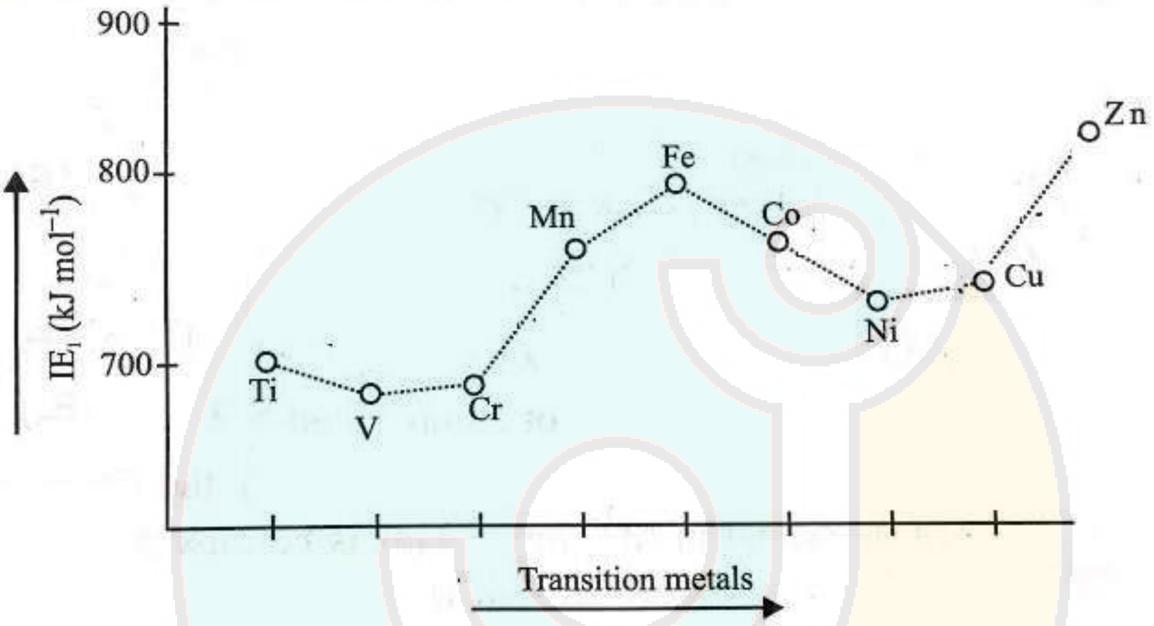
In the case of Mn^{3+} (d^4), it acts as an oxidizing agent and gets reduced to Mn^{2+} (d^5). This has an exactly half-filled d-orbital and has an extra-stability.

19. Compare the ionization enthalpies of first series of the transition elements.

1) As we move from left to right in a transition metal series, the ionization enthalpy increases as expected. This is due to increase in nuclear charge corresponding to the filling of d electrons.

2) The increase in first ionisation enthalpy with increase in atomic number along a particular series is not regular.

3) The added electron enters (n-1)d orbital and the inner electrons act as a shield and decrease the effect of nuclear charge on valence ns electrons. Therefore, it leads to variation in the ionization energy values



4) Chromium has low first ionization enthalpy because lose one electron gives stable configuration ($3d^5$)

While Zinc has very high ionization enthalpy because electron has to be removed from 4s orbitals.

20. Actinoid contraction is greater from element to element than the lanthanoid contraction, why?

i) In actinoids, 5f orbitals are filled. These 5f orbitals have a poorer shielding effect than 4f orbitals (in lanthanoids).

ii) Thus, the effective nuclear charge experienced by electrons in valence shells in case of actinoids is much more that than experienced by lanthanoids.

iii) Hence, the size contraction in actinoids is greater as compared to that in lanthanoids.

21. Out of $Lu(OH)_3$ and $La(OH)_3$ which is more basic and why?

$La(OH)_3$ is most basic and $Lu(OH)_3$ is least basic. Due to lanthanide contraction. As the size of lanthanide ions decreses from La^{3+} to Lu^{3+} , the covalent character of the hydroxides increases and hence the basic strength decreases.

22. Why europium (II) is more stable than Cerium (II)?

i) Europium (II) is more stable trhan Cerium (II) As we from left to right, effective nuclear charge increases due to which lanthanide contraction takes place. The inert pair effect becomes more dominative.

ii) In Eu^{2+}, 4f sub shell is half filled and Ce^{2+}, 4f and 5d sub shells are partially filled.so, Eu(II) more stable than Ce(II)

23. Why do zirconium and Hafnium exhibit similar properties?

Zr and Hf exhibit similar properties due to lanthanoid contraction.

Electrons present in f subshell didn't do good shielding due to which with the increasing atomic number or increasing effective nuclear charge size gets constricted .

The size of Halfenium and Zirconium becomes almost equal.

4d series	**Zr**	**145 pm**
5d Series	**Hf**	**144 pm**

24. Which is stronger reducing agent Cr^{2+} or Fe^{2+}?

Cr^{2+} is a stronger reducing agent than Fe^{2+}.

This can be explained on the basis of the standard electrode potential values

$$E^\circ(Cr^{3+}/Cr^{2+} = -0.41\ V) \quad \text{and} \quad E^\circ\ (Fe^{3+}/Fe^{2+} = +\ 0.77\ V).$$

Thus Cr^{2+} is easily oxidised to Cr^{3+} but Fe^{2+} cannot be as readily oxidised to Fe^{3+}.

25. The $E^0_{M2+\ /M}$ value for copper is positive. Suggest a possible reason for this.

1. Sublimation energy:
The energy needed to convert one mole of atoms from a solid state to gaseous state.

2. Ionization energy:

The energy supplied to remove electrons from one mole of atoms, which are in the gaseous state.

3. Hydration energy:

The energy emitted to hydrate one mole of ions.

Now,Copper has a high energy of atomization and low hydration energy. Hence, the $E^0(M^{2+}/M)$ value for copper is positive.

26. predict which of the following will be coloured in aqueous solution Ti^{2+} , V^{3+} , Cu^{+} ,Sc^{3+}, Fe^{3+}, Ni^{2+} and Co^{3+}

A transition metal ion in coloured if it has one or more unpaired electron in (n-1)d orbitals i.e. 3d orbitals in case of first transition series.When such species are exposed to visible radiation, d-d transition can take place.

(It does not contain unpaired electron in 3d orbitals so it is colourless)

ion	configuration	colour
Ti^{2+}	$3d^1 4s^0$	Violet
V^{3+}	$3d^2 4s^0$	Green
Cu+	$3d^{10}\ 4s^0$	colourless
Sc^{3+}	$3d^0 4s^0$	colourless
Fe^{3+}	$3d^5 4s^0$	brown to yellow
Ni^{2+}	$3d^8 4s^0$	green
Co^{3+}	$3d^6 4s^0$	blue

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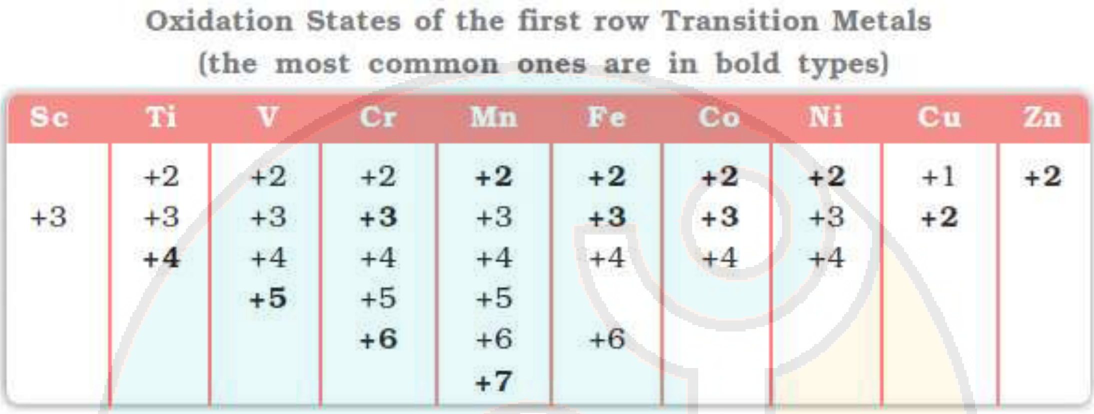
27. Describe the variable oxidation state of 3d series elements.

The first transition metal Scandium exhibits only +3 oxidation state, but all other transition elements exhibit variable oxidation states by loosing electrons from (n-1)d orbital and ns orbital as the energy difference between them is very small .

At the beginning of the series, +3 oxidation state is stable but towards the end +2 oxidation state be comes stable

For example, the first element Sc has only one oxidation state +3; the middle element Mn has six different oxidation states from +2 to +7. The last element Cu shows +1 and +2 oxidation states only.



Oxidation States of the first row Transition Metals
(the most common ones are in bold types)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	**+2**	**+2**	**+2**	**+2**	+1	**+2**
+3	+3	+3	**+3**	+3	**+3**	**+3**	+3	**+2**	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

The relative stability of different oxidation states of 3d metals is correlated with the extra stability of half filled and fully filled electronic configurations. Example: Mn^{2+} ($3d^5$) is more stable than Mn^{4+} ($3d^4$)

28. Which metal in the 3d series exhibits +1 oxidation state most frequently and why?

Cu is the only metal in the first transition series (3d series) which shows +1 oxidation state most frequently. This is because the electronic configuration of Cu is 3d10 4s1 and after losing one electron it acquires a stable 3d10 configuration.

29. Why first ionization enthalpy of chromium is lower than that of zinc?

The electronic configuration of Zn and Cr is given below :

Cr = [Ar] $3d^5 4s^1$ Zn = [Ar] $3d^{10} 4s^2$.

First ionisation enthalpy of Cr is lower than that of Zinc because in case of zinc first electron has to be remove from fulfilled orbital and full filled electronic configuration is most stable so it require high energy to remove electron from it. While in case of Chromium electron is easily removed from half filled orbital with less amount of energy.

30. Transition metals show high melting points why?

a) The melting-points of the transition metals are high due to the 3d electrons being available for metallic bonding.

b) This strength of the bond is due to the presence of unpaired or delocalized electrons in the outermost shell of the atom

c)The enthalpies of atomization and the densities of transition elements are also high that leads to high boiling and melting points.

S.SHANMUGAM

UNIT- 5
COORDINATION CHEMISTRY

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1. Write the IUPAC names for the following complexes.

i) $Na_2[Ni(EDTA)]$ ii) $[Ag(CN)_2]^-$ iii) $[Co(en)_3]_2(SO_4)_3$

iv)$[Co(ONO)(NH_3)_5]^{2+}$ v) $[Pt(NH_3)_2Cl(NO_2)]$

Ans:

i) $Na_2[Ni(EDTA)]$ - Sodium 2,2',2'',2'''-(ethane-1,2- diamminetetraacetate)nickelate(II)

ii) $[Ag(CN)_2]^-$ - Dicyanidoargentate(I) ion

iii) $[Co(en)_3]_2(SO_4)_3$ - tris (ethylenediamine)cobalt(III)sulphate.

iv) $[Co(ONO)(NH_3)_5]^{2+}$ - pentaammine (nitrito κ -O) cabalt (III) sulphate

v) $[Pt(NH_3)_2Cl(NO_2)]$ - diamminechloridonitrito κ -N- platinum(II)

2. Write the formula for the following coordination compounds.

a) potassiumhexacyanidoferrate(II) - $K_4[Fe(CN)_6]$

b) pentacarbonyliron(0) - $[Fe(CO)_5]$

c) pentaamminenitrito -N-cobalt(III)ion - $[Co(NH_3)_5NO_2]^{2+}$

d) hexaamminecobalt(III)sulphate - $[Co(NH_3)_6]_2(SO_4)_3$

e) sodiumtetrafluoridodihydroxidochromate(III) - $Na_3[Cr(F)_4(OH)_2]$

3. Arrange the following in order of increasing molar conductivity

i) $Mg [Cr(NH_3)(Cl)_5]$ ii) $[Cr(NH_3)Cl]_3[CoF_6]_2$ iii) $[Cr(NH_3)_3Cl_3]$

i) $Mg [Cr(NH_3)(Cl)_5] \rightarrow Mg^{2+} + [Cr(NH_3)(Cl)_5]^{2-}$ Total no of ions = 2

ii) $[Cr(NH_3)Cl]_3[CoF_6]_2 \rightarrow 3[Cr(NH_3)_5Cl]^{2+} + 2[CoF_6]^{3-}$ Total no of ions = 5

iii) $[Cr(NH_3)_3Cl_3] \rightarrow$ no dissociation occurs Total no of ions = 0

More the number of ions given out by the complex on dissociation and their molar conductivity also increases

increasing order of molar conductivity

$[Cr(NH_3)_3Cl_3] < Mg [Cr(NH_3)(Cl)_5] < [Cr(NH_3)Cl]_3[CoF_6]_2$

4. Ni^{2+} is identified using alcoholic solution of dimethyl glyoxime. Write the structural formula for the rosy red precipitate of a complex formed in the reaction

Addition of an alcoholic solution of dimethylglyoxime to an ammoniacal solution of Ni(II) gives a rose-red precipitate, abbreviated **$Ni(dmg)_2$:**

$$[Ni(NH_3)_6]^{2+}{}_{(aq)} + 2(CH_3CNOH)_2(alc) \rightleftharpoons \mathbf{Ni[ONC(CH_3)C(CH_3)NOH]_2}(s) + 2NH_4^+{}_{(aq)} + 4NH_{3\,(aq)}$$

5. $[CuCl_4]^{2-}$ exists while $[Cu\,I_4]^{2-}$does not exist why?

Both the species contains Cu^{2+} ions but only iodide ion (not chloride ion) reduces Cu^{2+} to cuprous iodide and I_2. Hence, $[CuI_4]^{2-}$ does not exist.

In [CuI4]2-complex iodide ion reduces Cu2+ to Cu+ therefore the complex is unstable.

so , $2CuI_2 \rightarrow Cu_2I_2 + I_2$

6 **Calculate the ratio of $\frac{[Ag^+]}{[Ag(NH_3)_2]^+}$ in 0.2 M solution of NH_3. If the stability constant for the complex $[Ag(NH_3)_2]^+$ is 1.7×10^7**

$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$ $(\beta) = 1.7 \times 10^7$, $[NH_3] = 0.2M$

$$\text{i) } (\beta) = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2}, \quad \frac{[Ag(NH_3)_2]^+}{[Ag^+]} = \beta \times [NH_3]^2 = 1.7 \times 10^7\ (0.2)^2 = 6.8 \times 10^5$$

$$\text{ii) } \frac{[Ag^+]}{[Ag(NH_3)_2]^+} = \frac{1}{\beta\,[NH_3]^2} = \frac{1}{6.8 \times 10^5} = 1.47 \times 10^{-5} \quad \textbf{ratio} = 1.47 \times 10^{-5}$$

7. Give an example of coordination compound used in medicine and two examples of biologically important coordination compounds.

Used in medicine

(1) Ca-EDTA chelate, is used in the treatment of lead and radioactive poisoning

(2) Cis-platin is used as an antitumor drug in cancer treatment.

Biologically important coordination compounds.

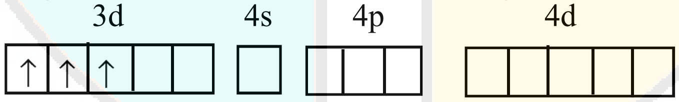
i) (RBC) is composed of heme group, which is Fe^{2+}- Porphyrin complex It plays an important role in carrying oxygen from lungs to tissues and carbon dioxide from tissues to lungs.

ii) Carboxypeptidase is a protease enzyme that hydrolytic enzyme important in digestion, contains a zinc ion coordinated to the protein

8. Based on VB theory explain why $[Cr(NH_3)_3]^{3+}$ is paramagnetic, while $[Ni(CN)_4]^{2-}$ diamagnetic.

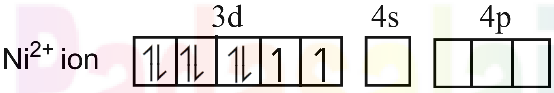
i) Cr is in the +3 oxidation state i.e., d^3 configuration. Also,

NH_3 is a weak field ligand that does not cause the pairing of the electrons in the 3d orbital.



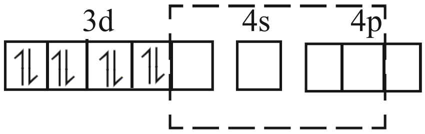
Therefore, it undergoes d^2sp^3 hybridization and the electrons in the 3d orbitals remain unpaired. Hence, **it is paramagnetic in nature.**

ii) In $[Ni(CN)_4]^{2-}$, Ni exists in the +2 oxidation state i.e., d^8 configuration.



CN^- is a strong field ligand. It causes the pairing of the 3d orbital electrons.

Then, Ni^{2+} under goes dsp^2 hybridization.

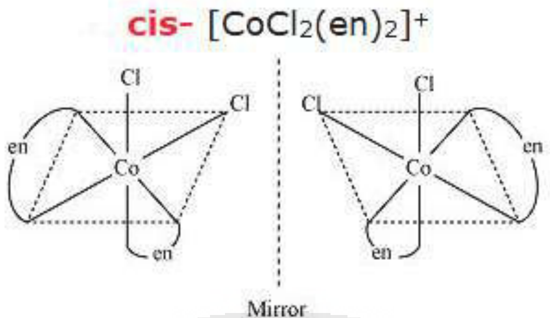


As there are **no unpaired electrons, it is diamagnetic.**

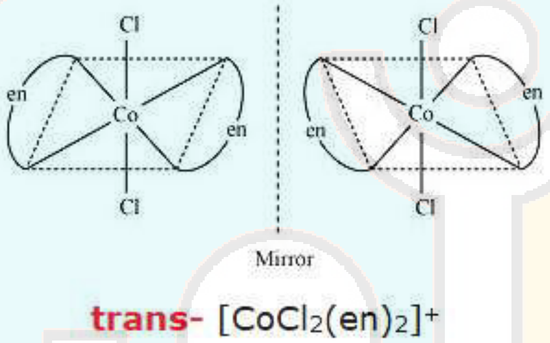
9. Draw all possible geometrical isomers of the complex $[Co(en)_2Cl_2]^+$ and identify the optically active isomer.

Cis - $[Co(en)_2Cl_2]^+$ is shows both geometrical as well as optical isomerism.

Its cis form is unsymmetrical,



Cis-$[Co(en)_2Cl_2]^+$ - **optically active** [Non - superimposable mirror image]



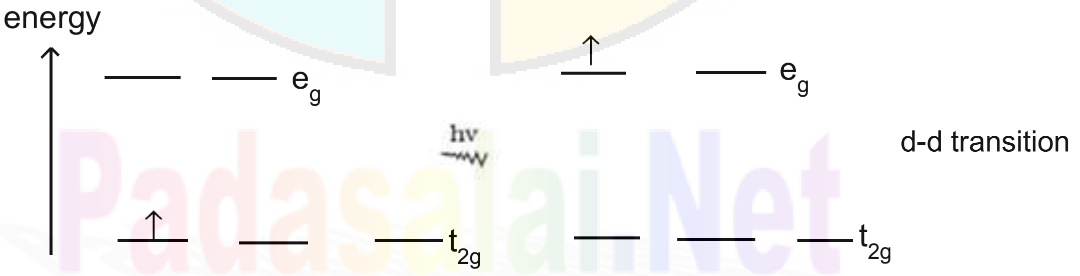
trans-$[Co(en)_2Cl_2]^+$ is symmetrical because it contains a **plane of symmetry**

Hence,***optically in active***

In total , Three isomers are possible

10. $[Ti(H_2O)_6]^{3+}$ is coloured, while $[Sc(H_2O)_6]^{3+}$ is colourless- explain .

i) $[Ti(H_2O)_6]^{3+}$ is coloured because of configuration is Ti^{3+} - $3d^1$ $\boxed{\uparrow}\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }$



has one unpaired electron for d-d transition, hence it is coloured

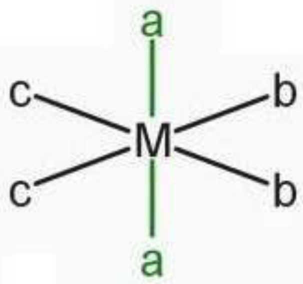
i) **$[Sc(H_2O)_6]^{3+}$ is colourless because of** configuration is Configuration Sc^{3+} - $3d^0$ $\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }$

No unpaired electron, so d-d transition is not possible hence it is not coloured

11. Give an example for complex of the type [$Ma_2b_2c_2$] where a, b, c are monodentate ligands and give the possible isomers.

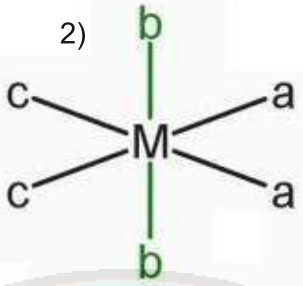
The combination are as follows for **[$Ma_2b_2c_2$] are (a,a)(b,b),(c,c)** - this means in the octahedral structure of the compound a lies directly opposite of **a** ,and **b** lies opposite of **b** , same followed for **c**. these are the five possible combination e**g) [$Cr((NH_3)_2(H_2O)_2(Br)_2]^+$**

1)



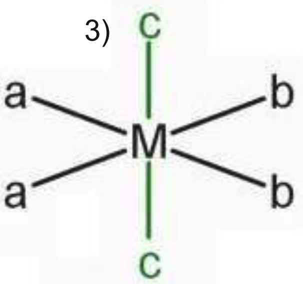
a-a trans

2)



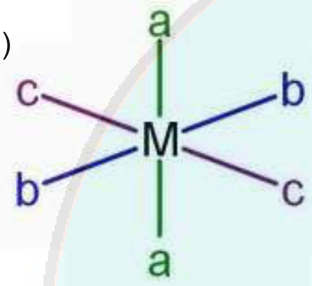
b-b trans

3)



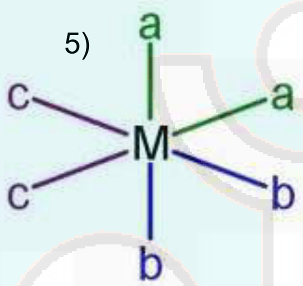
c-c trans

4)



all trans

5)



all cis

[$Ma_2b_2c_2$]
5 - Geometrical isomers

1. (a,a)(b,c)(b,c) -trans
2. (b,b) (a,c) (a,c) -trans
3. (c,c) (a,b) (a,b)- trans
4.(a,a)(b,b),(c,c) -all trans
5. (a,c)(a,b) (b,c) - all cis

(5th , isomer - shows optical isomerism d and l form)

7- isomers out of which 5 are geometrical and 2 are optical isomers.

12. Give one test to differentiate [$Co(NH_3)_5Cl]SO_4$ and [$Co(NH_3)_5SO_4]Cl$.

This can be tested by using $AgNO_3$solution and $BaCl_2$

Barium chloride test

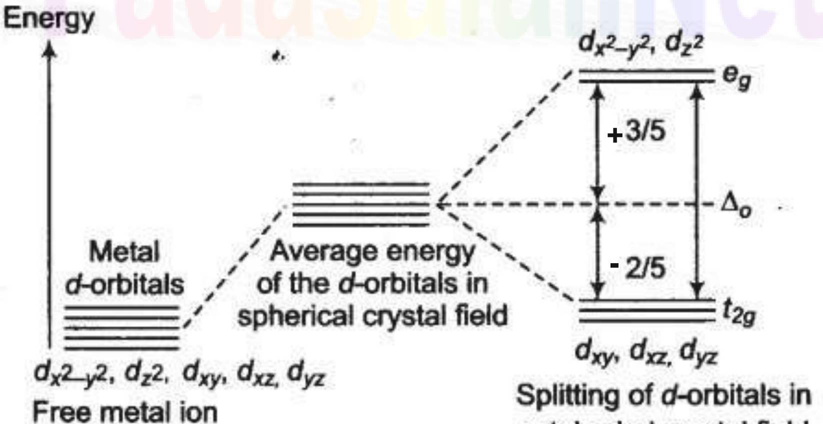
i) $[Co(NH_3)_5Cl]SO_{4(aq)} + BaCl_{2(aq)} \rightarrow BaSO_{4(ppt)}$ **ii)** $[Co(NH_3)_5(SO_4)]Cl_{(aq)} + BaCl_{2(aq)} \rightarrow$ no reaction

Silver nitrate test

i)$[Co(NH_3)_5Cl]SO_{4(aq)} + AgNO_{3(aq)} \rightarrow$ no reaction **ii)**$[Co(NH3)5(SO4)]Cl_{(aq)} + AgNO3_{(aq)} \rightarrow AgCl_{(ppt)}$

Hence they give different precipitates with different solutions. Thus they are ionisation isomers.

13. In an octahedral crystal field, draw the figure to show splitting of d orbitals.

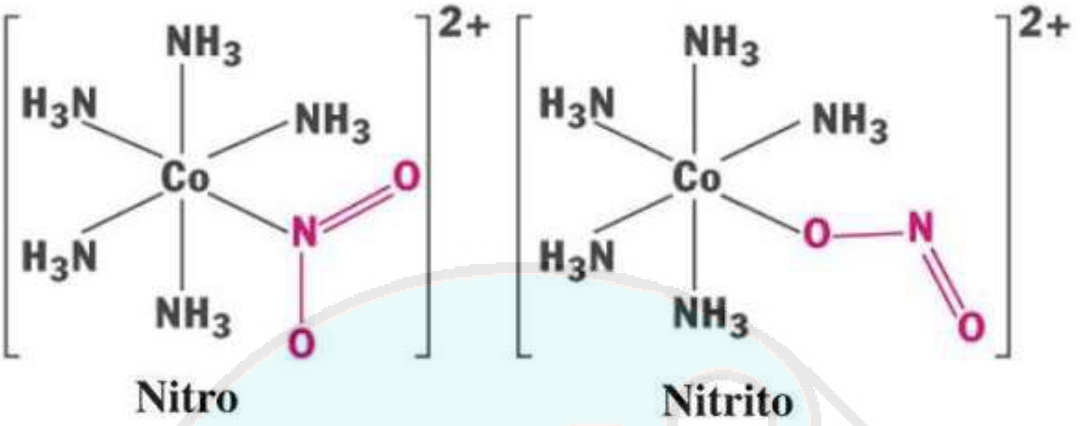


Splitting of d-orbitals in octahedral crystal field

14. What is linkage isomerism? Explain with an example.

This type of isomers arises when an ambidentate ligand is bonded to the central metal atom/ion through either of its two different donor atoms.

Example - $[Co(NH_3)_5(NO_2)]^{2+}$



15. Write briefly about the applications of coordination compounds in volumetric analysis.

a) Colour Tests :

Since many complexes are highly coloured they can be used as colourimetric reagents

e.g. formation of red 2,2'-bipyridyl and 1,10-phenanthroline complexes as a test for Fe^{2+}

b) Gravimetric Analysis : Here chelating ligands are often used to form insoluble complexes

e.g. $Ni(DMG)_2$ and $Al(oxine)_3$.

c) Complexometric Titrations and Masking Agents :

An example of this is the use of EDTA in the volumetric determination of a wide variety of metal ions in solution,

e.g. Zn^{2+}, Pb^{2+},Ca^{2+},Co^{2+},Ni^{2+},Cu^{2+}, etc. By careful adjustment of the pH and using suitable indicators, mixtures of metals can be analysed, e.g. Bi^{3+} in the presence of Pb^{2+}.

Alternatively, EDTA may be used as a masking agent to remove a metal ion which would interfere with the analysis of a second metal ion present.

16. Classify the following ligand based on the number of donor atoms.

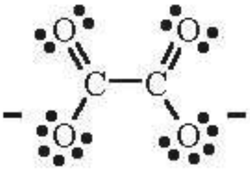
a) NH_3 b) en c) ox^{2-} d) triaminotriethylamine e) pyridine

a) $\ddot{N}H_3$ **- Monodentate** : The ligands which have only one donor atom.

b) en **- Bidentate ligands :** $H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2$ **ethane-1,2-diamine**

Bidentate ligands have two lone pairs and both of which can bond to the central metal ion. Bidentate ligands may be neutral molecules or anions

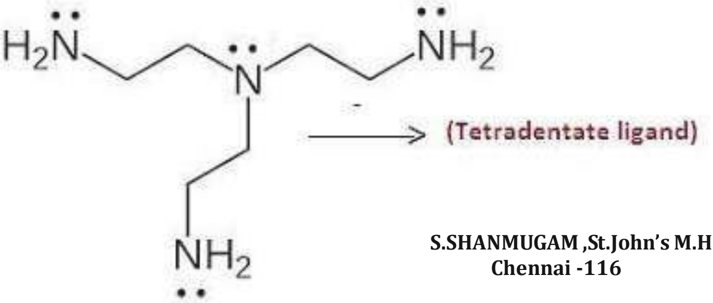
c) ox^{2-} **- Bidentate ligands**



oxalato

d) triaminotriethylamine - Tetradentate ligands :

Tetradentate ligands have two lone pairs and the four lone pair can bond to the central metal ion.



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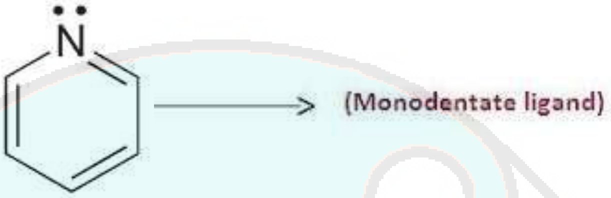
e) pyridine



17. Give the difference between double salts and coordination compounds.

i) Double salts are molecular compounds which are formed by the evoporation of solution containing 2 or more salts in stoichiometric proportions. They dissociate into their constituent ions in solution

eg: $K_2SO_4.Al_2(SO_4)_3.24H_2O \rightarrow 2K+ + 2Al^{3+} + 4SO_4^{2-} + 24H_2O$

ii) A complex compound is a compound formed from a lewis acid and a lewis base.

They do not dissociate into its constituent ions in solutions

eg: $Fe(CN)_2 + 4KCN \rightarrow K_4[Fe(CN)_6]$

$K_4[Fe(CN)_6]$ on dissociation gives 4K+ + $[Fe(CN)_6]^{4-}$ In $K_4[Fe(CN)_6]$ the individual components lose their identity. The metal of the complex ion is not free in solution unlike the metal in double salt solution.

18. Write the postulates of Werner's theory.

i) Most of the elements exhibit, two types of valence namely primary valence and secondary valence

ii) primary valence is referred as the oxidation state of the metal atom and the secondary valence as the coordination number.

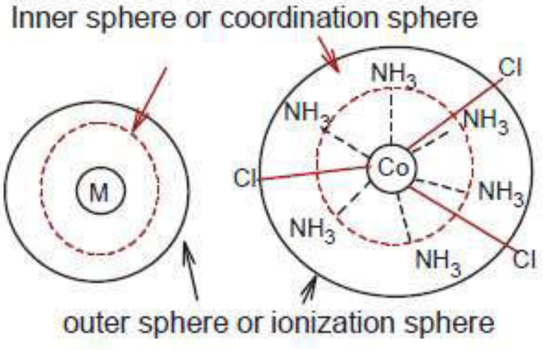
iii) The primary valence of a metal ion is positive in most of the cases and zero in certain cases. They are always satisfied by negative ions.

iv) The secondary valence is satisfied by negative ions, neutral molecules, positive ions or the combination of these.

v) Two spheres of attraction around a metal atom/ion in a complex.

1) The inner sphere is known as coordination sphere

2) The outer sphere is called ionisation sphere.



two sphere of attraction of metal

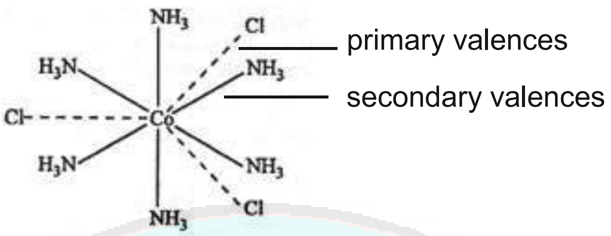
vi) i)The primary valences - non-directional

ii) Secondary valences - directional

vii) The geometry of the complex is determined by the spacial arrangement of the groups which satisfy the secondary valence.

6 - octahedral geometry. 4 -either tetrahedral or square planar geometry.

Werner's representation



CoCl$_3$.6NH$_3$ Complex

19. [Ni(CN)$_4$]$^{2-}$ is diamagnetic, while [Ni(Cl)$_4$]$^{2-}$ is paramagnetic using crystal field theory?

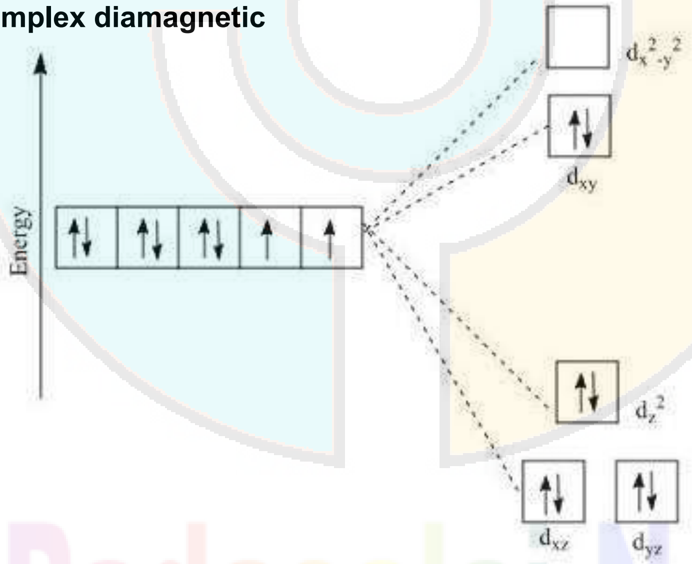
The [Ni(CN)$_4$]$^{2-}$ is a low-spin square planar complex, since it contains the strong-field CN– ligand in it.

The oxidation state number of Ni in the complex +2 and the electronic configuration of Ni^{2+}is 3d^8.

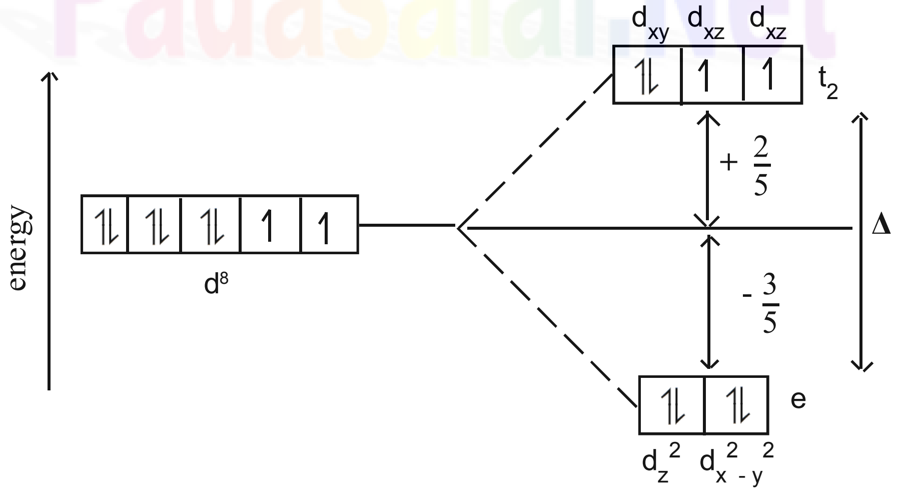
In the splitting pattern for a square-planar complex, the orbital possess the highest energy, followed by the dxy and orbitals. **The dxz and dyz are symmetrically equivalent.**

All the eight electrons will enter these five orbitals, such that no electron remains unpaired.

This makes the complex diamagnetic



[NiCl4]2-: Splitting in the tetrahedral field



8 electrons, then fill
The d orbitals, but instead, with high spin.

So, the dz^2 and dx^2-y^2 fill with one electron each, then the dxy, dxz, and dyz with one electron each, and then pairing occurs only after that, filling the dz^2, dx^2-y^2, and dxy completely. This leaves two unpaired electrons in the t2 orbitals, and thus this complex is **paramagnetic** with two unpaired electrons, as expected

20. Why tetrahedral complexes do not exhibit geometrical isomerism.

In tetrahedral complex metal atom or ion is at the Centre of a tetrahedron and four ligands are at four corners of tetrahedron this type of complex does not exhibit geometrical isomerism since all four ligands are at the equidistance having bond angle $109^{o}28'$

OR

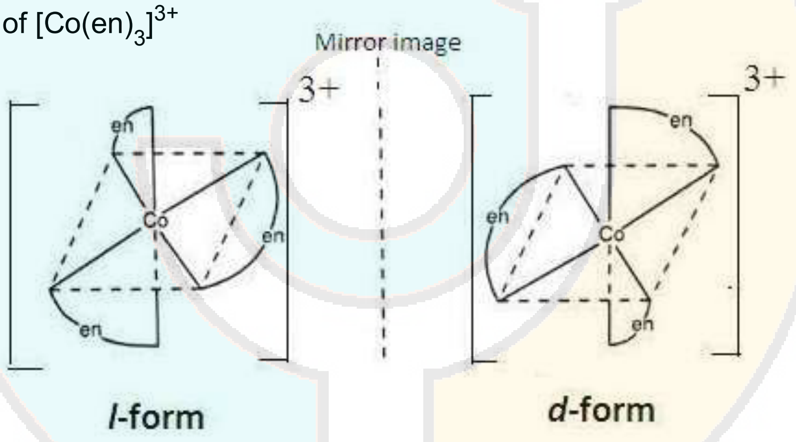
Tetrahedral complexes do not show geometrical isomerism because the relative positions of unidentate ligands attached to the central atom are same with respect to each other

21. Explain optical isomerism in coordination compounds with an example.

The pair of two optically active isomers which are mirror images of each other are called enantiomers. Their solutions rotate the plane of the plane polarised light either clockwise or anticlockwise and the corresponding isomers are called ‘d’ (dextro rotatory) and ‘l’ (levo rotatory) forms respectively .

Examples:

The optical isomers of $[Co(en)_3]^{3+}$



The octahedral complexes of type $[M(xx)_3]^{n\pm}$, $[M(xx)_2AB]^{n\pm}$ and $[M(xx)_2B_2]^{n\pm}$ exhibit optical isomerism

22. What are hydrate isomers? Explain with an example.

The exchange water molecules in the crystal lattice with a ligand in the coordination entity will give different isomers. These type of isomers are called hydrate isomers.

For example

$[Cr(H_2O)_6]\ Cl_3$ - is a violet colour compound and gives $3Cl^-$ ions in solution

$[CrCl(H_2O)_5]\ Cl_2.H_2O$ - is a pale green colour compound and gives $2Cl^-$ ions in solution

$[CrCl_2(H_2O)_4]Cl.\ 2H_2O$ is a dark green colour compound and gives one Cl^- ion in solution

23. What is crystal field splitting energy?

The degenerate d-orbitals (in a spherical field environment) split into two levels i.e., e_g and t_{2g} in the presence of ligands. The splitting of the degenerate levels due to the presence of ligands is called the crystal-field splitting while the energy difference between the two levels (e_g and t_{2g}) is called the crystal-field splitting energy. It is denoted by Δo.

24. What is crystal field stabilization energy (CFSE) ?

The crystal field stabilisation energy is defined as the energy difference of electronic configurations in the ligand filed (E_{LF}) and the isotropic field/barycentre (E_{iso}).

$$CFSE\ (.\Delta E_o) = \{E_{LF}\} - \{E_{iso}\}$$

$$= \{ [\ nt_{2g}(-0.4) + n_{eg}\ (0.6)]\ \Delta o + n_p P\} - \{n'_p\ P\}$$

nt_{2g} - is the number of electrons in t_{2g} orbitals

n_{eg} - is number of electrons in eg orbitals

n_p is number of electron pairs in the ligand field

n'_p is the number of electron pairs in the isotropic field (barycentre).

25. A solution of $[Ni(H_2O)_6]^{2+}$ is green, whereas a solution of $[Ni(CN)_4]^{2-}$ is colorless – Explain.

in $[Ni(H_2O)_6]^{2+}$, Ni is +2 state with the configuration is $3d^8$ i.e it has two unpaired electrons which do not pair up in the presence of the week H_2O ligand. Hence, it is coloured, For d-d transition, red is absorbed and complementary light emitted is green

In case **$[Ni(CN)_4]^{2-}$** Ni is again in + 2 state with with the configuration is $3d^8$ but in the presence of the strong CN- ligand , the two unpaired electrons in the 3d orbitals pair up.Thus, there is no unpaired electron present. Hence, it is colourlesss (no d-d transition)

26. Discuss briefly the nature of bonding in metal carbonyls.

The metal-carbon bonds in metal carbonyls have both **σ** and **π** characters.

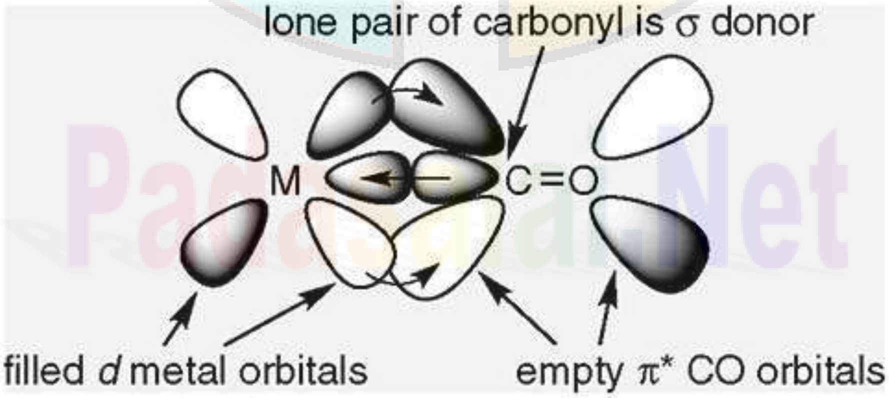
A **σ** bond is formed when the carbonyl carbon donates a lone pair of electrons to the vacant orbital of the metal.

A π bond is formed by the donation of a pair of electrons from the filled metal d orbital into the vacant anti- bonding **π** orbital (also known as back bonding of the carbonyl group).

The **σ** bond strengthens the **π** bond and vice-versa.

Thus, a synergic effect is created due to this metal-ligand bonding.

This synergic effect strengthens the bond between CO and the metal.



27. What is the coordination entity formed when excess of liquid ammonia is added to an aqueous solution of copper sulphate?

When excess of liquid ammonia is added to an aqueous solution of copper sulphate it gives tetraammine copper (II) sulphate.

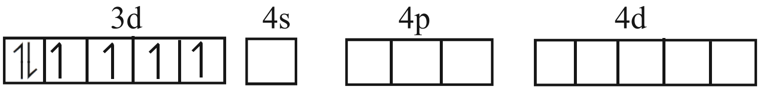
$$CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$$

Thus, the coordination entity formed in the process is $[Cu(NH_3)_4]SO_4$ is a very stable complex, which does not ionize to give Cu^{2+} ions when added to water

28. On the basis of VB theory explain the nature of bonding in $[Co(C_2O_4)_3]^{3-}$

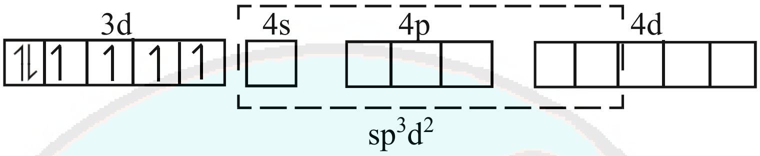
$[Co(C_2O_4)_3]^{3-}$
Cobalt exists in the +3 oxidation state in the given complex.

Orbitals of Co^{3+} ion

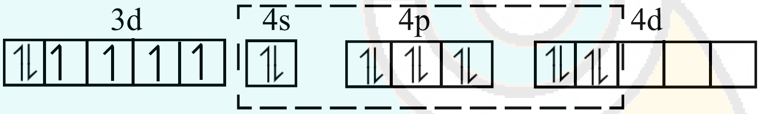


Oxalate is a weak field ligand. Therefore, it cannot cause the pairing of the 3d orbital electrons. As there are 6 ligands, hybridization has to be either sp^3d^2 or d^2sp^3 hybridization.

sp^3d^2 hybridization of Co^{3+}:



The 6 electron pairs from the 3 oxalate ions (oxalate anion is a bidentate ligand) occupy these sp^3d^2 orbitals.



6 electron pairs from 3 oxalate ions

Hence, the geometry of the complex is found to be octahedral.

29. What are the limitations of VB theory?

1. It does not explain the colour of the complex
2. It considers only the spin only magnetic moments and does not consider the other components of magnetic moments.
3. It does not provide a quantitative explanation as to why certain complexes are inner orbital complexes and the others are outer orbital complexes for the same metal.

30. Write the oxidation state, coordination number , nature of ligand, magnetic property and electronic configuration in octahedral crystal field for the complex $K_4[Mn(CN)_6]$

$K_4[Mn(CN)_6]$ - Potassium hexacyanomanganate(II)

Oxidation state of manganese = +2 { 4(+1) + x + 6(-1) = 0; x = +2 }

Coordination number - 6

Nature of ligand - CN^- Monodentate ligand

Magnetic property : Paramagnetic

$$\text{Magnetic moment, } \mu = \sqrt{n(n+2)}$$
$$= \sqrt{1(1+2)}$$
$$= \sqrt{3}$$
$$= 1.732 \text{ BM}$$

Electronic configuration - d5$^+$: t_{2g}^{5}

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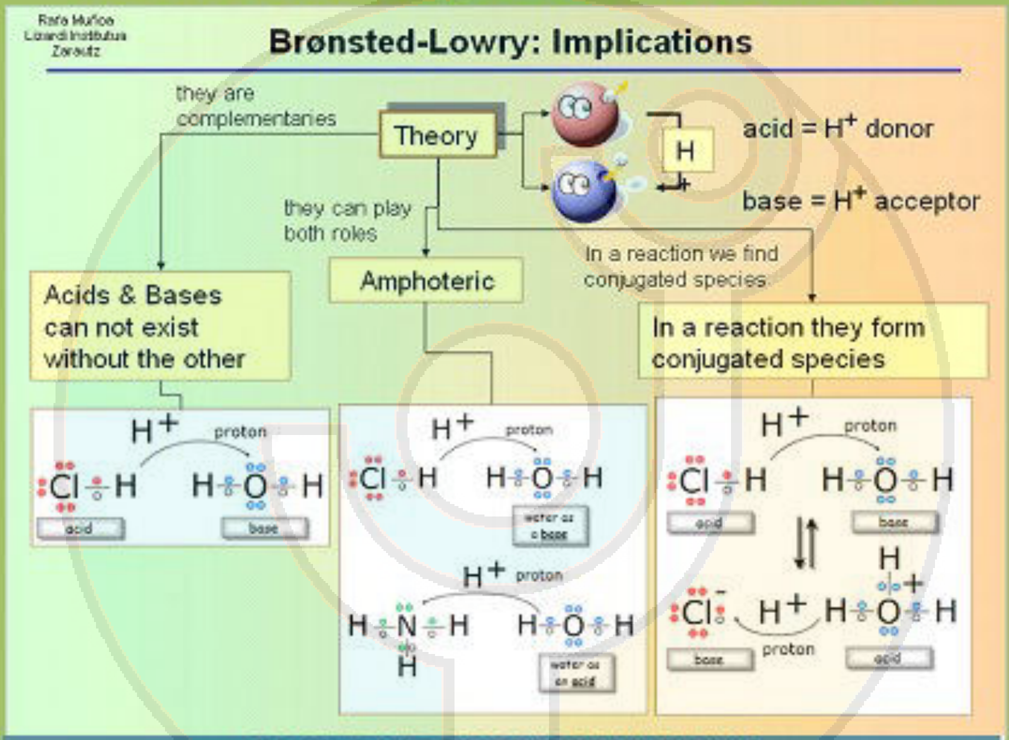
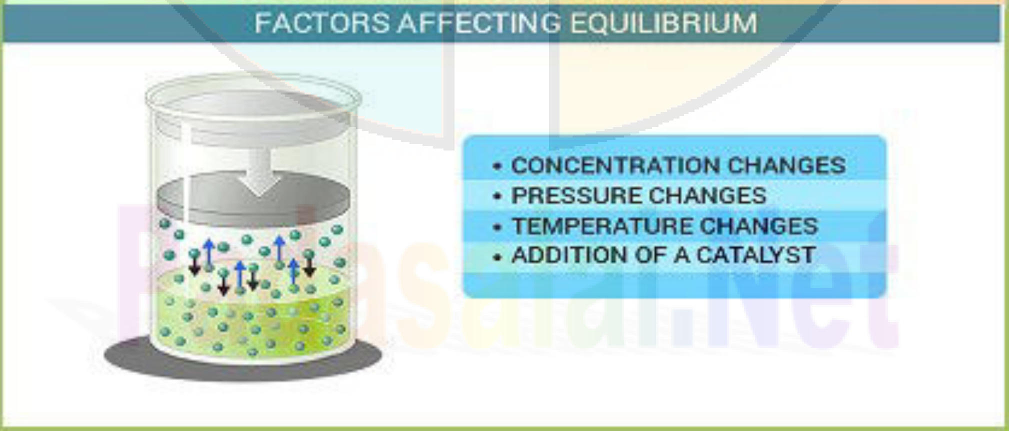
PHYSICAL CHEMISTRY

Plus two

Unit-8

IONIC EQUILIBRIUM





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UNIT- 8

IONIC EQUILIBRIUM

1. **What are Lewis acids and bases? Give two example for each.**

i) Lewis acid is a species that accepts an electron pair and it is a positive ion (or) an electron deficient molecule

example :Electron deficient molecules BF_3 ,$AlCl_3$.etc

All metal ions (or) atoms : Fe^{2+} , Cr^{3+}, Cu^{2+} and Carbonium ion

ii) Lewis base is a species that donates an electron pair and it is a anion (or) neutral molecule with at least one lone pair of electrons.

example :more lone pairs of electrons: NH_3, H_2O, R-O-H, R-O-R, $R\text{-}NH_2$

All anions : F^- , Cl^-, CN^- and Carbanion ..

2. **Discuss the Lowry – Bronsted concept of acids and bases.**

According to their concept,

An Acid is defined as a substance that has a tendency to donate a proton to another substance

Base is a substance that has a tendency to accept a proton from other substance.

In other words, an acid is a proton donor and a base is a proton acceptor.

In general, Lowry – Bronsted (acid – base) reaction is represented as

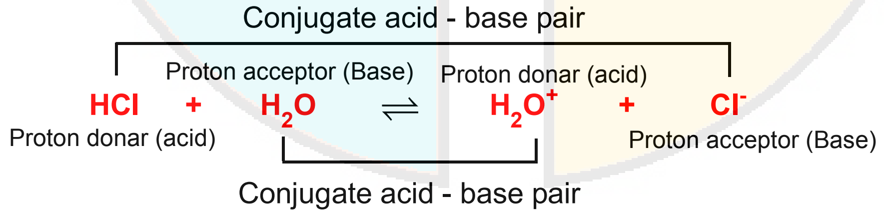
$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1$$

$\text{Acid}_1 \longrightarrow$ conjugate acid - (Proton donar)

$\text{Base}_2 \longrightarrow$ conjugate base - (Proton acceptor)

$\text{Acid}_2 \longrightarrow$ conjugate acid - (Proton donar)

$\text{Base}_1 \longrightarrow$ conjugate base - (Proton acceptor)



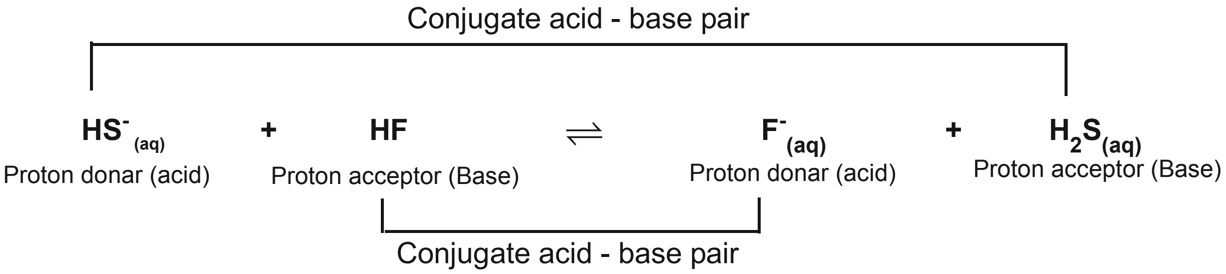
3. **Indentify the conjugate acid base pair for the following reaction in aqueous solution**

i) $HS^-(aq) + HF \rightleftharpoons F^-(aq) + H_2S(aq)$

ii) $HPO_4^-(aq) + SO_3^{2-} \rightleftharpoons PO_4^{3-}(aq) + HSO_3^-(aq)$

Iii) $NH_4^+(aq) + CO_3^{2-} \rightleftharpoons NH_3^{3-}(aq) + HCO_3^-(aq)$

i)



ii)

Conjugate acid - base pair

$$HPO_4^{-}{}_{(aq)} + SO_3^{2-} \rightleftharpoons PO_4^{3-}{}_{(aq)} + HSO_3^{-}{}_{(aq)}$$

Proton donar (acid) Proton acceptor (Base) Proton donar (acid) Proton acceptor (Base)

Conjugate acid - base pair

iii)

Conjugate acid - base pair

$$NH_4^{+}{}_{(aq)} + CO_3^{2-} \rightleftharpoons NH_3^{3-}{}_{(aq)} + HCO_3^{-}{}_{(aq)}$$

Proton donar (acid) Proton acceptor (Base) Proton donar (acid) Proton acceptor (Base)

Conjugate acid - base pair

4. **Account for the acidic nature of $HClO_4$. In terms of Bronsted – Lowry theory, identify its conjugate base.**

$$HClO_4 + H_2O \rightleftharpoons H_3O^+ + ClO_4^-$$

When an acid dissociates in water into H_3O^+ ions and the anion of the acid, the anion (ClO_4^-) is termed the conjugate base of that acid.

In this case, the acid is perchloric acid and its conjugate base is the perchlorate ion (ClO_4^-)

5. **When aqueous ammonia is added to $CuSO_4$ solution, the solution turns deep blue due to the formation of tetramminecopper (II) complex, $[Cu(H_2O)_4]^{2+} + 4NH_3 (aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}$,among H_2O and NH_3 which is stronger Lewis base**

H_2O has two nonbonding electron pairs and is, therefore, a stronger Lewis base than NH_3 which only has one.

H_2O is a stronger Lewis base because the extra hydrogen in NH_3 shields the lone pair of the central nitrogen atom.

H_2O should be a stronger Lewis base because oxygen is more electronegative than nitrogen.

6. **The concentration of hydroxide ion in a water sample is found to be 2.5×10^{-6}M. Identify the nature of the solution**

$[OH^-] = 2.5\times10^{-6}M$

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

$pOH = -\log[2.5\times10^{-6}]$

$pOH = -[\log 2.5 - 6\log 10]$

$pOH = -0.3979 - (-6\times1)$

$pOH = -0.3979 + 6\times1$

$pOH = 5.6021$

$pOH + pH = 14$ $pH = 14 - 5.6021 = 8.3979$

pH = 8.3979 pH > 7 , The nature of the solution is basic

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7. **A lab assistant prepared a solution by adding a calculated quantity of HCl gas 25°C to get a solution with $[H_3O^+] = 4\times10^{-5}M$. Is the solution neutral (or) acidic (or) basic.**

$$[H_3O^+] = 4\times10^{-5}M$$
$$pH = -\log[H_3O^+]$$
$$pH = -\log[4\times10^{-5}]$$
$$pH = -[\log 4 - 5\log 10]$$
$$pH = -\log 4 + 5\log 10$$
$$pH = -0.6020 + 5\times1 = 4.398$$

pH = 4.398 , pH < 7 , The solution is acidic nature

8. **Calculate the pH of 0.04 M HNO_3 Solution.**

$$pH = -\log[H_3O^+]$$
$$pH = -\log[0.04]$$
$$pH = -\log[4\times10^{-2}]$$
$$pH = -[\log 4 - 2\log 10]$$
$$pH = -\log 4 + 2\log 10$$
$$pH = -0.6021 + 2\times1$$
$$pH = 1.3979 \simeq 1.40$$

9. **Define solubility product**

The solubility product of a compound is defined as the product of the molar concentration of the constituent ions, each raised to the power of its stoichiometric co – efficient in a balanced equilibrium equation.

10. **Define ionic product of water. Give its value at room temperature.**

The product of concentrations of H^+ and OH^- ions in water at a particular temperature is known as ionic product of water.

Therefore, the ionic product of water at 25°C is

$$K_w = [H_3O] + [OH^-]$$
$$K_w = (1\times10^{-7})(1\times10^{-7})$$
$$K_w = 1\times10^{-14}\ mol^2dm^{-6} \text{ at } 298\ K$$

11. **Explain common ion effect with an example**

The dissociation of a weak acid is suppressed in the presence of a salt containing an ion common to the weak electrolyte. It is called the common ion effect.

For example,

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$
$$CH_3COONa \rightleftharpoons Na^+ + CH_3COO^-$$

the addition of sodium acetate to acetic acid solution leads to the suppression in the dissociation of acetic acid which is already weakly dissociated. In this case, CH_3COOH and CH_3COONa have the **common ion, CH_3COO^-.**

12. Derive an expression for Ostwald's dilution law

Ostwald's dilution law relates the dissociation constant of the weak acid (K_a) with its degree of dissociation (α) and the concentration (c).

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{total number of moles}}$$

The dissociation of acetic acid can be represented as

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

	CH_3COOH	H^+	CH_3COO^-
Initial number of moles	1	-	-
Degree of dissociation	α		
Number of moles at equilibrium	$1 - \alpha$	α	α
Equilibrium concentration	$C(1 - \alpha)$	$C\alpha$	$C\alpha$

$$Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$K_a = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

$$K_a = \frac{C\alpha^2}{1-\alpha}, (1-\alpha \simeq 1)$$

$$K_a = C\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{C}}$$

$[H+] = C\alpha$ $\quad$ $[H+] = C\sqrt{\frac{K_a}{C}}$ $\quad$ for weak acid is $[H+] = \sqrt{K_a.C}$

13. Define pH

pH of a solution is defined as the negative logarithm of base 10 of the molar concentration of the hydronium ions present in the solution.

$$\mathbf{pH = -log [H_3O^+]}$$

14. Calculate the pH of 1.5×10^{-3}M solution of Ba (OH)$_2$

$$Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$$

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

$pOH = - \log [2 \times 1.5\times10^{-3}]$

$pOH = - \log [3 \times 10^{-3}]$

$pOH = -[\log 3 - 3 \log 10]$

$pOH = - \log 3 + 3 \log 10$

$pOH = - \log 3 + 3 \times 1$

$pOH = - 0.4771 + 3 = 2.53$ $\quad$ $\therefore$ **pH = 14 - 2.53 = 11.47**

15. **50ml of 0.05M HNO_3 is added to 50ml of 0.025 M KOH.Calculate the pH of the resultant solution.**

Mole = Concentration x Volume

mole of KOH = 50 ml x 0.025 = 1.25

mole of HNO_3 = 50 ml x 0.05M = 2.5

Total volume of solution (50+50 ml = 100 ml)

1.25 mole of KOH exactly neutralized by 1.25 mole of HNO_3

$$KOH + HNO_3 \longrightarrow KNO_3 + H_2O$$

that is 2.5 -1.25 = 1.25 HNO_3mole

$$\text{Conc of } H^+ = \frac{\text{no of mole of } H^+}{\text{total volume of solution } (50 + 50\text{ ml} = 100\text{ ml})}$$

$$\text{Conc of } [H^+] = \frac{1.25}{100} = 0.0125$$

pH = - log [H^+]

pH = - log [0.0125]

pH = - log [1.25 x 10^{-2}]

pH = - [log 1.25 - 2 log10]

pH = - log 1.25 + 2 log10

pH = - 0.0969 + 2 x1

pH = 1.9031

16. **The K_a value for HCN is 10^{-9} .What is the pH of 0.4M HCN solution?**

$K_a = 10^{-9}$ C= 0.4 M

$[H^+] = \sqrt{K_a.C}$

$[H^+] = \sqrt{10^{-9} \text{ x } 0.4}$

$[H^+] = 2\text{x}10^{-5}$

pH = - log [H^+]

pH = - log [2 x 10^{-5}]

pH = - [log 2 - 5 log10]

pH = - log 2 + 5 log10

pH = - 0.3010 + 5 x1

pH = 4.699

17. **Calculate the extent of hydrolysis and the pH of 0.1M ammonium acetate Given that $K_a = K_b = 1.8 \times 10^{-5}$**

For hydrolysis of salt of weak acid and weak base,

$$K_h = \frac{K_w}{K_a x K_b}$$

$$K_h = \frac{\alpha^2}{(1-\alpha)^2}$$

$$K_h = \frac{1 \ x10^{-14}}{1.8x10^{-5}x1.8x10^{-5}}$$

$$\frac{\alpha^2}{(1-\alpha)^2} = \frac{1 \ x10^{-14}}{1.8x10^{-5}x1.8x10^{-5}}$$

$$\frac{\alpha}{(1-\alpha)} = \sqrt{\frac{1 \ x10^{-14}}{1.8x10^{-5}x1.8x10^{-5}}} = \sqrt{\frac{1 \ x10^{-4}}{3.24}} = \frac{1 \ x10^{-2}}{1.8} = 0.55 \ x \ 10^{-2}$$

hydrolysis = 0.55×10^{-2}

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

$$\frac{1}{2}pK_w = -\frac{1}{2}\log(1 \ x10^{-14}) = 7$$

$$\frac{1}{2}pK_a = -\frac{1}{2}\log K_a = -\frac{1}{2}\log(1.8x10^{-5}) = \frac{1}{2}4.7447 = 2.3723$$

$$\frac{1}{2}pK_b = -\frac{1}{2}\log K_b = -\frac{1}{2}\log(1.8x10^{-5}) = \frac{1}{2}4.7447 = 2.3723$$

pH = 7 + 2.3723 – 2.3723 = 7 + 0

pH = 7

18. **Derive an expression for the hydrolysis constant and degree of hydrolysis of salt of strong acid and weak base.**

Weak base - NH_4OH and strong acid - HCl

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

Hydrolysis constant : Applying the Law of Mass Action

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+][H_2O]}$$

Since $[H_2O]$ is very large, it is taken to be constant and the hydrolysis constant expression is reduced to

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \quad \text{----------------} 1$$

Relation between K_h, K_w and K_b. We know that the ionic product of water K_w is expressed as :

$$K_w = [H^+][OH^-] \quad \text{-------------}2$$

For the dissociation of a weak base, NH_4OH

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

The dissociation constant, K_b, can be expressed as

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_4OH]} \text{ -------------------------------- } 3$$

Dividing (2) by (3)

$$\frac{K_w}{K_b} = [H^+][OH^-] \times \frac{[NH_4OH]}{[NH_4^+]\,[OH^-]} = \frac{[NH_4OH][H^+]}{[NH_4^+]} = K_h$$

$$\frac{K_w}{K_b} = K_h$$

As discussed in the salt hydrolysis of strong base and weak acid. In this case also, we can establish a relationship between the K_h and K_b as

$$K_h . K_b = K_w$$

Let us calculate the K_h value in terms of degree of hydrolysis (h) and the concentration of salt

$$K_h = h^2C \text{ and}$$

$$[H^+] = \sqrt{K_h.C}$$

$$[H^+] = \sqrt{\frac{K_w}{K_b}.C}$$

$$pH = -\log [H^+]$$

$$pH = -\log\sqrt{\frac{K_w}{K_b}.C} \quad \text{(or)} \quad pH = -\log\left(\frac{K_w}{K_b}.C\right)^{\frac{1}{2}}$$

$$pH = -\frac{1}{2}\log K_w - \frac{1}{2}\log C + \frac{1}{2}\log K_b$$

$$pH = 7 + \frac{1}{2}pK_b - \frac{1}{2}\log C \quad \text{(or)} \quad pH = 7 + \frac{1}{2}pK_b = \frac{1}{2}\log C$$

In this case it is evident that pH will always be less than 7. Thus, **the solution of a salt of weak base and strong acid will always be acidic.**

19. Solubility product of Ag_2CrO_4 is 1 x10^{-12}. What is the solubility of Ag_2CrO_4 in 0.01M $AgNO_3$ solution?

$$K_{sp} = 1 \times 10^{-12}$$

$$Ag_2CrO_4\,(s) \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

$$Ag\,NO_3\,(s) \rightleftharpoons 2Ag^+ + NO_3^-$$

$$0.01\text{ M} \qquad 0.01\text{ M} \qquad 0.01\text{ M}$$

$$[Ag^+] = 2s + 0.01$$

$$\because 0.01 >> 2s$$

$$\therefore [Ag^+] = 0.01\text{ M}$$

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

$$K_{sp} = (s)^2(s)$$

$$1 \times 10^{-12} = (0.01)^2\,(s)$$

$$[CrO_4^{2-}] = (s) = \frac{1 \times 10^{-12}}{(10^{-2})^2} = 1 \times 10^{-8}$$

20. Write the expression for the solubility product of $Ca_3(PO_4)_2$

$Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2\ PO_4^{3-}$

$K_{sp} = [Ca^{2+}]^3 . [\ PO_4^{3-}]^2$

$K_{sp} = (3s)^3.(2s)^2$

$K_{sp} = (27s^3\ ).(4s^2)$

$K_{sp} = 108s^5$.

21. A saturated solution, prepared by dissolving $CaF_{2(s)}$ in water, has $[Ca^{2+}]= 3.3\ x10^{-4}$ What is theK_{sp} of CaF_2?

$CaF_{2\ (s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + \ 2\ F^-{}_{(aq)}$

(breaks into 2 F^- ions not F_2)

$[F^-]$ is double the $[Ca^{2+}]$

$[2\ F^-\ ] = 2[Ca^{2+}] = 2 \times 3.3 \times 10^{-4}$

$[2\ F^-\ ] = 6.6 \times 10^{-4}$ M

$K_{sp} = [Ca^{2+}]\ .\ [\ F^-\ ]^2$

$K_{sp} = 3.3 \times 10^{-4}\ .\ (6.6 \times 10^{-4}\ )^2$

$K_{sp} = 1.44 \times 10^{-10}$.

22. K_{sp} of AgCl is 1.8×10^{-10}.Calculate molar solubility in 1 M $AgNO_3$.

$AgCl_{(s)} \rightleftharpoons Ag^+{}_{(aq)} + Cl^-{}_{(aq)}$

x = solubility of AgCl in 1M $AgNO_3$.

$AgNO_{3\ (aq)} \rightleftharpoons Ag^+{}_{(aq)} + NO_3^-{}_{(aq)}$

1 M   1 M

$[Ag^+] = x + 1\ M \simeq 1M \quad (\because\ x << 1\ )$

$[Cl^-] = x$

$K_{sp} =[Ag^+].\ [Cl^-]$

$1.8 \times 10^{-10} = (1\ )\ (x)$

$x = 1.8 \times 10^{-10}M$

23. A particular saturated solution of silver chromate Ag_2CrO_4 has $[Ag^+] = 5 \times 10^{-5}$ and $[\ CrO_4^{2-}\ ] = 4.4 \times 10^{-4}$ What is the value of K_{sp} for Ag_2CrO_4 ?

$Ag_2CrO_4\ (s) \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$K_{sp} = [\ Ag^+]^2[\ CrO_4^{2-}\ ]$

$K_{sp} = (5 \times 10^{-5})^2\ (\ 4.4 \times 10^{-4}\ )$

$K_{sp} = (\ 25 \times 10^{-10}\ )\ (4.4 \times 10^{-4})$

$K_{sp} = (25 \times 4.4) \times 10^{-10} \times 10^{-4}$

$K_{sp} = 110 \times 10^{-14}$

$\mathbf{K_{sp} = 1.10 \times 10^{-12}}$

24. Write the expression for the solubility product of Hg_2Cl_2.

$$Hg_2Cl_2 \rightleftharpoons Hg_2^{2+} + 2Cl^-$$

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2$$

$$K_{sp} = [s].[2s]^2$$

$$K_{sp} = 4s^3$$

25. K_{sp} of Ag_2CrO_4 is 1.1×10^{-12}. What is solubility of Ag_2CrO_4 in 0.1M K_2CrO_4.

$$Ag_2CrO_4\,(s) \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

x 2x x

x is the solubility of Ag_2CrO_4 in 0.1M K_2CrO_4.

$$K_2CrO_4\,(s) \rightleftharpoons 2K^+ + CrO_4^{2-}$$

0.1 M 0.1 M 0.1 M

$$[Ag^+] = 2x$$

$$[CrO_4^{2-}] = (x + 0.1) \simeq 0.1 \quad (\because x << 0.1)$$

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

$$1.1 \times 10^{-12} = (2x)^2\,(0.1)$$

$$1.1 \times 10^{-12} = 0.4x^2$$

$$x^2 = \frac{1.1 \times 10^{-12}}{0.4} \qquad x = \sqrt{\frac{1.1 \times 10^{-12}}{0.4}}$$

$$x = \sqrt{2.75 \times 10^{-12}} \qquad \mathbf{x = 1.658 \times 10^{-6} M}$$

26. Will a precipitate be formed when 0.150 L of 0.1M $Pb(NO_3)_2$ and 0.100L of 0.2 M NaCl are mixed? $K_{sp}(PbCl_2) = 1.2 \times 10^{-5}$.

Precipitation reaction : $Pb(NO_3)_{2(aq)} + 2NaCl_{(aq)}$ ----------> $PbCl_{2(s)} + 2NaNO_{3(aq)}$

Solubility reaction : $PbCl_2(s)$ -----> $Pb^{2+} + 2Cl^-$

K_{sp} is given and in order to find out if a precipitate form we need to find out Q **$Q = [Pb^{2+}][Cl^-]^2$**

1:1 mole ratios so initial $[Pb^{2+}] = [Pb(NO_3)_2] = 0.1$ M ; initial $[Cl^-] = [NaCl] = 0.2$ M

After we combine the solution the total volume becomes .250 L ,

so the concentration of Pb^{2+} and Cl^- ions is :

Number of moles Pb^{2+}= molarity x Volume of the solution in lit= 0.1 × 0.150 L

$$[Pb^{2+}] = \frac{0.1\ M\ Pb^{2+}\ x\ 0.150L}{0.250\ L} = 0.06\ M\ Pb^{2+}$$

$$[Cl^-] = \frac{0.2\ M\ Cl^-\ x\ 0.100L}{0.250\ L} = 0.08\ M\ Cl^-$$

$Q = [Pb^{2+}].[Cl^-]^2$ $Q = (0.060)(0.080)^2 = 3.8 \times 10^{-4}$

$Q > K_{sp}$, [$3.8 \times 10^{-4} < 1.2 \times 10^{-5}$] so $PbCl_2$ does precipitate.Eq shifts to the left .

27. K_{sp} of $Al(OH)_3$ is $1x10^{-15}$M. At what pH does $1.0x10^{-3}$M Al^{3+} precipitate on the addition of buffer of NH_4Cl and NH_4OH solution?

1) Write the dissociation equation: $Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$

2) Write the Ksp expression: $K_{sp} = [Al^{3+}][OH^-]^3$

3. Plug into the K_{sp} expression: $1x10^{-15}M = (1.0x10^{-3}M)\ [OH^-]^3$

4) Solve for s, which is the $[OH^-]$: $[OH^-]^3 = \frac{K_{sp}}{[Al^{3+}]}$

$$[OH^-] = 3\sqrt{\frac{K_{sp}}{[Al^{3+}]}}$$

$$[OH^-] = 3\sqrt{\frac{1x10^{-15}}{1x10^{-3}}}$$

$$[OH^-] = 3\sqrt{1x10^{-12}}$$

$$[OH^-] = (1x10^{-12})^{\frac{1}{3}}$$

$$\mathbf{[OH^-] = 1 \times 10^{-4}}$$

5) Calculate the pH:

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

$pOH = -\log(1x10^{-4}) = 4$

$pH = 14 - pOH = 14 - 4 = 10$

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UNIT 9

Electro Chemistry

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1. Define anode and cathode

The anode of a device is the terminal where current flows in from outside. The cathode of a device is the terminal where current flows out. By current we mean the positive conventional current. Since electrons are negatively charged, positive current flowing in is the same as electrons flowing out.

2. Why does conductivity of a solution decrease on dilution of the solution

The conductivity of a solution is directly proportional to number of ions present in a unit volume of the solution because current is carried forward by the ions. With dilution number of ions in unit volume decreases so that conductivity also decreases. Hence with dilution conductivity decreases.

3. State Kohlrausch Law. How is it useful to determine the molar conductivity of weak electrolyte at infinite dilution.

At infinite dilution, the limiting molar conductivity of an electrolyte is equal to the some of the limiting molarconductivities of its constituent ions. i.e., the molar conductivity is due to the independent migration of cations in one direction and anions in the opposite direction.

Determination of for weak electrolytes : The molar conductivity of a weak electrolyte at infinite dilution cannot be determined by extrapolation method. However, values for weak electrolytes can be deter mined by using the Kohlrausch's equation.

$$\alpha = \frac{\Lambda_m}{\Lambda_m^o}$$

Λ_m - Molar conductivity

Λ_m^o - Molar conductivity at infinite dilution

4. Describe the electrolysis of molten NaCl using inert electrodes

Electrolysis of Molten NaCl. If sodium chloride is melted (above 801 °C), two electrodes are inserted into the melt, and an electric current is passed through the molten salt, then chemical reactions take place at the electrodes. Chlorine gas bubbles out of the melt above the anode.

5. State Faraday's Laws of electrolysis

Faraday's first law

The mass of the substance (m) liberated at an electrode during electrolysis is directly proportional to the quantity of charge (Q) passed through the cell.

$$m \alpha Q \qquad m = Z\ It$$

Faraday's second law

When the same quantity of charge is passed through the solutions of different electrolytes, the amount of substances liberated at the respective electrodes are directly proportional to their electrochemical equivalents.

6. Describe the construction of Daniel cell. Write the cell reaction.

Anodic oxidation

The electrode at which the oxidation occurs is called the anode. In Daniel cell, the oxidation take place at zinc electrode, i.e., Electrons are liberated at zinc electrode and hence it is negative (- ve).

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ (loss of electron-oxidation)

Cathodic reduction

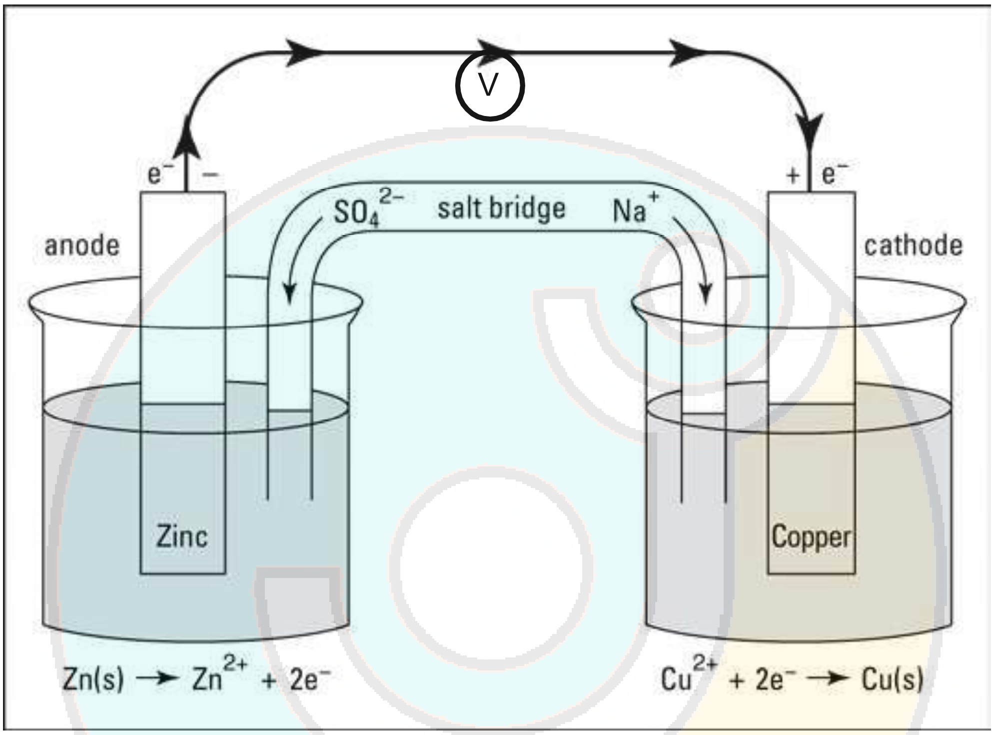
As discussed earlier, the electrons flow through the circuit from zinc to copper, where the Cu2+ ions in the solution accept the electrons, get reduced to copper and the same get deposited on the electrode. Here, the electrons are consumed and hence it is positive (+ve).

$Cu^{2+}(aq) + 2e^- \rightarrow Cu\ (s)$ (gain of electron-reduction)

The total reaction is: $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

Salt bridge

The electrolytes present in two half cells are connected using a salt bridge To maintain the electrical neutrality in both the compartments, the non reactive anions SO_4^{2-} (from Na_2SO_4 taken in the salt bridge) move from the salt bridge and enter into the anodic compartment, at the same time some of the $2Na^+$ ions move from the salt bridge into the cathodic compartment.



7. **Why is anode in galvanic cell considered to be negative and cathode positive electrode?**

The anode is the electrode where oxidation (loss of electrons) takes place; in a galvanic cell, it is the negative electrode, as when oxidation occurs, electrons are left behind on the electrode. This is why the cathode is a positive electrode; because positive ions are reduced to metal atoms there

8. **The conductivity of a 0.01M solution of a 1 :1 weak electrolyte at 298K is 1.5×10^{-4} S cm^{-1}.**

i) molar conductivity of the solution

ii) degree of dissociation and the dissociation constant of the weak electrolyte

Given that : λ^o_{cation} = 248.2 S cm^2 mol^{-1} and λ^o_{anion} = 51.8 Scm^2 mol^{-1}

i) Molar conductivity $\Lambda_m = \dfrac{\kappa \times 10^{-3}}{C}$ $\quad \Lambda_m = \dfrac{1.5\times10^{-2}\times10^{-3}}{0.01} = 1.5\times10^{-3}\,S\,m^{-2}mol^{-1}$

ii) **degree of dissociation** $\Lambda^o_m = \Lambda^o_{cation} + \Lambda^o_{anion}$, $\quad \Lambda^o_m = (248.2+51.8) = 300\ cm^2mol^{-1}$

(or) $\Lambda^o_m = 300\times10^{-4}Sm^2mol^{-1}$ $\quad \alpha = \dfrac{1.5\times10^{-3}S\,m^{-2}mol^{-1}}{300\times10^{-4}Sm^2mol^{-1}} = 0.05$

dissociation constant of the weak electrolyte $K_a = \dfrac{C\alpha^2}{1-\alpha}$,

$$K_a = \frac{0.01\times(0.05)^2}{1-0.05} = \frac{0.01\times0.025}{0.95} = \frac{0.000025}{0.95} = 2.63\times10^{-5}$$

9. Which of 0.1M HCl and 0.1 M KCl do you expect to have greater Λ^o_m and why?

0.1 M HCl will have greater Λ^o_m because, H^+ (aq) being smaller in size than Na^+(aq) and have greater mobility.

10. Arrange the following solutions in the decreasing order of specific conductance.

i) 0.01M KCl ii) 0.005M KCl iii) 0.1M KCl iv) 0.25 M KCl v) 0.5 M KCl

0.5 M KCl > 0.25 M KCl > 0.1M KCl > 0.01M KCl > 0.005M KCl

Conductivity changes with the concentrationof the electrolyte. The number of ions per unit volume carrying the current decreases on dilution, so conductivity always decreases with decrease in concentration. Hence the number of ions per unit volume that carry charge in a solution decreases

11. Why is AC current used instead of DC in measuring the electrolytic conductance?

Using DC causes polarisation of the electrodes and electrolyte which leads to error in measured conductance values over a period of time. In AC there is no polarisation due to non-continuous flow of current, hence,AC is used

12. 0.1M NaCl solution is placed in two different cells having cell constant 0.5 and 0.25cm^{-1} respectively. Which of the two will have greater value of specific conductance.

So the cell with higher cell constant has greater value of specific conductance i. e 0.5 cm^{-1} .

$\frac{1}{\rho}$ is called specific conductance which is directly proportional to the cell constant .

13. A current of 1.608A is passed through 250 mL of 0.5M solution of copper sulphate for 50 minutes. Calculate the strength of Cu^{2+} after electrolysis assuming volume to be constant and the current efficiency is 100%.

V= 250 mL , (η) efficiency is 100% Q = I x t

Q= 1.608 x 50 x 60= 4824 C

Number of faraday's of electricity= $\frac{4824}{96500}=0.5F$

Electrolysis of $CuSO_4$: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$, 1 mole of Cu^{2+} = 2F

At 0.5 F electricity will deposit = $\frac{1\text{mol}}{2F}$ x 0.5 = 0.025 mol

before number of molar of Cu^{2+} in 250 ml of solution = $\frac{0.5}{1000}\times 250 = 0.125\text{mol}$

Number of molar of Cu^{2+} after electrolysis = 0.125 - 0.025 = 0.1 mol

Conc of Cu^{2+} = $\frac{0.1\text{mol}}{250\text{ mL}}\times 1000 = 0.4\text{ M}$

14. Can Fe^{3+} oxidises bromide to bromine under standard conditions?

Given: $E^o_{Fe^{3+}/Fe^{2+}}$ = 0.771 $E^o_{Br_2/Br^-}$ = -1.09 V

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ (oxidation)

$Br^- \rightarrow \frac{1}{2}Br_2 + e^-$ (reduction)

Net reaction : $Fe^{3+} + Br^- \rightarrow Fe^{2+} + \frac{1}{2}Br_2$ E^o_{cell} = -1.09 V+ 0.771 = - 0.319 V

E^o_{cell} value is negative the reaction is not feasible , So Fe^{3+} will not oxidize Br^- to Br_2.

15. Is it possible to store copper sulphate in an iron vessel for a long time?

$E_{Cu2+/Cu}$ = 0.34V and E V $_{Fe2+ /Fe}$ = -0.44 .

No we can't store copper sulphate in an iron vessel. Iron is more reactive than copper and it will displace copper from its sulphate solution. No,we can't store $CuSO_4$ solution in an iron vessel.Because iron is more reactive than copper.

16. Two metals M_1 and M_2 have reduction potential values of -*x*V and +yV respectively.Which will liberate H_2 and H_2SO_4.

$M_1^+ + e^- \rightarrow M_1$ E°= -0.76V

$M_2 + e^- \rightarrow M_2$ E°= +0.80V.

The first metal has a negative reduction potential and so more reactive than Hydrogen, whose reduction potential is given as

$H^+ + e^- \rightarrow \frac{1}{2}H_2$ E°= 0.00V.

So the metal with negative reduction potential will liberate H_2- gas from Dil. H_2SO_4. Here the metal with electrode potential of - 0.76V, is Zinc and with + 0.80 V is Silver.Zinc will liberate Hydrogen gas from dilute H_2SO_4 and Silver will not

17. Reduction potential of two metals M_1 and M_2 are $E^o_{M12+ /M1}$ = - 2.3 V and $E^o_{M2^{2+} /M2}$ = 0.2 V Predict which one is better for coating the surface of iron. Given : $E^o_{Fe2+ /Fe}$ = -0.44 V

M_1 is more positive oxidation potential than the oxidation potential of Fe which due to indicates that it will better for coating the surface of iron.

18. Calculate the standard emf of the cell:Cd /Cd^{2+} || Cu^+ / Cu (s),and determine the cell reaction.The standard reduction potentials of Cu^{2+} / Cu and Cd^{2+}/ Cd are 0.34V and -0.40 volts respectively. Predict the feasibility of the cell reaction.

$Cd (s) \rightarrow Cd^{2+}_{(aq)} + 2 e-$ oxidation $E^o_{cd /cd2+}$ = - 0.40 V

$Cu^{2+}_{(aq)} + 2 e- \rightarrow Cu(s)$ reduction $E^o_{Cu2+ /Cu}$ = 0.34 V

$Cd (s) + Cu^{2+} \rightarrow Cd^{2+}_{(aq)} + Cu(s)$

$E^o_{cell} = E^o_{Cu2+ /Cu} - E^o_{cd /cd2+}$ E^o_{cell} = =0.34 - (-0.40) = 0.74 V

E^o_{cell} is + ve , But ΔG i s - ve so the reaction is feasible

19. In fuel cell H_2 and O_2 react to produce electricity. In the process, H_2 gas is oxidised at the anode and O_2 at cathode. If 44.8 litre of H_2 at 25°C and 1atm pressure reacts in 10 minutes, what is average current produced? If the entire current is used for electro deposition of Cu from Cu^{2+} , how many grams of Cu deposited?

Oxidation of anode : $2H_2 (g) + 4OH^-_{(aq)} \rightarrow 4H_2O + 4e^-$

1 mole of H_2 gas = 2 moles of electron at 25°C , 1 atm

1 mole of H_2 gas = 22.4 liters

no of moles of H_2 gas produced = $\frac{1 \text{ mole}}{22.4 \text{ lits}}$ x 44.8 litre = 2 moles of H_2 gas

2 moles of H_2 gas = 4 moles of electron at 25°C , 1 atm = 4F

Q = I x t $I=\frac{Q}{t}=\frac{4\times96500}{10\times60}=643.3A$ $Cu^{2+}_{(aq)}+2e^-\rightarrow Cu(s)$, 1 mole of Cu^{2+} = 63.5 g

The fuel cell entire current is used for electro deposition of Cu from Cu^{2+} is 4F is used for electrolysis = 2 x 63.5 g = 127 g Cu deposited

20. The same amount of electricity was passed through two separate electrolytic cells containing solutions of nickel nitrate and chromium nitrate respectively. If 2.935 g of Ni was deposited in the first cell. The amount of Cr deposited in the another cell? Give : molar mass of Nickel and chromium are 58.74 and 52 gm^{-1} respectively.

Molar mass of Nickel= 58.74 and Molar mass of Chromium = 52 gm^{-1}

$$\frac{m_{Ni}}{m_{Cr}}=\frac{Z_{Ni}}{Z_{Cr}}$$

(Z) $\text{equivalent weight of Cr}=\frac{52}{3}=17.33$ and (Z) $\text{equivalent weight of } Ni=\frac{58.84}{2}=29.35$

$$\frac{2.935}{m_{Cr}}=\frac{29.35}{17.33} \qquad m_{Cr}=\frac{2.935\times17.33}{29.35}=1.733g$$

21. A copper electrode is dipped in 0.1M copper sulphate solution at 25°C.Calculate the electrodepotential of copper. [Given: $E^o_{Cu2+/Cu}$ **= 0..34 V]**

$Cu^{2+}+2e^-\rightarrow Cu$ $$E^o_{red}=E^o_{red}-\frac{0.0591}{n_{cell}}\log\frac{[P]}{[R]} \qquad E^o_{red}=0.34-\frac{0.0591}{2}\log\frac{[Cu]}{[Cu^{2+}]}$$

$$E^o_{red}=0.34-\frac{0.0591}{2}\log\frac{1}{0.1} \qquad E^o_{red}=0.34-0.03=0.31\text{ V}$$

22. For the cell Mg (s) /Mg^{2+}(aq) || Ag^+ (aq)/ Ag (s), calculate the equilibrium constant at 25°C and maximum work that can be obtained during operation of cell. Given :

$E^o_{Mg2+/Mg}$ = - 2.37 V and $E^o_{Ag2+/Ag}$ = 0.80V

Soln:

E^o_{Cell} = + 0.80 - (- 2.37 V) = 3.17 V

$\Delta_rG^o = -nFE^o$, $\Delta_rG^o = -2\times96500\times3.17$

Δ_rG^o = - 611810 CV = - 611810 J

Calculate the value of equilibrium constant.

$\Delta_rG^o = -2.303\times RT\times\log K_c$ $\log K_c=\frac{-\Delta_rG^o}{2.303RT}$

$\log K_c=(-)\frac{(-611810\text{ J})}{2.303\times(8.314\text{ JK}^{-1})\times(298\text{ K})}$ $\log K_c = 107.2250$

K_c = Antilog (107.2250) = ? **$K_c = 1.679\times10^{107}$**

23. **8. 2 x10¹² litres of water is available in a lake. A power reactor using the electrolysis of water in the lake produces electricity at the rate of 2 ×10⁶ Cs⁻¹ at an appropriate voltage. How many years would it like to completely electrolyse the water in the lake. Assume that there is no loss of water except due to electrolysis.**

At anode : $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

At cathode : $2 \times (2H_2O + 2e^- \rightarrow H_2 + 2OH^-)$

Net reaction : $6H_2O \rightarrow 4H^+ + 2H_2 + 4OH^- + O_2$

4 Faraday ⇒ 2 mole of H_2O = 36 g = 36 mL

density of water = 1000 g/lit

Volume of water in lake = 8.2×10^{12} litres

$$\text{volume of water} = \frac{36}{1000} = 3\times10^{-3}$$

$$1\text{mL of } H_2O = \frac{4\times96500}{36} \text{ faraday}$$

Electrolysis of water in the lake produces electricity at the rate of 2 ×10⁶ Cs⁻¹

$$t = \frac{4\times 96500\times 8.2 \times10^{12}}{36\times10^{-3}\times2\times10^{6}} = \frac{3165200 \times10^{12}}{72\times10^{3}} = 43961\times10^{9} \text{ sec}$$

Number of years required completely electrolyse the water in the lake

(Number of years required) $t = \dfrac{43961\times10^{9} \text{ sec}}{31.5\times10^{6}} = 1.3955\times10^{6}$ years

24. **Derive an expression for Nernst equation (refer text book)**

25. **Write a note on sacrificial protection.**

Sacrificial protection is the protection of iron or steel against corrosion by using a more reactive metal. Pieces of zinc or magnesium alloy are attached to pump bodies and pipes. The protected metal becomes the cathode and does not corrode. The anode corrodes, thereby providing the desired sacrificial protection.

26. **Explain the function of H_2 - O_2 fuel cell.(refer text book)**

27. **Ionic conductances at infinite dilution of Al^{3+} and SO_4^{2-} are 189 ohm⁻¹ cm² gm.equiv.⁻¹ and 160 ohm⁻¹ cm² gm.equiv.⁻¹. Calculate equivalent and molar conductance of the electrolyte at infinite dilution.**

Al^{3+} = 189 ohm⁻¹ cm² gm.equiv.⁻¹

SO_4^{2-} = 160 ohm⁻¹ cm² gm.equiv.⁻¹

$$\Lambda_{eq}\, Al_2(SO_4)_3 \longrightarrow \frac{1}{3} Al^{3+} + \frac{1}{2} SO_4^{2-}$$

Equivalent conductance

$$\Lambda_m\ Al_2(SO_4)_3 = 2\times189 + 3\times160 = 63 + 80 = 858 \text{ mho cm}^2 \text{ mol}^{-1}$$

Molar conductance

$$\Lambda_{eq}\ Al_2(SO_4)_3 = \frac{189}{3} + \frac{160}{2} = 63 + 80 = 143 \text{ mho cm}^2 \text{ gm.equi}^{-1}$$

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Unit-10

SURFACE CHEMISTRY

1. Give two important characteristics of physiscorption

(i) It is reversible.

(ii) It takes place at low temperature and decreases with increase in temperature.

(iii) It forms multimolecular layer.

2. Differentiate physisorption and chemisorption

physisorption	chemisorption
1. It is instantaneous	1. It is very slow
2. It is non-specific	2. It is very specific depends on nature of adsorbent and adsorbate.
3. Heat of adsorption is low in the order of 40kJ/mole.	3. Heat of adsorption is high i.e., from 40-400kJ/mole.
4. Multilayer of the adsorbate is formed on the adsorbent.	4. Monolayer of the adsorbate is formed.
5. It occurs on all sides.	5. Adsorption occurs at fixed sites called active centres. It depends on surface area

3. **In case of chemisorption, why adsorption first increases and then decreases with temperature?**

Chemisorption involves a high activation energy,so also reffered to as activated adsorption.It is found in chemisorption that it first increases and than decreases

4. Which will be adsorbed more readily on the surface of charcoal and why; NH_3 or CO_2?

Among CO_2 and NH_3, NH3 will be more readily absorbed on the surface of the charcoal. This is because the critical temperature of ammonia gas is quite high than the carbon dioxide

5. Heat of adsorption is greater for chemisorptions than physisorption. Why?

Chemisorption has higher enthalpy (from 40 - 400 kJ) of adsortion because in chemisorption the chemical bonds are much stronger. In adsorbed state the adsorbate is held on the surface of adsorbent by attractive forces (bond).

6. In a coagulation experiment 10 mL of a colloid (X) is mixed with distilled water and 0.1M solution of an electrolyte AB so that the total volume is 20 mL. It was found that all solutions containing more than 6.6 mL of AB coagulate with in 5 minutes. What is the flocculation values of AB for sol (X)?

A minimum of 6.6 mL of AB is required to coagulate the sol .

The moles of AB in the sol is = $\frac{6.6\times0.1}{20}=0.033$

This means that a minimum of 0.033 moles or 0.033×1000=33 milli moles are required for coagulating 1 litre of sol .Therefore , Flocculation value of AB sol = 33 .

7. Peptising agent is added to convert precipitate into colloidal solution. Explain with an example.

When peptising agent is added to freshly prepared precipitate, it changes into colloidal sol. It is called peptisation. During peptisation, the precipitate adsorbs one of the ions of the electrolyte on its surface

For example,when we add a small volume of very dilute hydrochloric acid solution(peptizing agent) to a fresh precipitate of aluminum hydroxide

8. What happens when a colloidal sol of $Fe(OH)_3$ and As_2O_3 are mixed?

Mutual coagulation occurs which causes precipitation. This is because $Fe(OH)_3$ is postively charged and As_2S_3 is negatively charged When they are mised, the particles gets neutralised and get precipitated. No new compound is formed.

9. What is the difference between a sol and a gel?

In sol, dispersion medium is liquid and the dispersed phase is solid. In gel, dispersion medium is solid and dispersed phase is liquid

10. Why are lyophillic colloidal sols are more stable than lyophobilc colloidal sol.

In a lyophobic colloids, no attractive force exists between the dispersed phase and dispersion medium. They are less stable and precipitated readily, but not be produced again by just adding the dispersion medium. They themselves undergo coagulation after a span of characteristic life time.They are called irreversible sols

examples: sols of gold, silver, platinum and copper

11. Addition of Alum purifies water. Why?

Purification of drinking water is activated by coagulation of suspended impurities in water using alums containing Al^{3+}

12. What are the factors which influence the adsorption of a gas on a solid?

The adsorption is well understood by considering the various factors affecting it. Qualitatively, the extent of surface adsorption depends on

(i) Nature of adsorbent

(ii) Nature of adsorbate

(iii) Pressure

(iv) Concentration at a given temperature.

13. What are enzymes? Write a brief note on the mechanism of enzyme catalysis.

Enzymes are complex protein molecules with three dimensional structures. They catalyse the chemical reaction in living organism. They are often present in colloidal state and extremely specific in catalytic action.

Mechanism of enzyme catalysed reaction

The following mechanism is proposed for the enzyme catalysis

$$E + S \rightleftharpoons ES \rightarrow P + E$$

Where E is the enzyme, S the substrate (reactant), ES represents activated complex and P the products.

14. What do you mean by activity and selectivity of catalyst?

(a) Activity of a catalyst:

The activity of a catalyst is its ability to increase the rate of a particular reaction. Chemisorption is the main factor in deciding the activity of a catalyst. The adsorption of reactants on the catalyst surface should be neither too strong nor too weak. It should just be strong enough to make the catalyst active.

(b) Selectivity of the catalyst:

The ability of the catalyst to direct a reaction to yield a particular product is referred to as the selectivity of the catalyst. **For example**, by using different catalysts, we can get different products for the reaction between H_2 and CO.

i) $CO_{(g)} + 3H_{2\,(g)} \xrightarrow{Ni} CH_{4\,(g)} + H_2O_{(g)}$ ii) $CO_{(g)} + 2H_{2\,(g)} \xrightarrow{Cu/ZnO-CrO_3} CH_4OH_{(g)}$

iii) $CO_{(g)} + H_{2\,(g)} \xrightarrow{Cu} H\text{-}CHO_{(g)}$

15. Describe some feature of catalysis by Zeolites.

Zeolites are, crystalline, microporous, hydrated alumino silicates, made of silicon and aluminium tetrahedra.

i) There are about 50 natural zeolites and 150synthetic zeolites.

ii) As silicon is tetravalent and aluminium is trivalent, the zeolite matrix carries extra negative charge.

iii) To balance the negative charge, there are extra framework cations for example, H^+ or Na^+ ions.

iv) Zeolites carring protons are used as solid acids, catalysis and they are extensively used in the

v) petrochemical industry for cracking heavy hydrocarbon fractions into gasoline, diesel,etc.,

vi) Zeolites carring Na+ ions are used as basic catalysis.

vii) One of the most important applications of zeolites is their shape selectivity. In zeolites, the active sites namely protons are lying inside their pores. So, reactions occur only inside the pores of zeolites.

16. Give three uses of emulsions.

(i) Cleansing action of soaps is based on the formation of emulsions.

(ii) Digestion of fats in intestines takes place by the process of emulsification.

(iii) Antiseptics and disinfectants when added to water form emulsions.

(iv) The process of emulsification is used to make medicines.

17. Why does bleeding stop by rubbing moist alum

Blood is a colloidal sol. When we rub the injured part with moist alum then coagulation of blood takes place. Hence, main reason is coagulation, which stops the bleeding

18. Why is desorption important for a substance to act as good catalyst?

Desorption is important for a substance to act as a good catalyst so that after the reaction, the products formed on the surface separate out (desorbed) to create free surface again for other reactant molecules.

If desorption does not occur then other reactants are left with no space on the catalyst's surface for adsorption and reaction will stop.

19. Comment on the statement: Colloid is not a substance but it is a state of substance.

Common salt (a typical crystalloid in an aqueous medium) behaves as a colloid in a benzene medium. Hence, we can say that a colloidal substance does not represent a separate class of substances. When the size of the solute particle lies between 1 nm and 1000 nm, it behaves as a colloid.

Hence, we can say that colloid is not a substance but a state of the substance which is dependent on the size of the particle. A colloidal state is intermediate between a true solution and a suspension.

20. Explain any one method for coagulation

Clotting is what prevents excessive bleeding when you cut yourself. But the blood moving through your vessels shouldn't clot. If such clots form, they can travel through your bloodstream to your heart, lungs, or brain. This can cause a heart attack, stroke, or even death.

Coagulation tests measure your blood's ability to clot, and how long it takes to clot. Testing can help your doctor assess your risk of excessive bleeding or developing clots (thrombosis) somewhere in your blood vessels.

21. Write a note on electro osmosis

Electro-osmosis is the migration of water (and whatever is contained in the water) through a porous membrane resulting from a potential difference caused by the flow of electric charge through the membrane.

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22. Write a note on catalytic poison

Thecertain substances when added to a catalysed reaction decreases or completely destroys the activity of catalyst and they are often known as catalytic poisons.

23. Explain intermediate compound formation theory of catalysis with an example

The intermediate compound formation theory

A catalyst acts by providing a new path with low energy of activation. In homogeneous catalysed reactions a catalyst may combine with one or more reactant to form an intermediate

which reacts with other reactant or decompose to give products and the catalyst is regenerated.

Consider the reactions:

$$A + B \rightarrow AB \qquad (1)$$

$$A + C \rightarrow AC \text{ (intermediate)} \qquad (2)$$

C is the catalyst

$$AC + B \rightarrow AB + C \qquad (3)$$

Activation energies for the reactions (2) and (3) are lowered compared to that of (1). Hence the formation and decomposition of the intermediate accelerate the rate of the reaction.

Example

Formation of water due to the reaction of H_2 and O_2 in the presence of Cu can be given as

$$2Cu + \frac{1}{2}O_2 \rightarrow Cu_2O$$

It is an intermediate.

$$Cu_2O + H_2O \rightarrow H_2O + 2Cu$$

24. What is the difference between homogenous and hetrogenous catalysis?

Homogeneous catalysis

In a catalysed reaction, the reactants, products and catalyst are present in the same phase.

Illustration

$$2SO_2 + O_2 + [NO] \rightarrow 2SO_3 + [NO]$$

In this reaction the catalyst NO, reactants, SO_2 and O_2 , and product, SO_3 are present in the gaseous form.

Heterogeneous catalysis

n a reaction, the catalyst is present in a different phase i.e. It is not present in the same phase as that of reactants or products.

Decomposition of H_2O_2 occurs in the presence of the Pt catalyst

$$H_2O_2 \xrightarrow{Pt} H_2O + O_2$$

25. Describe adsorption theory of catalysis.

Adsorption theory

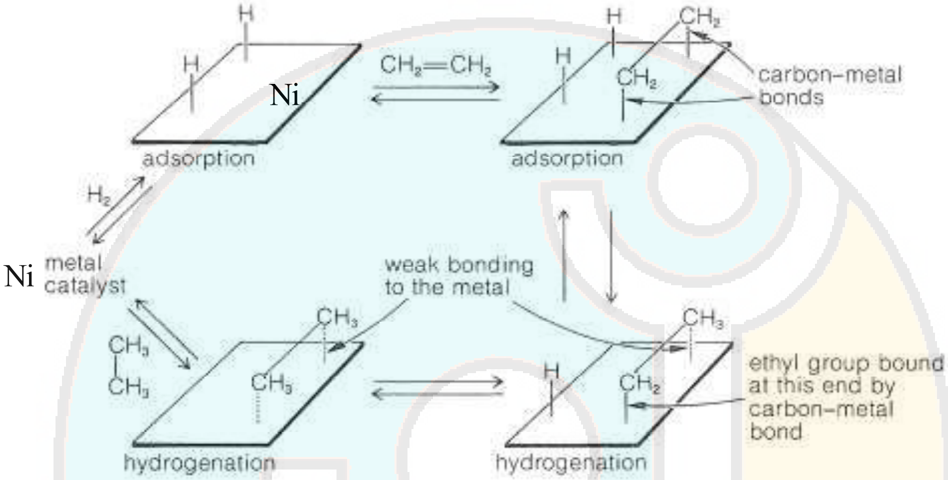
Langmuir explained the action of catalyst in heterogeneous catalysed reactions based on adsorption. The reactant molecules are adsorbed on the catalyst surfaces, so this can also be called as contact catalysis.

According to this theory, the reactants are adsorbed on the catalyst surface to form an activated complex which subsequently decomposes and gives the product.

The various steps involved in a heterogeneous catalysed reaction are given as follows:

1. Reactant molecules diffuse from bulk to the catalyst surface.
2. The reactant molecules are adsorbed on the surface of the catalyst.
3. The adsorbed reactant molecules are activated and form activated complex which is decomposed to form the products.
4. The product molecules are desorbed.
5. The product diffuse away from the surface of the catalyst.

eg) Hydrogenation of ethylene in presence of a nickel catalyst.



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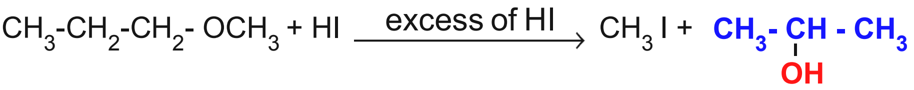
UNIT - 11

HYDROXY COMPOUNDS AND ETHERS

1. **Identify the product (s) is / are formed when 1 – methoxy propane is heated with excess HI. Name the mechanism involved in the reaction**

The carbon-oxygen bond is ethers can be cleaved by heating with HI to form an alcohol and an alkyl halide at 373K.In case of unsymmetrical ethers which contains two different alyl groups,the site of cleavege is such that the halide is formed from the alkyl group which is smaller in size.

Thus the products formed in this case are iodomethane and Propan-2-ol



$$CH_3\text{-}CH_2\text{-}CH_2\text{-}OCH_3 + HI \xrightarrow{\text{excess of HI}} CH_3I + CH_3\text{-}\underset{OH}{\underset{|}{CH}}\text{-}CH_3$$

i) **Name the mechanism involved in the reaction** - S_N1 reaction.

In the presence of conc.HI I think $(CH_3)_2CH\text{-}OH$ changes to $(CH_3)_2CH$ - I. Also since a secondary carbon is present SN_1 mechanism may occur then the products are different (CH_3OH and $(CH_3)_2CH\text{-}I$).

2. **Draw the major product formed when 1-ethoxyprop-1-ene is heated with one equivalent of HI**

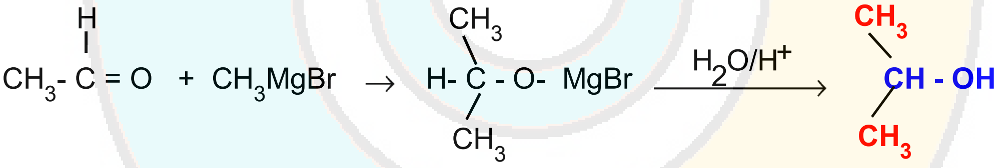
1-Ethoxyprop-1-ene reacts with HI to form iodoethane and prop-1-en-1-ol.

$$C_2H_5\text{-}OCH = CH - CH_3 + HI \xrightarrow{\text{one equivalent of HI}} C_2H_5\text{- I} + HO - CH = CH\text{-} CH_3$$

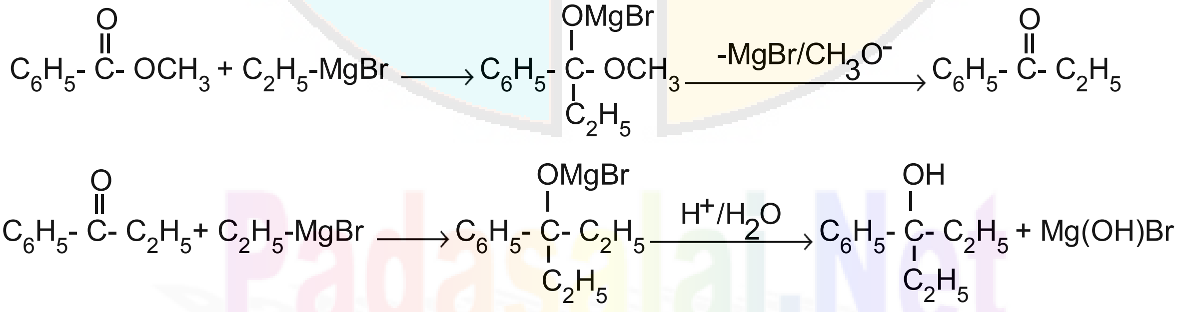
Not easy to break this bond as it is enaged in resonance so

$$HO - CH = CH\text{-} CH_3 \xleftrightarrow{\text{Tautomerism}} O = CH - CH_2\text{-} CH_3 \text{ (aldehyde)}$$

3. **Suggest a suitable reagent to prepare secondary alcohol with identical group using Grignard reagent.**



4. **What is the major product obtained when two moles of ethyl magnesium bromide is treated with methyl benzoate followed by acid hydrolysis.**



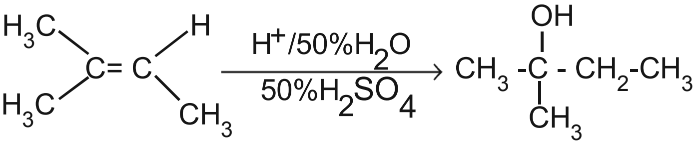
$$C_6H_5\text{-}\overset{O}{\overset{\|}{C}}\text{-} OCH_3 + C_2H_5\text{-}MgBr \longrightarrow C_6H_5\text{-}\overset{OMgBr}{\overset{|}{\underset{C_2H_5}{\underset{|}{C}}}}\text{-} OCH_3 \xrightarrow{\text{-MgBr/}CH_3O^-} C_6H_5\text{-}\overset{O}{\overset{\|}{C}}\text{-} C_2H_5$$

$$C_6H_5\text{-}\overset{O}{\overset{\|}{C}}\text{-} C_2H_5 + C_2H_5\text{-}MgBr \longrightarrow C_6H_5\text{-}\overset{OMgBr}{\overset{|}{\underset{C_2H_5}{\underset{|}{C}}}}\text{-} C_2H_5 \xrightarrow{H^+/H_2O} C_6H_5\text{-}\overset{OH}{\overset{|}{\underset{C_2H_5}{\underset{|}{C}}}}\text{-} C_2H_5 + Mg(OH)Br$$

3-phenyl-pentan-3-ol

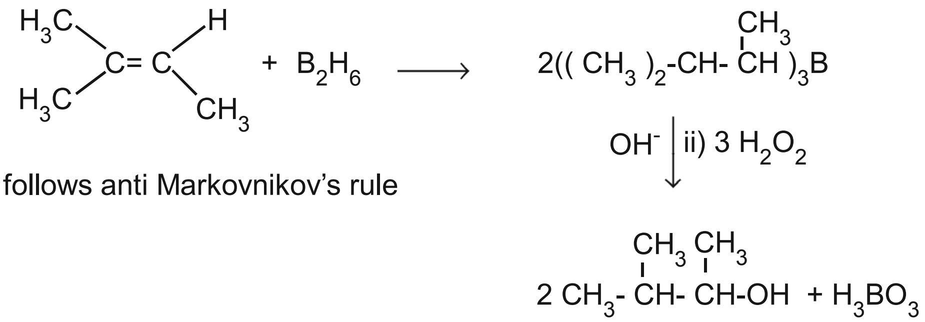
5. **Predict the major product, when 2-methyl but -2-ene is converted into an alcohol in each of the following methods.**
(i.) Acid catalysed hydration (ii.) Hydroboration (iii.) Hydroxylation using bayers reagent

i) 2-methyl but -2-ene is converted into an alcohol in Acid catalysed hydration

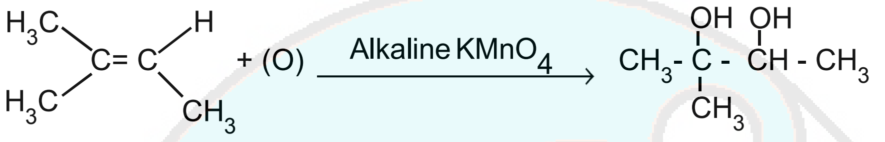


follows Markovnikov's rule 2-Methyl-butan - 2-ol

ii) 2-methyl but -2-ene is converted into an alcohol in Hydroboration



3-Methyl-butan - 2-ol



2-Methyl-butan - 2,3-diol

iii) 2-methyl but -2-ene is converted into an alcohol in Hydroxylation using bayers reagent

6. Arrange the following in the increasing order of their boiling point and give a reason for your ordering

(i) Butan – 2- ol, Butan -1-ol, 2 –methylpropan -2-ol

(ii) Propan -1-ol, propan -1,2,3-triol, propan -1,3 – diol, propan -2-ol

a) Among isomeric alcohols primary alcohols have higher boiling point and the tertiarly alcohols have lower boiling points

b) The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surfacearea).

i) increasing order of their boiling point

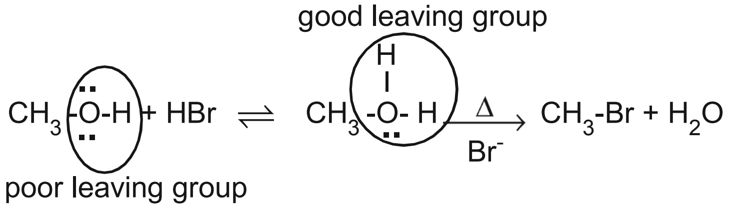
2 –methyl propan -2-ol < Butan – 2- ol < Butan -1-ol

ii) increasing order of their boiling point

propan -2-ol < Propan -1-ol < propan -1,3 – diol < propan -1,2,3-triol

7. Can we use nucelophiles such as NH_3 ,CH_3O^- for the Nucleophilic substitution of alcohols

Because the OH group of the alcohol must be protonated before it can be displaced by a nucleo-phile, only weakly basic nucleophiles (I^-, Br^-, Cl^-) can be used in the substitution reaction.Moderately and strongly basic nucleophiles (NH_3, RNH_2, and CH_3O^-) cannot be used because theytoo would be protonated in the acidic solution and, once protonated, would no longer be nucleo-philes (+ NH_4^+,RNH_3^+) or would be poor nucleophiles (CH_3OH).



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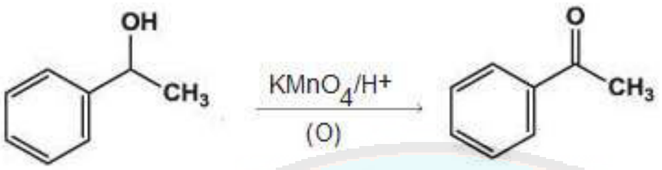
8. **Is it possible to oxidise t- butyl alcohol using acidified dichromate to form a carbonyl compound.**

i) Tertiary alcohol does not allow for their oxidation because of **absence α- hydrogen** atom.

ii) This is why tertiary alcohols are said to be resistant to oxidation

But at elevated temperatures **it possible to oxidise**, under strong oxidising agent like acidified $K_2Cr_2O_7$ / H^+ cleavage of C –C bond takes place to give a mixture of carboxylic acid like formic acid and acetic acid

9. **What happens when 1-phenyl ethanol is treated with acidified $KMnO_4$.**



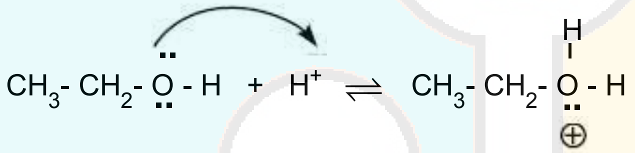
Acetophenone

10. **Write the mechanism of acid catalysed dehydration of ethanol to give ethene.**

The mechanism of acid dehydration of ethanol to yield ethene involves the following three steps:

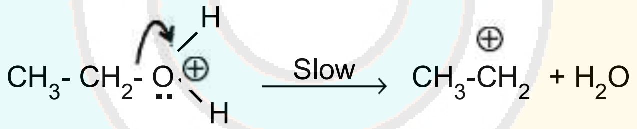
Primary alcohols undergo dehydration by E_2 mechanism

Step 1: Protonation of ethanol to form ethyl oxonium ion:



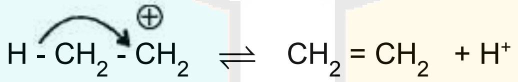
$$CH_3-CH_2-\ddot{\underset{..}{O}}-H + H^+ \rightleftharpoons CH_3-CH_2-\overset{H}{\underset{\oplus}{\underset{..}{O}}}-H$$

Step 2:F ormation of carbocation (rate determining step):



$$CH_3-CH_2-\underset{..}{O}\overset{\oplus}{<}^{H}_{H} \xrightarrow{Slow} CH_3-\overset{\oplus}{CH_2} + H_2O$$

Step 3:Elimination of a proton to form ethene:

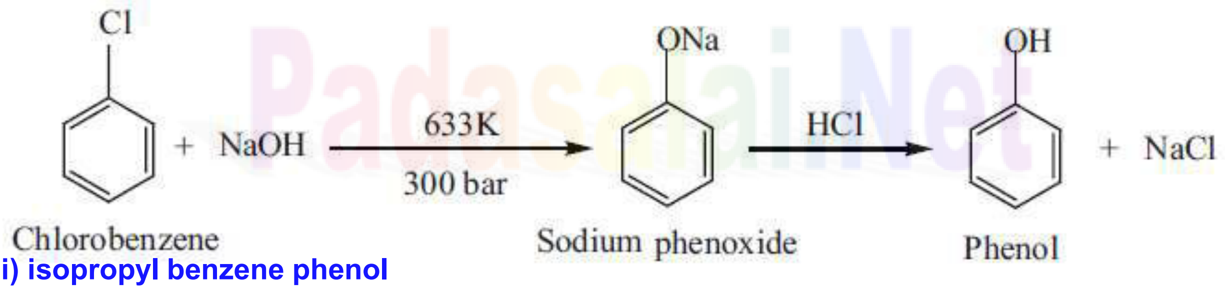


$$H-CH_2-\overset{\oplus}{CH_2} \rightleftharpoons CH_2=CH_2 + H^+$$

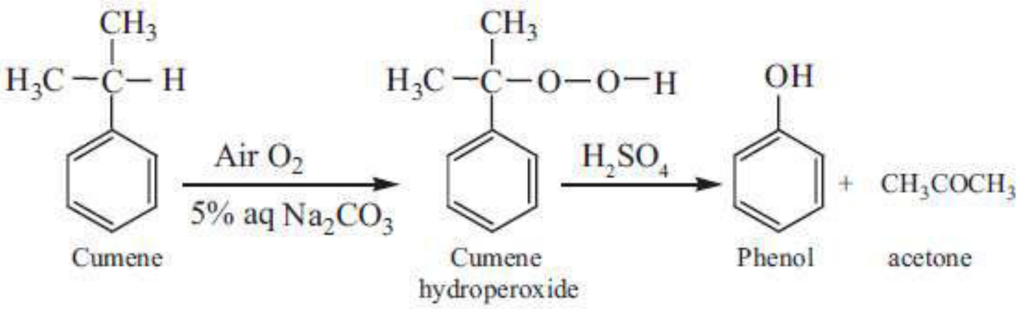
11. **How is phenol prepared form**

i) chloro benzene ii) isopropyl benzene

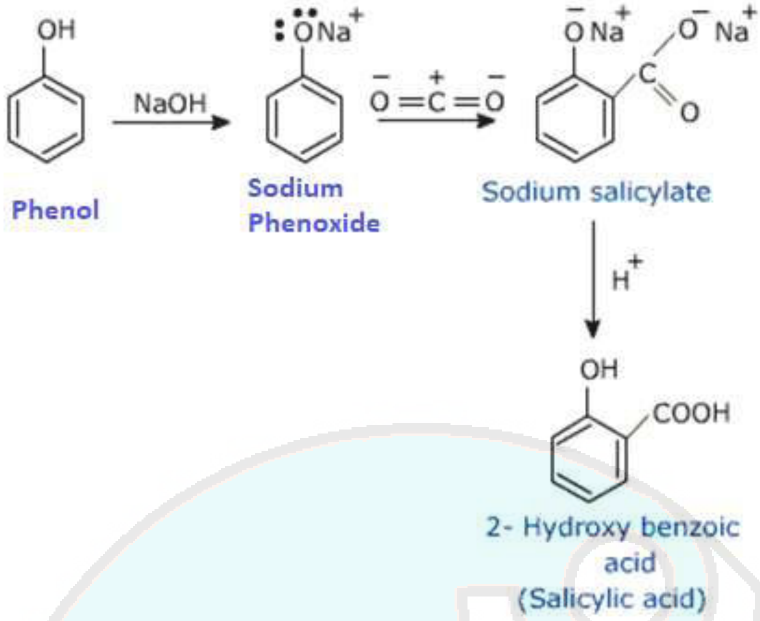
i) chloro benzene to phenol



ii) isopropyl benzene phenol



12. Explain Kolbe's reaction

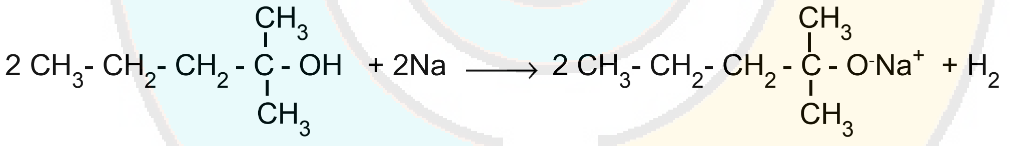


13. Write the chemical equation for Williamson synthesis of 2-ethoxy – 2- methyl pentane starting from ethanol and 2 – methyl pentan -2-ol

Step 1 : alcohol into alkylhalide

$$CH_3 - CH_2 - OH + HBr \xrightarrow{\Delta} CH_3 - CH_2 - Br + H_2O$$

Step 2 : 2 – methyl pentan -2-ol into sodium alkoxide

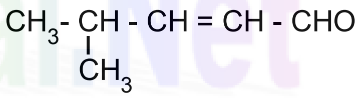

$$2\,CH_3 - CH_2 - CH_2 - \underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} - OH + 2Na \longrightarrow 2\,CH_3 - CH_2 - CH_2 - \underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} - O^-Na^+ + H_2$$

Step 3 : sodium alkoxide into 2-ethoxy – 2- methyl pentane

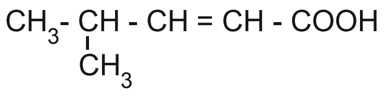

$$CH_3 - CH_2 - CH_2 - \underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} - O^-Na^+ + CH_3 - CH_2Br \longrightarrow CH_3 - CH_2 - CH_2 - \underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} - OCH_2 - CH_3 + NaBr$$

14. Write the structure of the aldehyde, carboxylic acid and ester that yield 4- methylpent-2-en-1-ol.

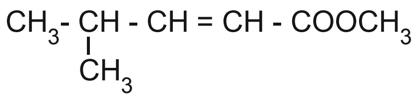
i) aldehyde yield 4- methylpent-2-en-1-ol


$$CH_3 - \underset{CH_3}{\underset{|}{CH}} - CH = CH - CHO$$

ii) carboxylic acid yield 4- methylpent-2-en-1-ol


$$CH_3 - \underset{CH_3}{\underset{|}{CH}} - CH = CH - COOH$$

iii) ester yield 4- methylpent-2-en-1-ol


$$CH_3 - \underset{CH_3}{\underset{|}{CH}} - CH = CH - COOCH_3$$

aldehyde, carboxylic acid and ester undergoes reduction that yield 4- methylpent-2-en-1-ol

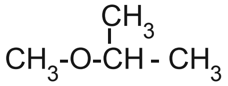

$$CH_3 - \underset{CH_3}{\underset{|}{CH}} - CH = CH - CH_2OH$$

15. What is metamerism? Give the structure and IUPAC name of metamers of 2-methyoxy propane

Metamerism :

It is a special isomerism in which molecules with same formula, same functional group, differing only in the nature of the alkyl group attached to oxygen.

For example an ether having molecular formula $C_4H_{10}O$ exhibits following **metamers**

	Comman Name	**IUPAC name**
 $CH_3-O-\overset{\displaystyle CH_3}{\overset{\vert}{C}H}-CH_3$	Methyl isopropyl ether	2- methoxy propane
$CH_3CH_2-O-CH_2CH_3$	dietyl ether	ethoxy ethane
$CH_3-O-CH_2CH_2CH_3$	methyl propyl ether	1 - methoxy propane

Ethoxy ethane and 1 - methoxy propane are metamers 2- methoxy propane

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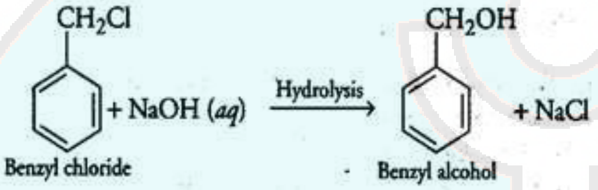
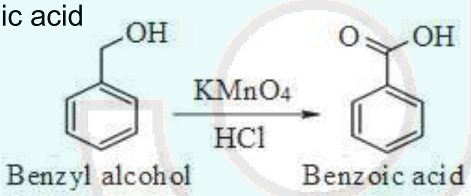
16. How are the following conversions effected

i) benzylchloride to benzylalcohol ii) benzyl alcohol to benzoic acid

i) benzylchloride to benzylalcohol :



ii) benzyl alcohol to benzoic acid



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17. Complete the following reactions

i) $CH_3-CH_2-OH \xrightarrow{PBr_3} A \xrightarrow{(aq)NaOH} B \xrightarrow{Na} C$

$$\mathbf{CH_3-CH_2-OH \xrightarrow{PBr_3} CH_3-CH_2-Br \xrightarrow{(aq)NaOH} CH_3-CH_2-OH \xrightarrow{Na} CH_3-CH_2-ONa + \frac{1}{2}H_2}$$

A - ethyl bromide **B - ethanol** **C - Sodium ethoxide**

---

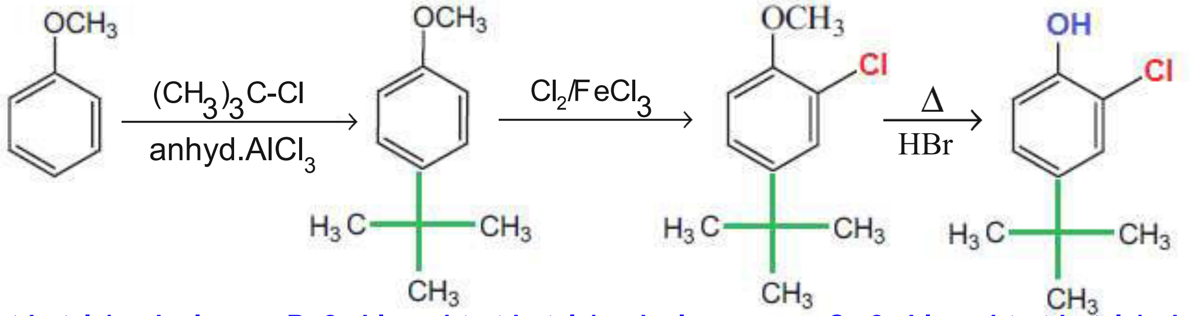
i) $C_6H_5-OH \xrightarrow{Zn} A \xrightarrow{CH_3Cl/anhydrous\ AlCl_3} B \xrightarrow{KMnO_4/H^+} C$

$$\mathbf{C_6H_5-OH \xrightarrow{Zn} C_6H_6 \xrightarrow{CH_3Cl} C_6H_5-CH_3 \xrightarrow{KMnO_4/H^+} C_6H_5-COOH}$$

A - benzene **B - Toluene** **C - Benzoic acid**

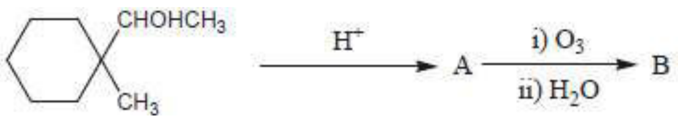
---

iii) Anisole $\xrightarrow{t\text{-}butylchloride/AlCl_3} A \xrightarrow{Cl_2/FeCl_3} B \xrightarrow{HBr} C$

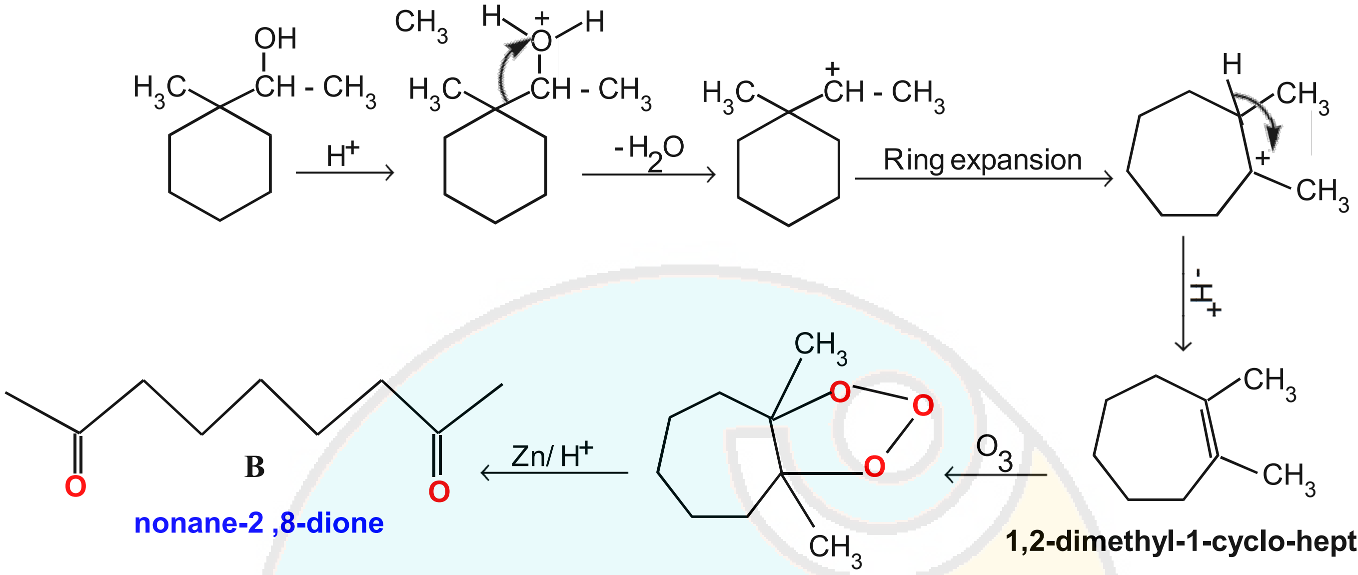


A - 4-tert-butyl-1-anisole **B - 2-chloro-4-tert-butyl-1-anisole** **C - 2-chloro-4-tert-butyl-1-phenol**

iv)



1-(1-methyl-cyclohexyl)-ethanol to nonane-2,8 -dione



B

nonane-2 ,8-dione

1,2-dimethyl-1-cyclo-heptene

A

18. 0.44g of a monohydric alcohol when added to methyl magnesium iodide in ether liberates at STP 112 cm^3 of methane with PCC the same alcohol form a carbonyl compound that answers silver mirror test. Identify the compound.

$$\text{Monohydric alcohol} + CH_3MgI \xrightarrow{\text{Ethers}} CH_4$$

$$\text{Monohydric alcohol} \xrightarrow{\text{PCC}} \text{Carbonyl compound} \longrightarrow \text{+ ve silver mirror test}$$

Monohydric alcohol means a alcohol which contains one hydroxyl group.PCC is an oxidising agent which convert alcohols to aldehyde or ketones. Aldehydes show silver mirror test not ketones. So, aldehyde is formed and primary alcohols give aldehyde on oxidation. Secondary alcohols give ketones.Consider the formula of monohydric alcohol is **$C_nH_{2n+1}OH$**. Alcohols react with grignard reagent form alkyl magnesium halide with the evolution of alkane.

$$CnH_{2n+1}OH + CH_3MgI \longrightarrow CH_4 + C_nH_{2n+1}OMgI$$

112 cm^3 of methane is produced from 0.44 g of alcohol

22400 cm3 of methane is produced from = $\frac{22400 \times 0.44}{112} = 88$ g

This is the molar mass of alcohol as 1 mole of alcohol which is equivalent to molar mass produces 22400 cm^3 of gas at STP.

Molar mass of alcohol = 81 g

Subtract the mass of hydroxyl group from it = 88 - (16 + 1) = 71 g

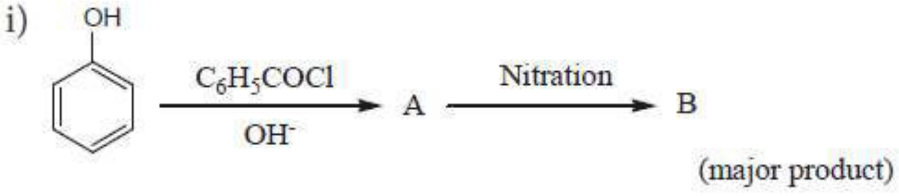
C_nH_{2n+1} = 71 g

Number of carbon can be possible with this molar mass is 5 which comprises mass 60 g and the rest mass is the mass of hydrogen.

So, the formula of alcohol is $C_5H_{11}OH$.

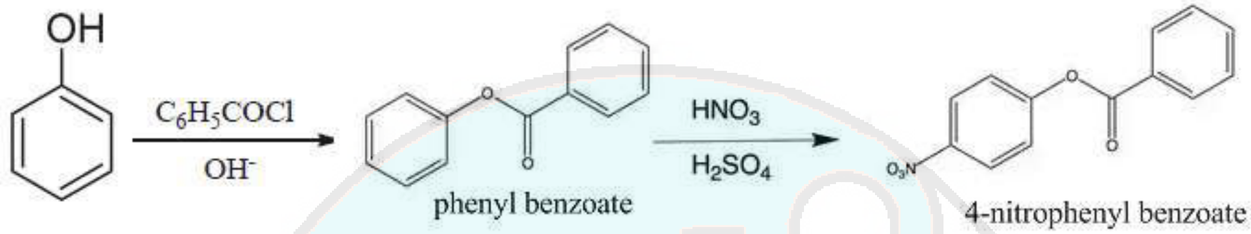
19. Complete the following reactions

i)



ii) $C_6H_5\text{-CHCH(OH)CH(CH}_3)_2 \xrightarrow{ConH_2SO_4}$

i) Phenol on treatment with acid chlorides gives esters.The acetylation and benzoylation of phenol are called **Schotten-Baumann reaction.**



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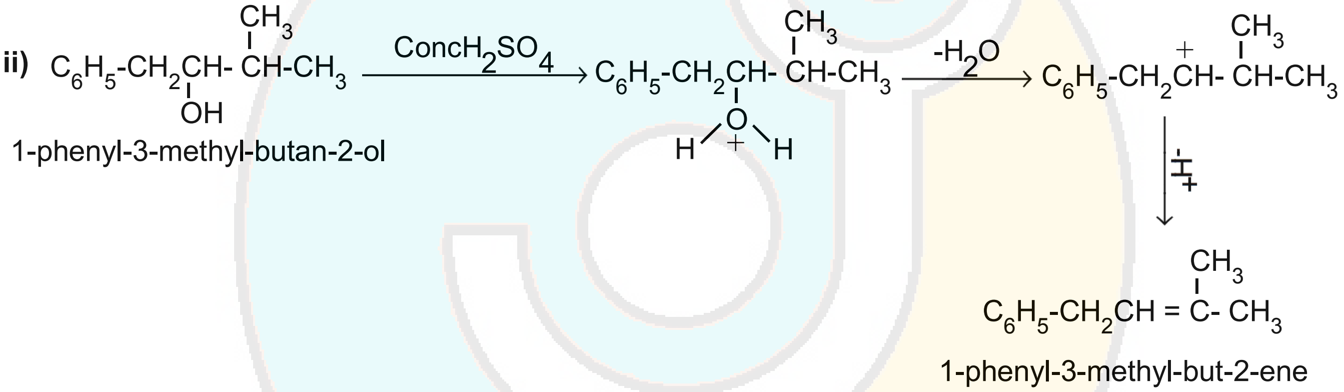
ii)



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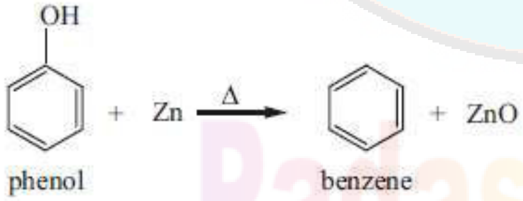
20. Phenol is distilled with Zn dust followed by friedel – crafts alkylation with propyl chloride to give a compound B, B on oxidation gives (c) Identify A,B and C.

i) Phenol to benzene

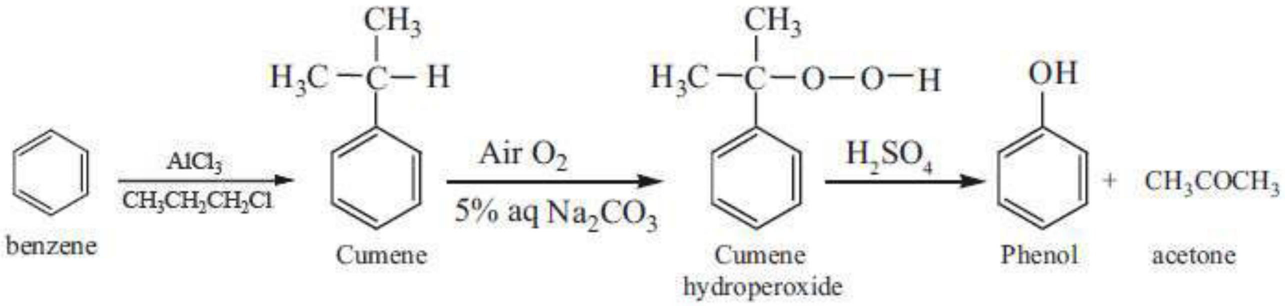


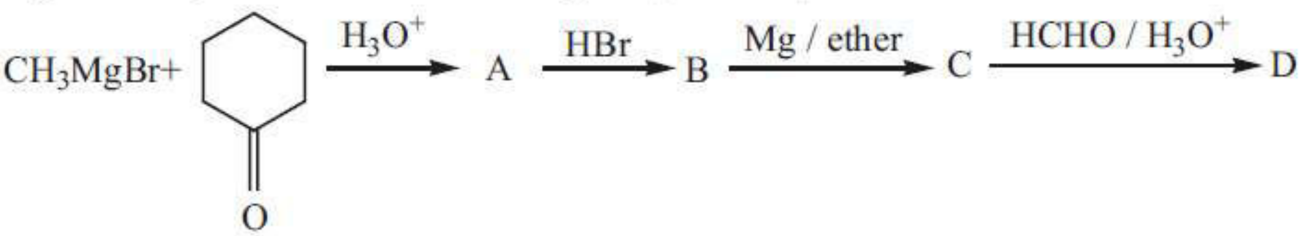
A- benzene

B- Cumene

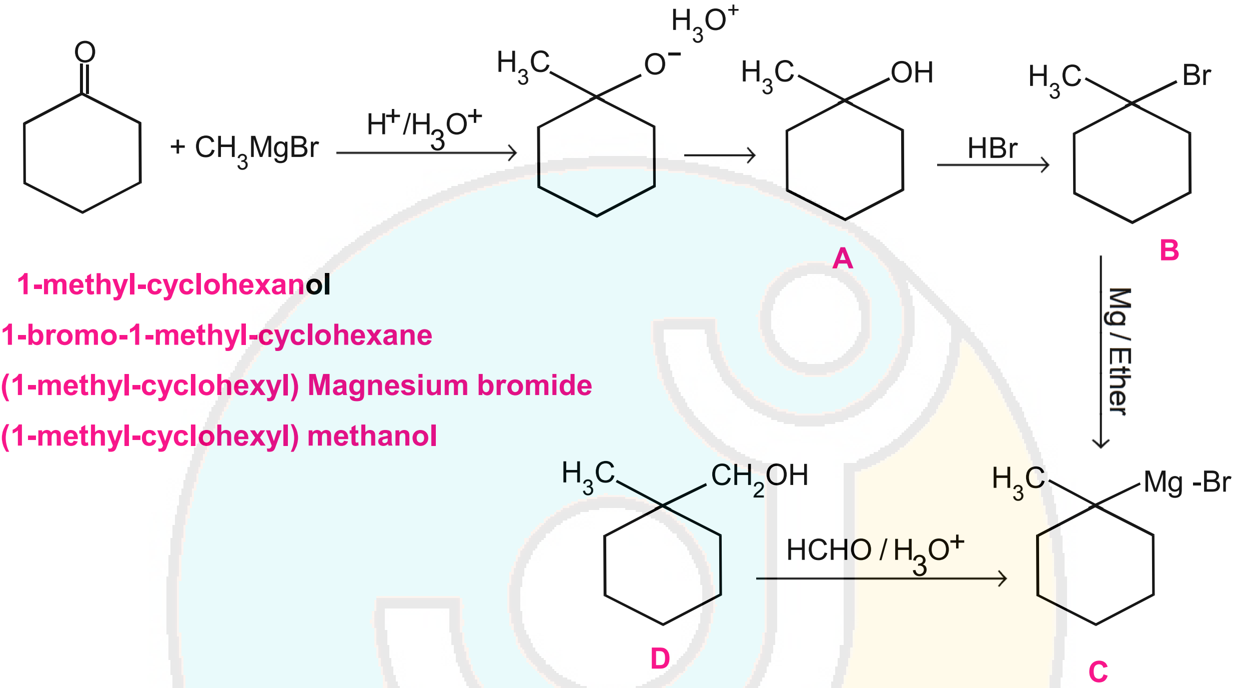
C- Cumene hydro peroxide

ii) benzene to phenol



21. 

Identify A,B,C,D and write the complete equation



A- 1-methyl-cyclohexanol

B-1-bromo-1-methyl-cyclohexane

C-(1-methyl-cyclohexyl) Magnesium bromide

D-(1-methyl-cyclohexyl) methanol

---

22. What will be the product (X and A)for the following reaction

acetylchloride $\xrightarrow[\text{ii) } H_3O^+]{\text{i) } CH_3MgBr} X \xrightarrow{\text{acid } K_2Cr_2O_7} A$

$CH_3\text{-}COCl \xrightarrow[\text{ii) } H_3O^+]{\text{i) } CH_3MgBr} CH_3\text{-}COCH_3 \xrightarrow{\text{acid } K_2Cr_2O_7} CH_3\text{-}COOH + H\text{-}COOH$

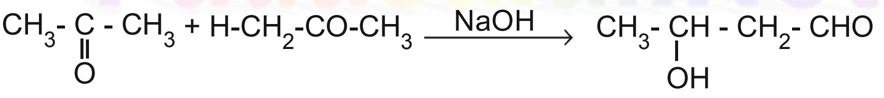
X - Acetone **A- Acetic acid**

---

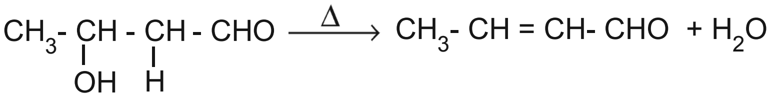
23. How will you convert acetylene into n-butyl alcohol.

step -1 : $H\text{-}C\equiv C\text{-}H \xrightarrow{42\%\, H_2SO_4 \,/\, 1\%Hg^{2+}} CH_3\text{-}COCH_3$

Aldol condesation

step-2 : 

$CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3 + H\text{-}CH_2\text{-}CO\text{-}CH_3 \xrightarrow{NaOH} CH_3\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CH_2\text{-}CHO$ **aldol**

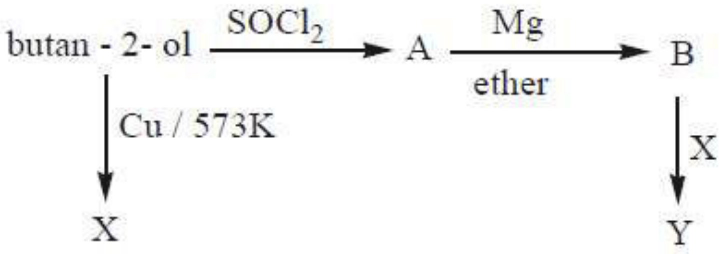
step- 3 : 

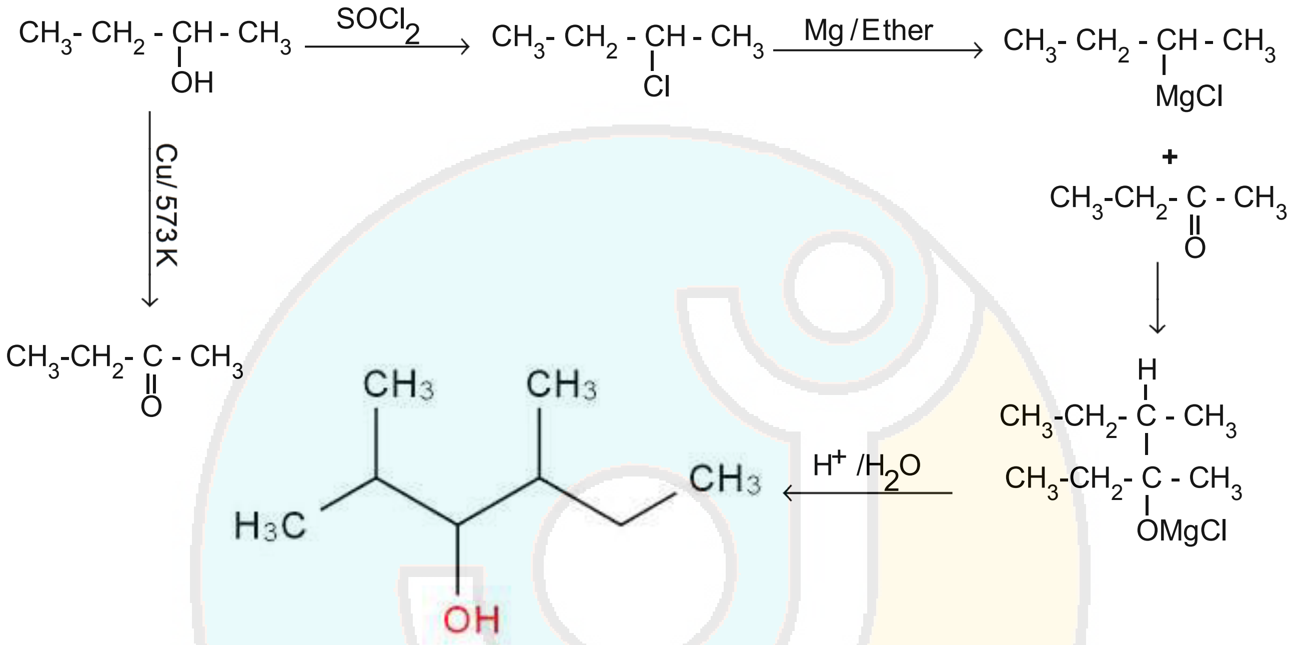
$CH_3\text{-}\underset{\underset{OH}{|}}{CH}\text{-}\underset{\underset{H}{|}}{CH}\text{-}CHO \xrightarrow{\Delta} CH_3\text{-}CH=CH\text{-}CHO + H_2O$

step-4 Reduction of crotonaldehyde to n-butyl alcohol.

$CH_3\text{-}CH=CH\text{-}CHO \xrightarrow{H_2/Ni} CH_3\text{-}CH_2\,CH_2\text{-}COOH$

24. **Predict the product A,B,X and Y in the following sequence of reaction**



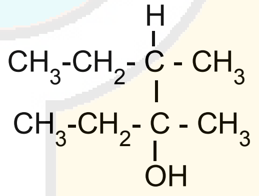


Compound- A : 2- chloro - butane

Compound- B : 2- butanone

Compound- X : 2- butanone

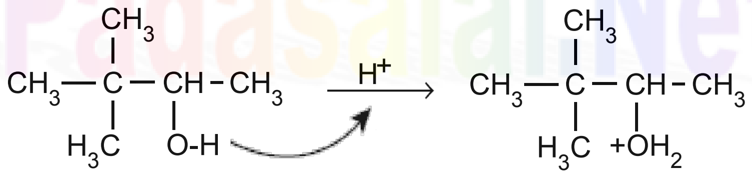
Compound- Y : 3, 4-dimethyl-hexan-3-ol



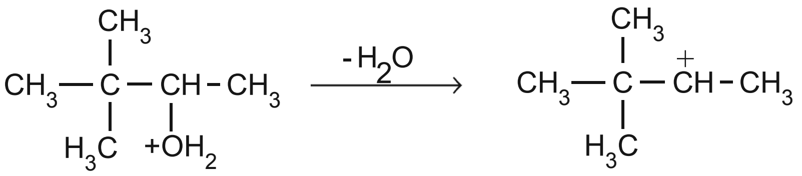
25. **3,3 – dimethylbutan-2-ol on treatment with conc. H_2SO_4 to give tetramethyl ethylene as a major product. Suggest a suitable mechanism**

The mechanism is as follows:

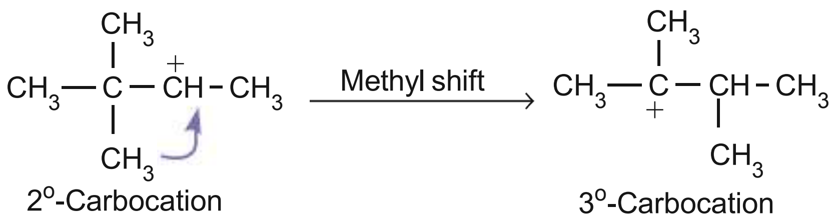
Step-1: protonation of 3,3-dimethylbutan-2-ol



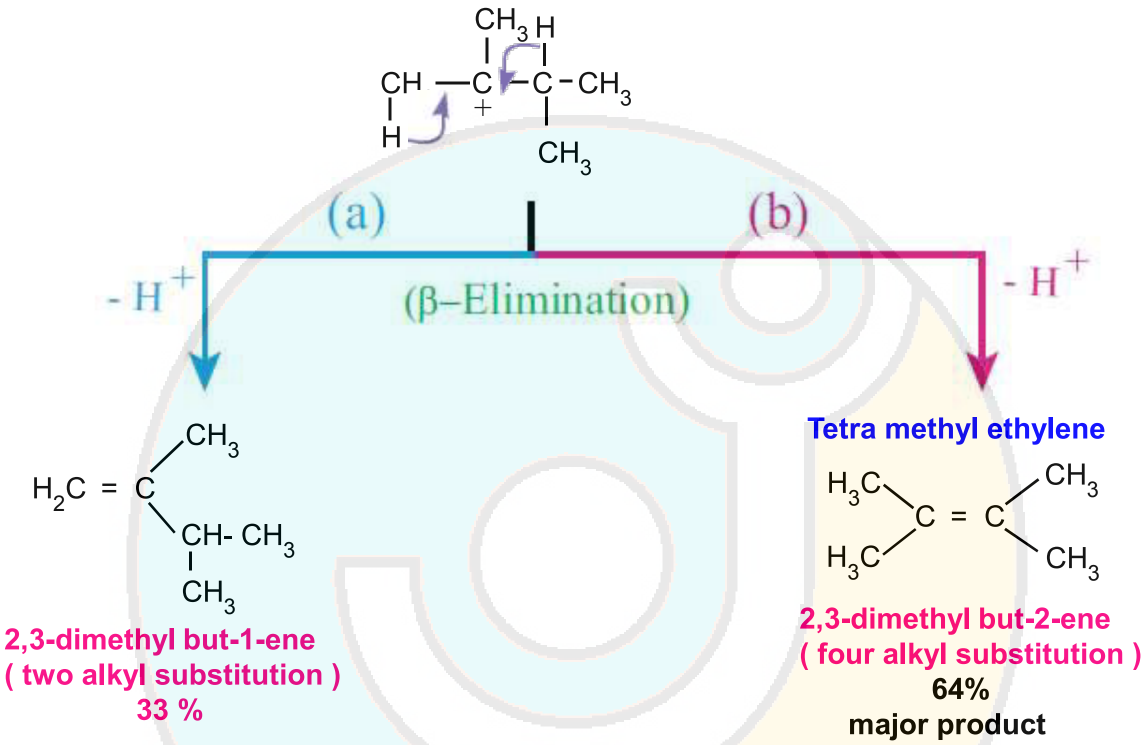
2) Removal of a water molecule from the carbonium ion formed above



3) Conversion of 2 degree carbonium to 3 degree carbonium by methyl shift:



4) Removal of H^+ ion to form a double bond:



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CARBONYL COMPOUNDS AND CARBOXYLIC ACIDS

1. How is propanoic acid is prepared starting from
(a) an alcohol (b) an alkylhalide (c) an alkene

a) An Alcohol converted in to propanoic acid

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}OH \xrightarrow{\text{Alkaline } KMnO_4} CH_3\text{-}CH_2\text{-}COOH$$

b) An alkyl halide converted in to propanoic acid

$$CH_3\text{-}CH_2\text{-}Cl \xrightarrow[\text{- KCl}]{\text{KCN/aq ethanol}} CH_3\text{-}CH_2\text{-}CN \xrightarrow[\text{Hydrolysis}]{H^+/H_2O} CH_3\text{-}CH_2\text{-}COOH$$

c) An alkene converted in to propanoic acid

$$CH_3\text{-}CH=CH_2 \xrightarrow{HBr/H_2O_2} CH_3\text{-}CH_2\text{-}CH_2Br \xrightarrow{\text{aq KOH}} CH_3\text{-}CH_2\text{-}CH_2OH$$

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}OH \xrightarrow{\text{Alkaline } KMnO_4} CH_3\text{-}CH_2\text{-}COOH$$

---

2. A Compound (A) with molecular formula C_2H_3N on acid hydrolysis gives(B) which reacts with thionylchloride to give compound(C). Benzene reacts with compound (C) in presence of anhydrous $AlCl_3$ to give compound(D). Compound (D) on reduction with gives (E). Identify (A), (B), (C) and D, E Write the equations.

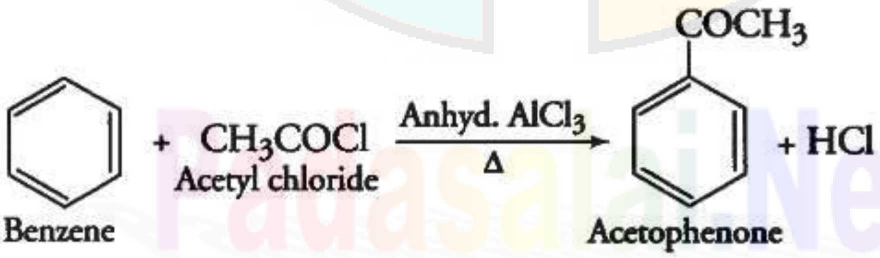
Compound(A) is nitrile (CH_3CN)

$$CH_3\text{- }CN + 2H_2O \xrightarrow{\text{dilute } HCl/H^+} CH_3\text{-}COOH \text{ (compound - B)}$$

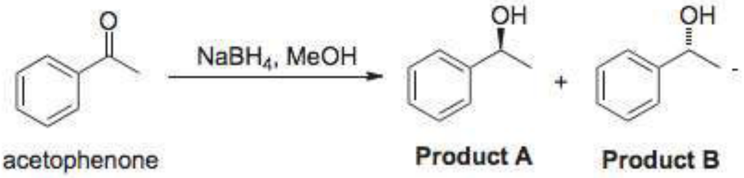
Compound (B) gives Compound (C)

$$CH_3\text{-}COOH + SOCl_2 \longrightarrow CH_3\text{-}COCl + SO_2 + HCl$$

Compound (C) gives Compound (D)

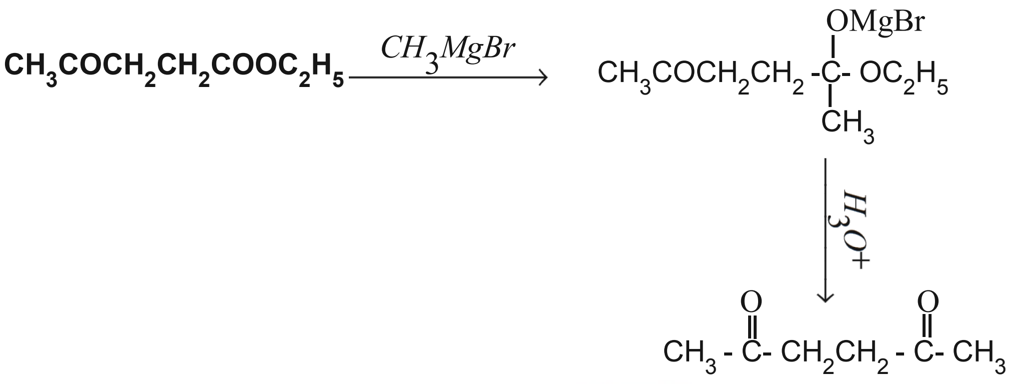


Compound (D) gives Compound (E)



Compound (A)- Nitrile
Compound (B) - Acetic acid
Compound (C)- Aceyl chloride
Compound (D) - Acetophenone
Compound (E) - Methyl phenyl carbinol

3. **Identify X and Y.** $\xrightarrow{CH_3MgBr} X \xrightarrow{H_3O^+}$



$$CH_3COCH_2CH_2COOC_2H_5 \xrightarrow{CH_3MgBr} CH_3COCH_2CH_2\text{-}\underset{\displaystyle CH_3}{\overset{\displaystyle OMgBr}{\overset{|}{\underset{|}{C}}}}\text{-}OC_2H_5 \xrightarrow{H_3O^+} CH_3\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}CH_2CH_2\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}CH_3$$

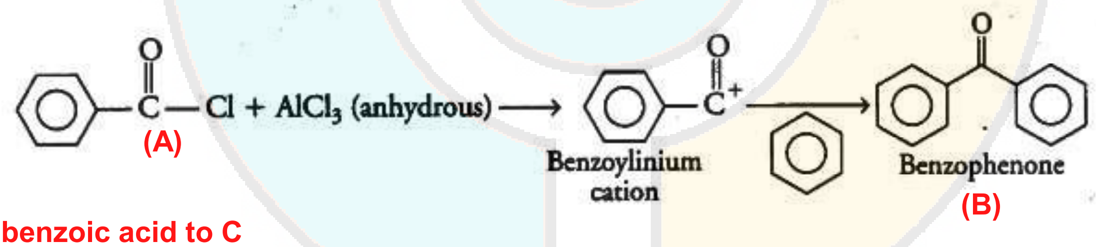
(diketone)

4. **Identify A, B and C, Benzoic acid**

$$\begin{tikzcd}
\text{Benzoic acid} \arrow[r, "PCl_5"] \arrow[d, "C_2H_5OH / H^+"] & A \arrow[r, "benzene", "\text{anhydrous } AlCl_3"'] & B \\
C \arrow[urr, "C_6H_5MgBr"'] & &
\end{tikzcd}$$

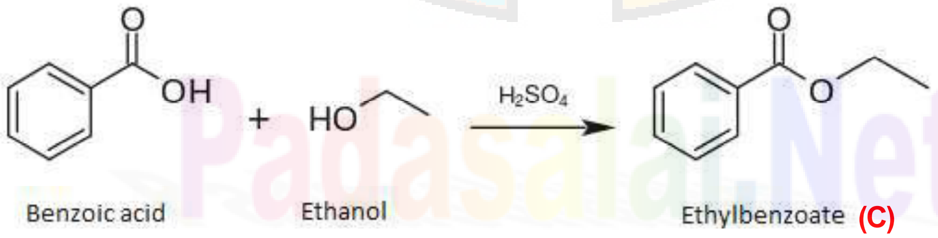
i) benzoic acid to A **i)** $C_6H_5COOH + PCl_5 \rightarrow C_6H_5COCl + PCl_3 + HCl$

ii) C_6H_5COCl (A) to Benzophenone (B)



iii) **benzoic acid to C**

Esterification Reaction

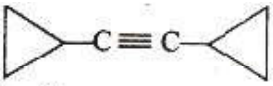


(C) to Benzophenone

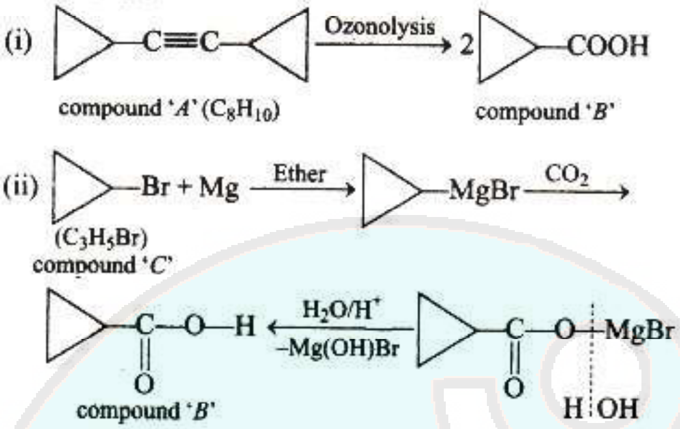
iv) $C_6H_5COOCH_2CH_3 + C_6H_5MgBr \xrightarrow{H_3O^+} C_6H_5CO\ C_6H_5 + MgBr(OCH_2CH_3)$

A - C_6H_5COCl (Benzoyl chloride)
B- Benzophenone
C - Ethyl benzoate

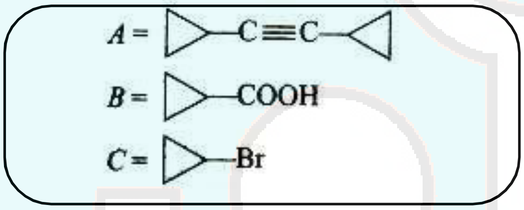
5. **A hydrocarbon A(molecular formula (C_8H_{10}) on ozonolysis gives B($C_4H_6O_2$)only. Compound C(C_3H_5Br) on treatment with magnesium in dry ether gives (D) which on treatment with CO_2 followed by acidification gives(C). Identify A, B and C.**



Reactions :



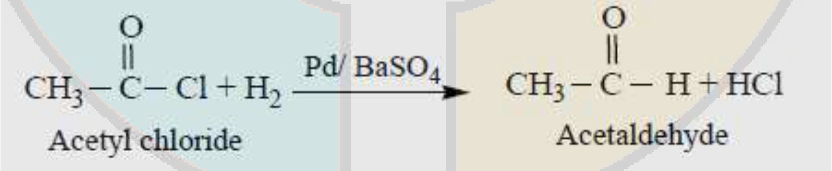
Thus, compounds



6. **Identify A, B, C and D** $\text{ethanoic acid} \xrightarrow{SOCl_2} A \xrightarrow{Pd/BaSO_4} B \xrightarrow{NaOH} C \xrightarrow[\Delta]{} D$

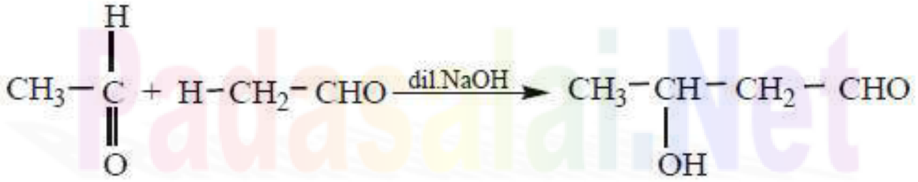
i) $CH_3COOH + SOCl_2 \rightarrow \underset{A}{CH_3COCl} + SO_2 + HCl$

ii) **Rosenmund resduction**



$$\underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{O}{\|}}{C}-Cl} + H_2 \xrightarrow{Pd/\ BaSO_4} \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H} + HCl$$

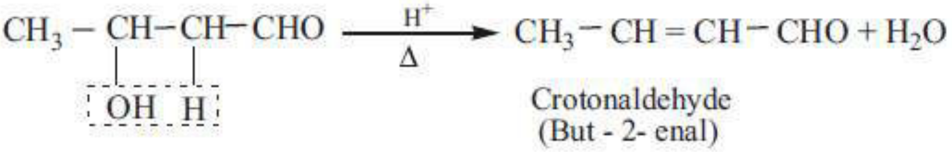
iii) Aldol condensation



$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{O}{\|}}{C}} + H-CH_2-CHO \xrightarrow{dil.NaOH} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO$$

Acetaldehyde
B

Acetaldol C
(3 - Hydroxy butanal)



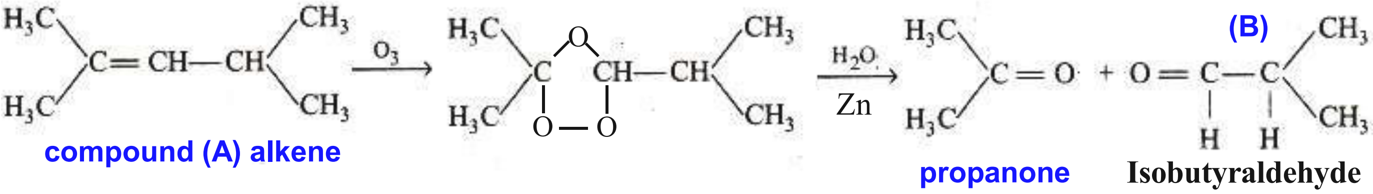
$$CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{H}{|}}{CH}-CHO \xrightarrow[\Delta]{H^+} CH_3-CH=CH-CHO+H_2O$$

Crotonaldehyde
(But - 2- enal)

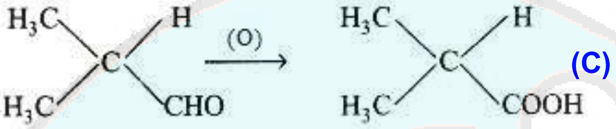
A- Acetyl Chloride B- Acetaldehyde C- Aldol D - Crotanoldehyde

7. **An alkene (A) on ozonolysis gives propanone and aldehyde (B). When (B) is oxidised (C) is obtained. (C) is treated with Br_2/red - P gives (D) which on hydrolysis gives (E). When propanone is treated with HCN followed by hydrolysis gives (E). Identify A, B, C, D and E.**

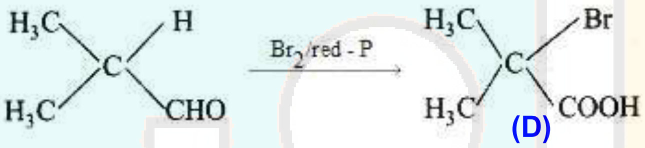
I) An alkene (A) on ozonolysis gives propanone and aldehyde (B) is



ii) (B) is oxidised to give (C) is Isobutyric acid

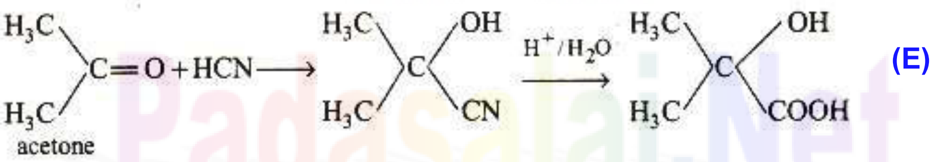


iii) Hell – Volhard – Zelinsky reaction (HVZ reaction) The α- Halogenated acids are convenient starting materials for preparing α - substituted acids.



iv) (D) which on hydrolysis gives (E). (hydrolysis of 'D' with aqueous alkali)

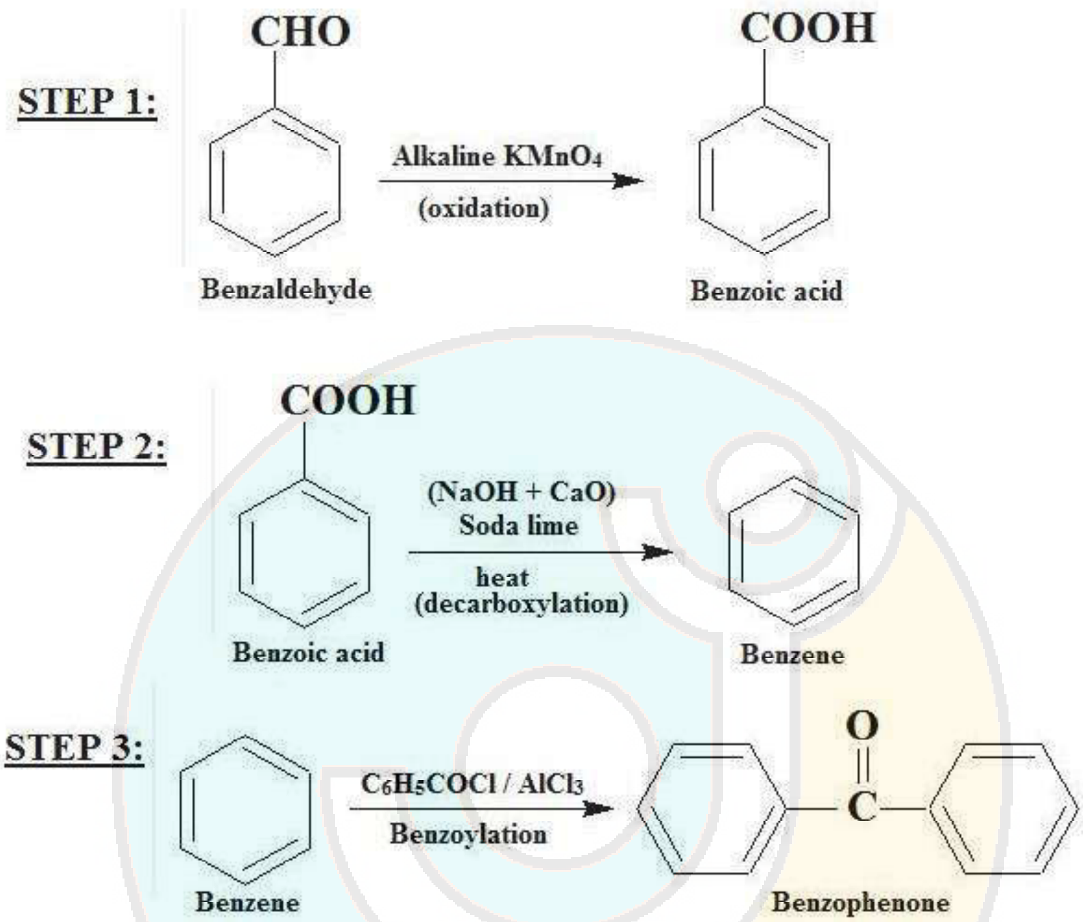
v) propanone is treated with HCN followed by hydrolysis gives (E)



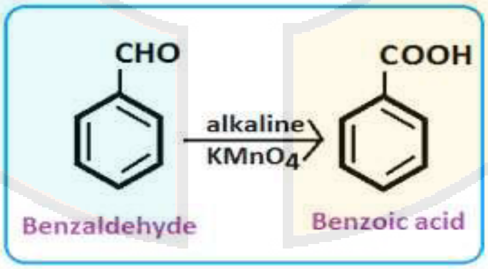
Compound - A	**- unsymetrical alkene**
Compound - B	**- Isobutyraldehyde**
Compound - C	**- Isobutyric acid**
Compound - D	**- 2-Bromo-2-methyl propionic acid**
Compound - E	**- 2-methyl -2- hydroxy propanoic acid**

8. How will you convert benzaldehyde into the following compounds?
(i) benzophenone (ii) benzoic acid (iii) α-hydroxyphenylaceticacid.

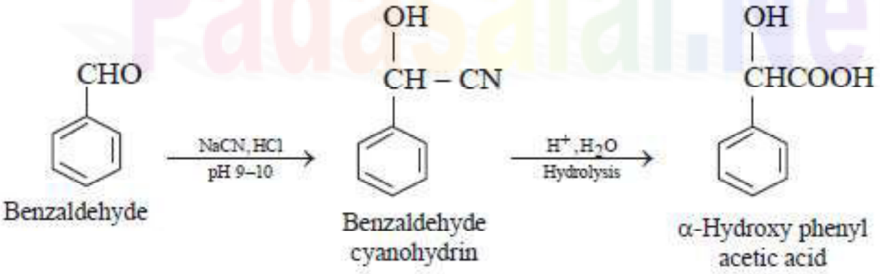
Conversion of benzaldehyde to benzophenone



i) Benzaldehyde into Benzoic acid



i) Benzaldehyde into Benzoic acid



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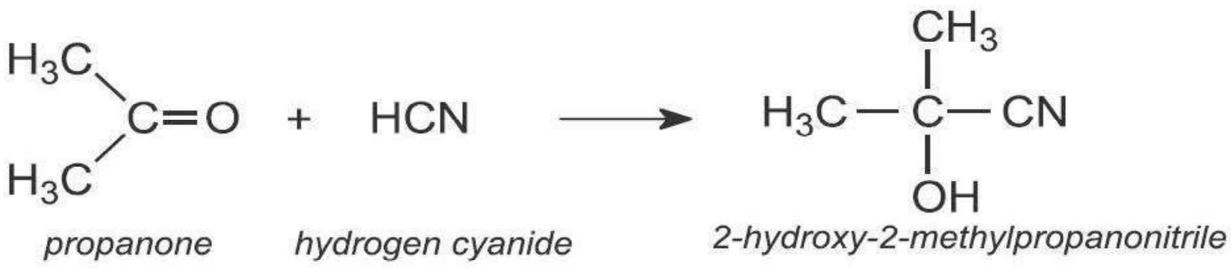
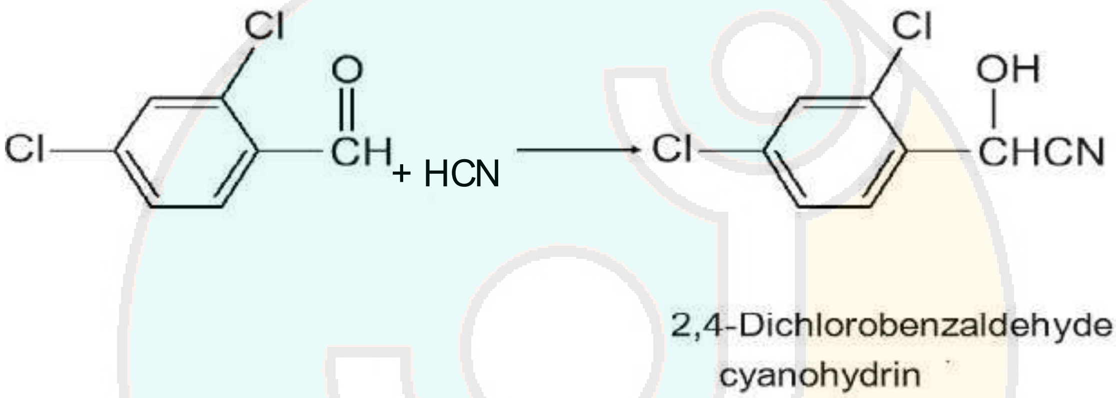
9. What is the action of HCN on
(i) propanone (ii) 2,4-dichlorobenzaldehyde. iii) ethanal

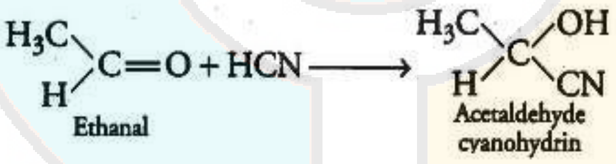
i) Action of HCN on propanone



ii) Action of HCN on 2,4-dichlorobenzaldehyde.



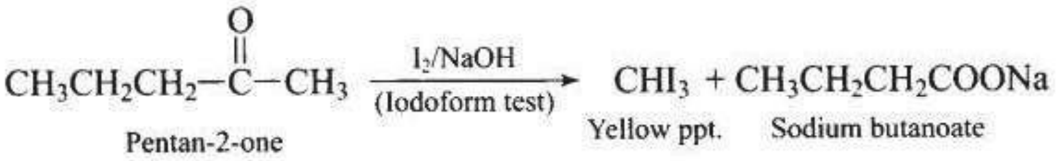
iii) Action of HCN on ethanal



10. A carbonyl compound A having molecular formula $C_5H_{10}O$ forms crystalline precipitate with sodium bisulphate and gives positive iodoform test. A does not reduce Fehling solution. Identify A.

It does not reduce fehling's solution but forms bisulpphite compound so it is a ketone therefore it gives positive iodoform test therefore it is methyl ketone.

Pentan-2-one having a $-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ group forms a yellow ppt. of iodoform with an alkaline solution of iodine (i.e., iodoform test) while pentan-3-one does not.

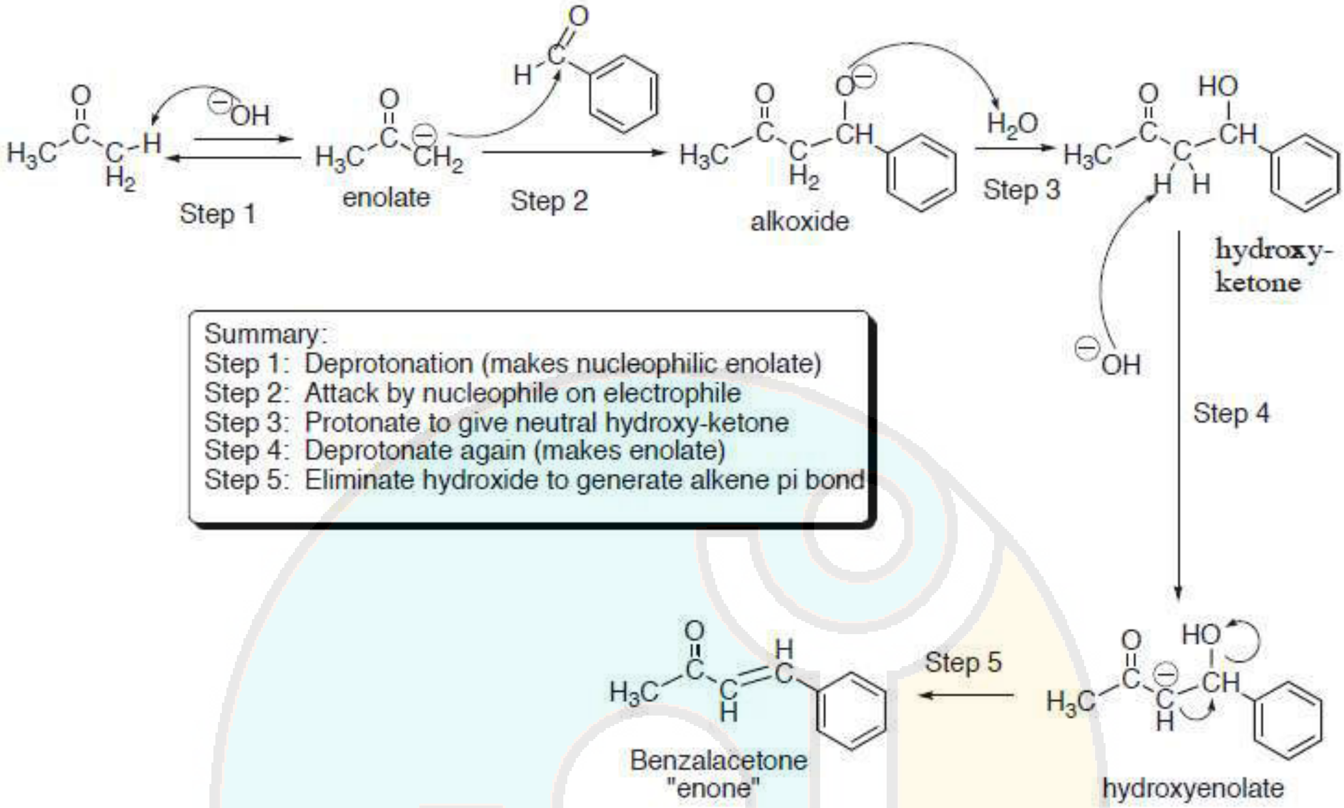


$$CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[\text{(Iodoform test)}]{I_2/NaOH} CHI_3 + CH_3CH_2CH_2COONa$$

Pentan-2-one Yellow ppt. Sodium butanoate

Ans: Compound A is Pentan-2-one

11. Write the structure of the major product of the aldol condensation of benzaldehyde with acetone.



Summary:
Step 1: Deprotonation (makes nucleophilic enolate)
Step 2: Attack by nucleophile on electrophile
Step 3: Protonate to give neutral hydroxy-ketone
Step 4: Deprotonate again (makes enolate)
Step 5: Eliminate hydroxide to generate alkene pi bond

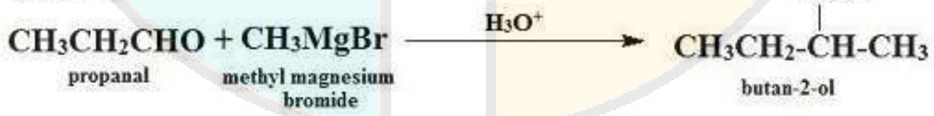
12. How are the following conversions effected

(a) propanal into butanone (b) Hex-3-yne into hexan-3-one.
(c) phenylmethanal into benzoic acid (d) phenylmethanal into benzoin

(a) propanal into butanone

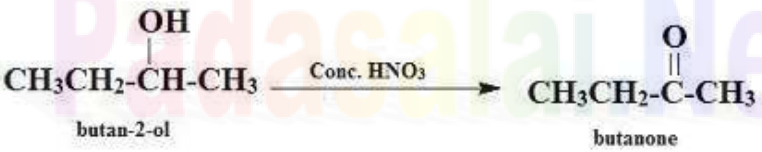
Conversion of propanal to butanone

STEP -1



$$\underset{\text{propanal}}{CH_3CH_2CHO} + \underset{\text{methyl magnesium bromide}}{CH_3MgBr} \xrightarrow{H_3O^+} \underset{\text{butan-2-ol}}{CH_3CH_2\text{-}\overset{OH}{\overset{|}{C}H}\text{-}CH_3}$$

STEP -2:



$$\underset{\text{butan-2-ol}}{CH_3CH_2\text{-}\overset{OH}{\overset{|}{C}H}\text{-}CH_3} \xrightarrow{\text{Conc. HNO}_3} \underset{\text{butanone}}{CH_3CH_2\text{-}\overset{O}{\overset{||}{C}}\text{-}CH_3}$$

(b) Hex-3-yne into hexan-3-one.

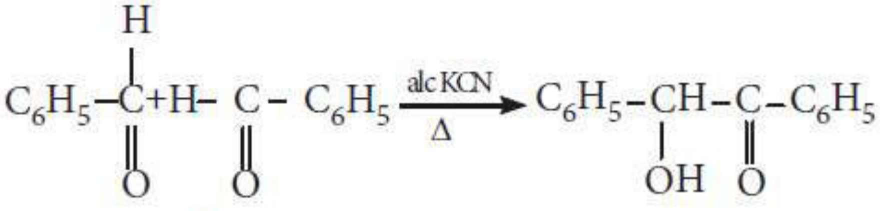
$$CH_3\text{-}CH_2\text{-}C \equiv C\text{-}CH_2\text{-}CH_3 \xrightarrow{H_2SO_4/\,HgSO_4} CH_3\text{-}CH_2\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

(c) phenylmethanal into benzoic acid

$$C_6H_5\text{-}CHO \xrightarrow[(O)]{\text{alkaline } KMnO_4} C_6H_5\text{-}COOH$$

(d) phenylmethanal into benzoin

Benzaldehyde reacts with alcoholic KCN to form benzoin



$$C_6H_5-\overset{H}{\underset{O}{C}}+H-\underset{O}{C}-C_6H_5 \xrightarrow[\Delta]{alc\,KCN} C_6H_5-\underset{OH}{CH}-\underset{O}{C}-C_6H_5$$

Benzaldehyde Benzoin

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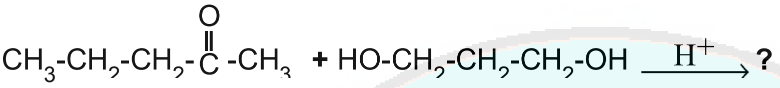
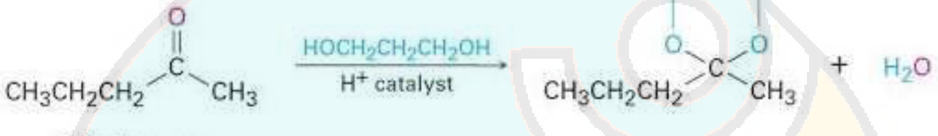
13. **Complete the following reaction.**



$$CH_3-CH_2-CH_2-\overset{O}{C}-CH_3 + HO-CH_2-CH_2-CH_2-OH \xrightarrow{H^+} ?$$



2-Pentanone acetal

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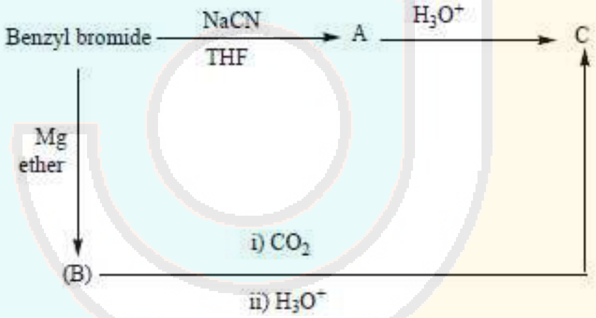
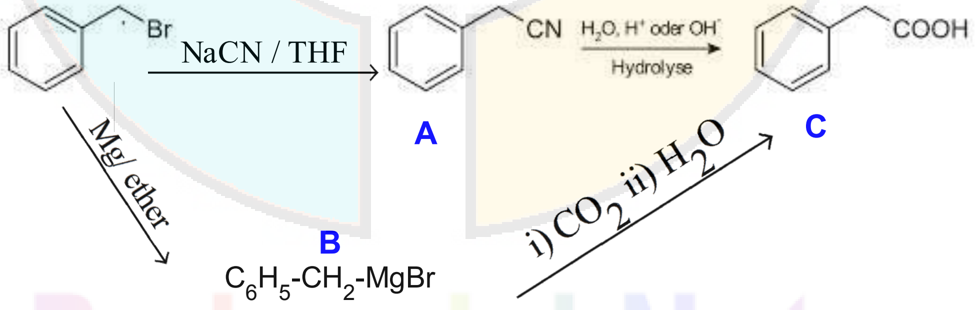
14. **Identify A, B and C**



Soln:

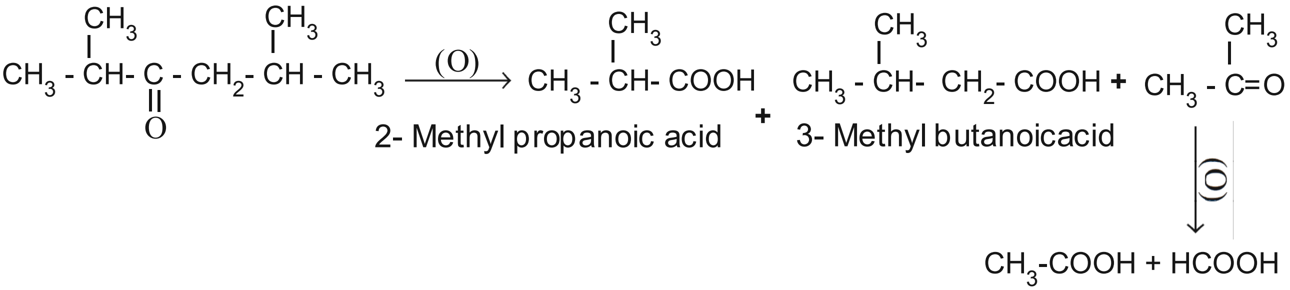


A - Benzyl cyanide B - Benzyl magnesium bromide C) 2 - Phenyl ethanoic acid

---

15. **Oxidation of ketones involves carbon – carbon bond cleavage. Name the product (s) is / are formed on oxidising 2,5 – dimethyhexan – 2- one using strong oxidising agent .**

According to Popoff's rule, the unsymmetrical ketone on oxidation, C-C bond cleavage and keto group goes with CH_3-CH(CH_3)-



$$CH_3-\overset{CH_3}{CH}-\underset{O}{C}-CH_2-\overset{CH_3}{CH}-CH_3 \xrightarrow{(O)} CH_3-\overset{CH_3}{CH}-COOH + CH_3-\overset{CH_3}{CH}-CH_2-COOH + CH_3-\overset{CH_3}{C}=O$$

2- Methyl propanoic acid 3- Methyl butanoicacid

$$CH_3-\overset{CH_3}{C}=O \xrightarrow{(O)} CH_3-COOH + HCOOH$$

16. How will you prepare

i. Acetic anhydride from acetic acid
ii. Ethylacetate from methylacetate
iii. Acetamide from methylcyanide
iv. Lactic acid from ethanal
v. Acetophenone from acetylchloride
vi. Ethane from sodium acetate
vii. Benzoic acid from toluene
viii. Malachitegreen from benzaldehyde
ix. Cinnamic acid from benzaldehyde
x. Acetaldehyde from ethyne

i. Acetic anhydride from acetic acid

$$CH_3\text{-}COOH + CH_3\text{-}COOH \xrightarrow{P_2O_5/\Delta} (CH_3\text{-}CO)_2O + H_2O$$

ii. Ethylacetate from methylacetate

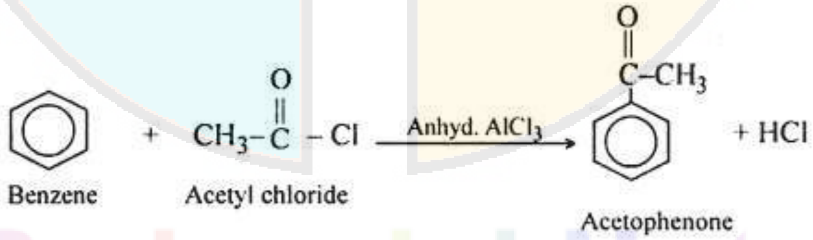
$$CH_3\text{-}COOCH_3 + CH_3\text{-}CH_2OH \xrightarrow{H^+} CH_3\text{-}COOCH_2CH_3 + H_2O$$

iii. Acetamide from methylcyanide

$$CH_3\text{-}CN \xrightarrow{H_2O/H^+} CH_3\text{-}CONH_2 + H_2O$$

iv. Lactic acid from ethanal

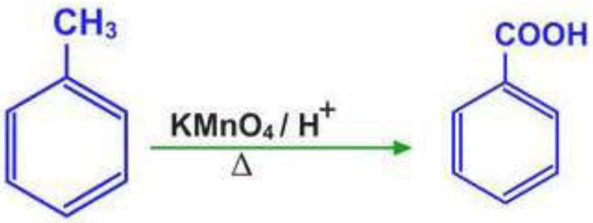
v. Acetophenone from acetylchloride



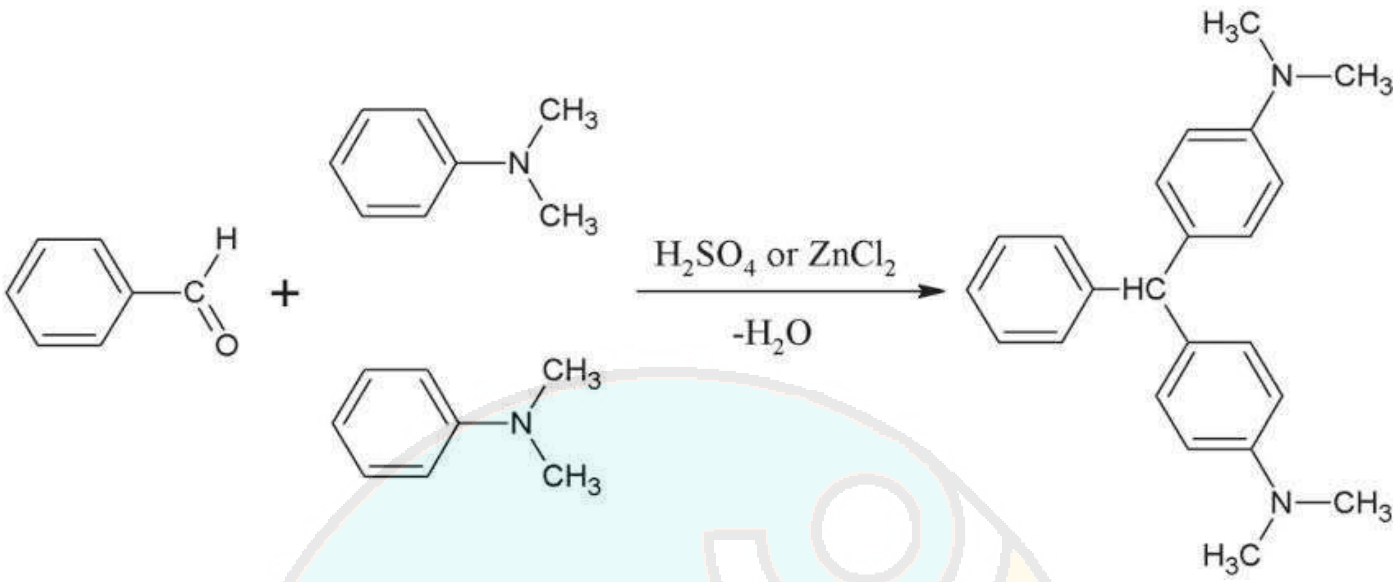
vi. Ethane from sodium acetate

$$2CH_3COONa + 2H_2O \xrightarrow{Electrolysis} \underset{Ethane}{CH_3-CH_3} + 2NaOH + H_2 + 2CO_2$$

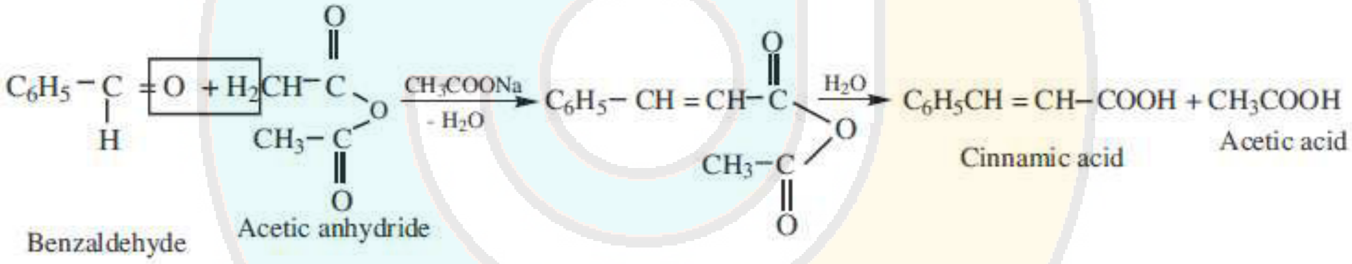
vii. Benzoic acid from toluene



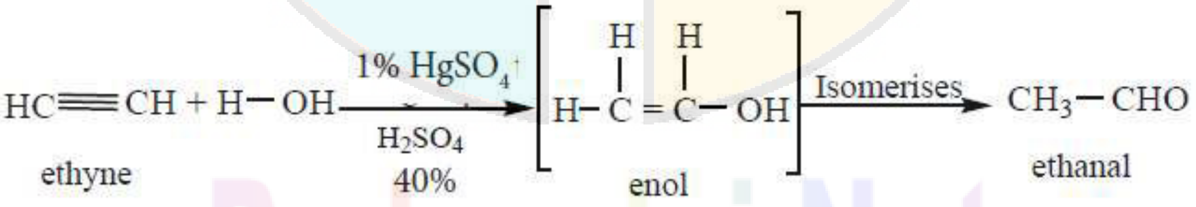
viii. Malachitegreen from benzaldehyde



ix. Cinnamic acid from benzaldehyde



x. Acetaldehyde from ethyne



$$HC{\equiv}CH + H{-}OH \xrightarrow[H_2SO_4\ 40\%]{1\%\ HgSO_4} \left[H{-}\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}{-}OH \right] \xrightarrow{\text{Isomerises}} CH_3{-}CHO$$

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UNIT – 13

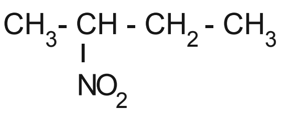
ORGANIC NITROGEN COMPOUNDS

1. Write down the possible isomers of the $C_4H_9NO_2$ give their IUPAC names

i) $CH_3-CH_2-CH_2-CH_2-NO_2$

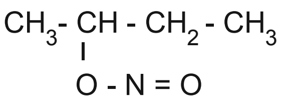
ii) $CH_3-CH_2-CH_2-CH_2-O-N=O$

iii)



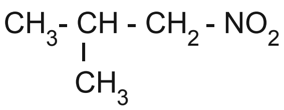
$CH_3-\underset{NO_2}{\underset{|}{CH}}-CH_2-CH_3$

iv)



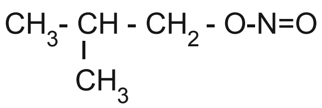
$CH_3-\underset{O-N=O}{\underset{|}{CH}}-CH_2-CH_3$

v)



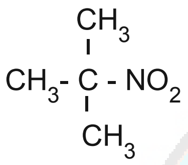
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-NO_2$

vi)



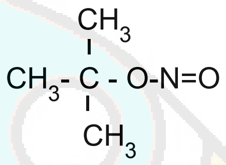
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-O-N=O$

vii)



$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-NO_2$

viii)



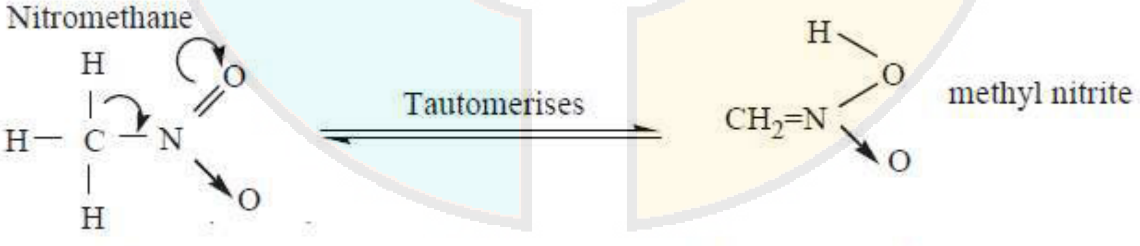
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-O-N=O$

i) 1- nitro butane	**ii) 1-nitrosooxybutane**
iii) 2 - nitro butane	**iv) 2- nitroso oxy butane**
v) 2- methyl - 1- nitro propane	**vi) 2 - methyl -1-nitroso oxy propane**
vii) 2- methy-2-nitro propane	**viii) 2-methyl-2-nitroso oxy propane**

2. There are two isomers with the formula CH_3NO_2 How will you distinguish between them?

Tautomerism:

Primary and secondary nitroalkanes, having α-H , also show an equilibrium mixture of two tautomers namely nitro and aci- form



nitro - form

Aci - form (or) isonitroform

Distinguish between two form

S.No.	Nitro form	Aci – form
1.	Less acidic	More acidic and also called pseudoacids (or) nitronic acids
2.	Dissolves in NaOH slowly	Dissolves in NaOH instantly
3.	Decolourises $FeCl_3$ solution	With $FeCl_3$ gives reddish brown colour
4.	Electrical conductivity is low	Electrical conductivity is high

3. What happends when

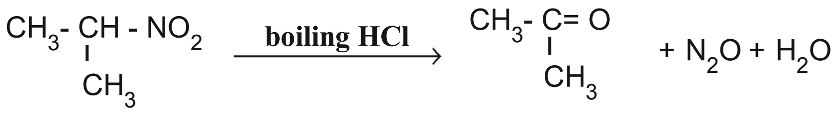
i. 2 - Nitropropane boiled with HCl

ii. Nitrobenzene undergo electrolytic-reduction in strongly acidic medium.

iii. Oxidation of tert - butylamine with $KMnO_4$

iv. Oxidation of acetoneoxime with trifluoroperoxy acetic acid.

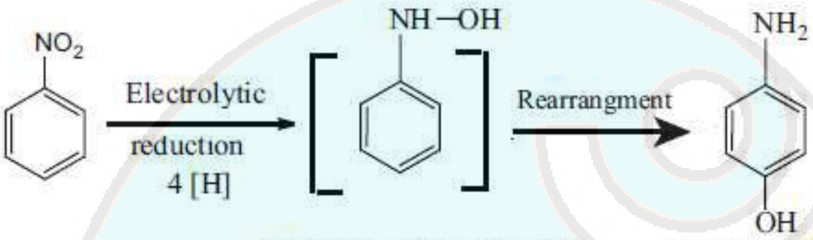
i. 2 - Nitropropane boiled with HCl



$$\underset{\displaystyle CH_3}{CH_3-CH-NO_2} \xrightarrow{\text{boiling HCl}} \underset{\displaystyle CH_3}{CH_3-C=O} + N_2O + H_2O$$

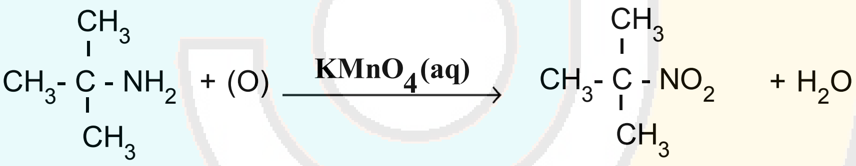
Acetone

ii. Nitrobenzene undergo electrolytic-reduction in strongly acidic medium.



Phenylhydroxyl amine p-aminophenol

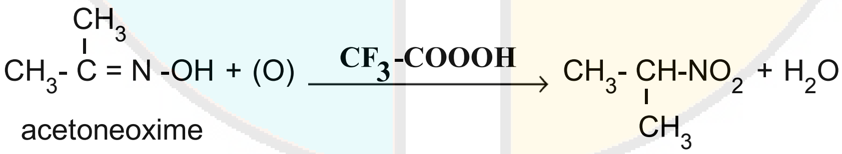
ii) Oxidation of tert - butylamine with $KMnO_4$



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-NH_2 + (O) \xrightarrow{KMnO_4(aq)} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-NO_2 + H_2O$$

iv. Oxidation of acetoneoxime with trifluoro peroxy acetic acid.

Oxidation of acetoneoxime with trifluoroperoxy acetic acid gives 2 - nitropropane (2^0) respectively.



$$CH_3-\overset{\displaystyle CH_3}{C}=N-OH + (O) \xrightarrow{CF_3-COOOH} \underset{\displaystyle CH_3}{CH_3-CH-NO_2} + H_2O$$

acetoneoxime

2 - nitropropane (2^0)

4. How will you convert nitrobenzene into

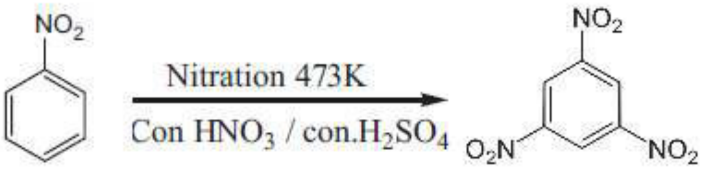
i. 1,3,5 - trinitrobenzene **ii. o and p- nitrophenol**

iii. m - nitro aniline **iv. azoxybenzene**

v. hydrozobenzene **vi. N - phenylhydroxylamine**

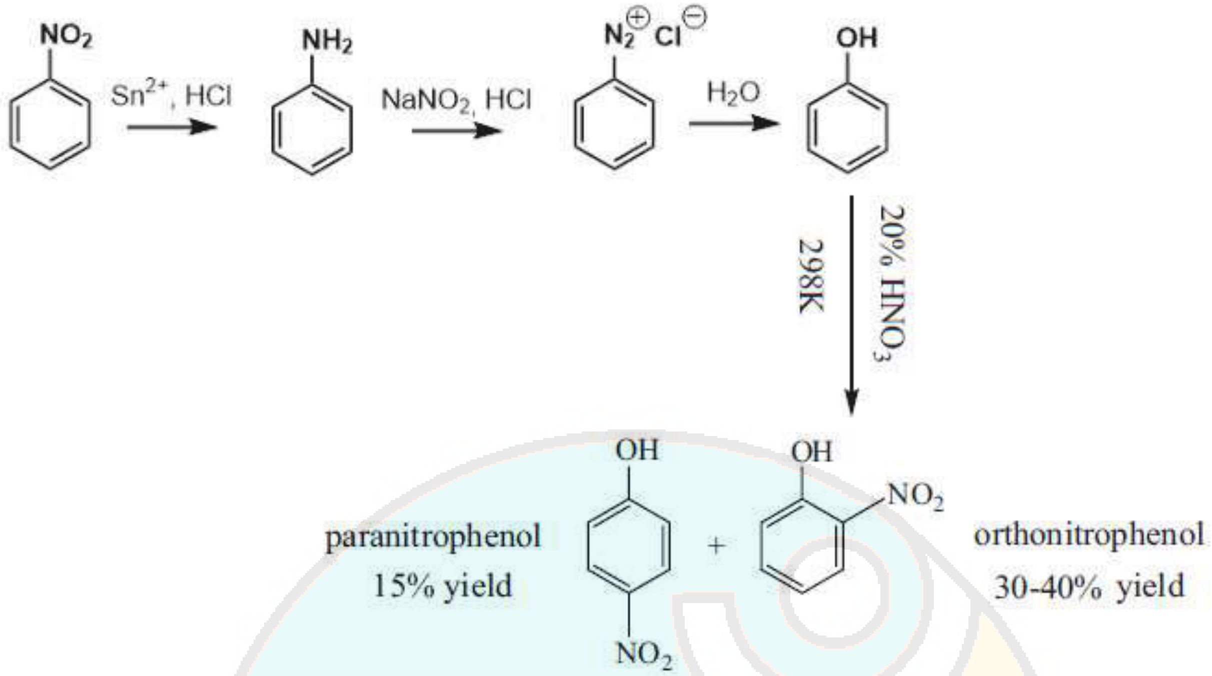
vii. aniline

i) Conversion of nitrobenzene into 1,3,5 - trinitrobenzene

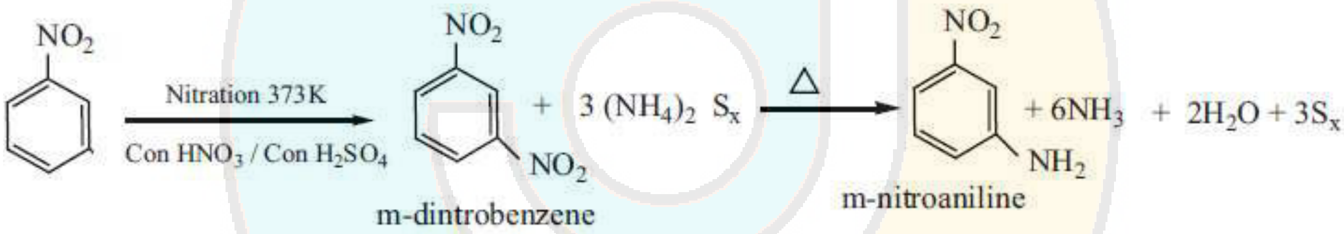


1,3,5 - trinitrobenzene (TNB)

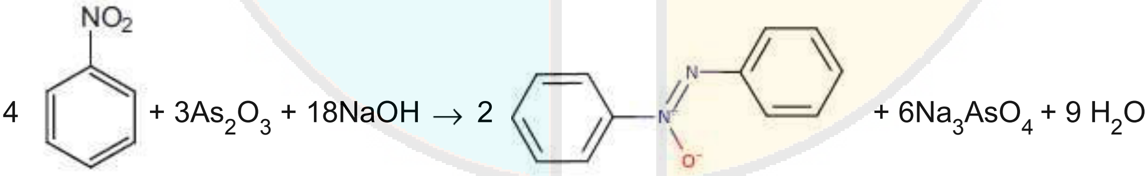
ji Conversion of nitrobenzene into o and p- nitrophenol



iii) Conversion of nitrobenzene into m - nitro aniline



iv) Conversion of nitrobenzene into azoxybenzene hydrozobenzene



iv) Conversion of nitrobenzene into hydrozobenzene

$$C_6H_5\text{-}NO_2 \xrightarrow[\text{basic medium}]{\mathbf{Zn\ /\ NaOH}} [C_6H_5\text{-}N{=}N\text{-}C_6H_5] \xrightarrow{\mathbf{2[H]}} C_6H_5\text{-}NH{=}NH\text{-}C_6H_5$$

iv) Conversion of nitrobenzene into N - phenylhydroxylamineaniline

$$C_6H_5\text{-}NO_2 + 2[H] \xrightarrow[\text{Neutral medium}]{\mathbf{Zn\ /NH_4Cl}} C_6H_5\text{-}NH\text{-}OH + ZnO$$

iv) Conversion of nitrobenzene into aniline

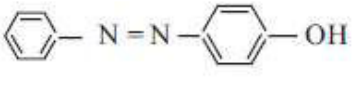
$$C_6H_5\text{-}NO_2 + 6[H] \xrightarrow[\text{Acid medium}]{\mathbf{Sn\ /\ HCl]}} C_6H_5\text{-}NH_2$$

5. **Identify compounds A,B and C in the following sequence of reactions.**

i) $C_6H_5\text{-}NO_2 \xrightarrow{Fe\ /\ HCl} A \xrightarrow{HNO_2/273K} B \xrightarrow{C_6H_5OH} C$

Ans: $C_6H_5\text{-}NO_2 \xrightarrow{Fe\ /\ HCl} C_6H_5\text{-}NO_2 \xrightarrow{HNO_2/273K} C_6H_5\text{-}N_2Cl$

$\xrightarrow[\text{Coupling reaction}]{C_6H_5OH}$



p- hydroxy azobenzene

A- Aniline **B - Benzene diazonium chloride** **C - p - hydroxy azobenzene**

---

ii) $C_6H_5\text{-}N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[288\ K]{NH_3} C$

Ans: $C_6H_5\text{-}N_2Cl \xrightarrow{CuCN} C_6H_5\text{-}CN \xrightarrow{H_2O/H^+} C_6H_5\text{-}COOH \xrightarrow[288\ K]{NH_3} C_6H_5\text{-}CONH_2$

A- Cyanobenzene **B - Benzoic acid** **C - Benzamide**

---

iii) $CH_3\text{-}CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{partial hydrolysis}]{OH^-} B \xrightarrow{NaOH + Br_2} C$

Ans: $CH_3\text{-}CH_2I \xrightarrow{NaCN} CH_3\text{-}CH_2CN \xrightarrow[\text{partial hydrolysis}]{OH^-} CH_3\text{-}CH_2CONH_2 \xrightarrow[\text{Hoffmann bromamide reaction}]{NaOH + Br_2} CH_3\text{-}NH_2$

A- Ethyl cyanide **B - Acetamide** **C - Methyl amine**

---

iv) $CH_3\text{-}NH_2 \xrightarrow{CH_3Br} A \xrightarrow{CH_3COCl} B \xrightarrow{B_2H_6} C$

Ans: $CH_3\text{-}NH_2 \xrightarrow{CH_3Br} (CH_3)_2NH \xrightarrow{CH_3COCl} (CH_3)_2N\text{-}CO\text{-}CH_3$

$\xrightarrow{B_2H_6} (CH_3)_2N\text{-}CH(OH)\text{-}CH_3$

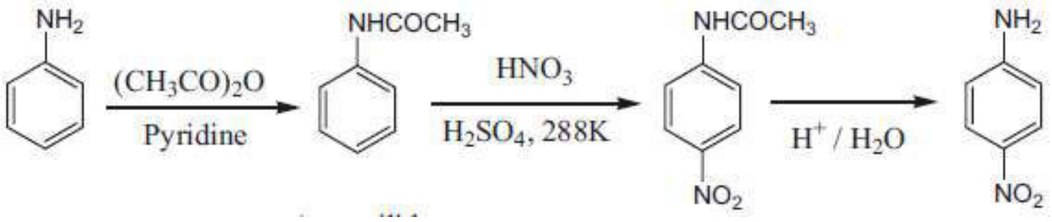
A- N,N dimethyl amine **B - N,N-dimethyl acetamide**

C - N,N-dimethyl 2- hydroxy ethan amine

---

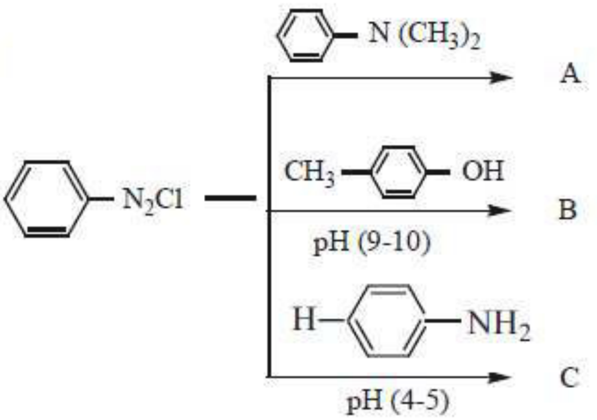
v) $C_6H_5\text{-}NH_2 \xrightarrow{(CH_3CO)_2O/\ pyridine} A \xrightarrow{HNO_3/H_2SO_4} B \xrightarrow{H_2O/H^+} C$

Ans:

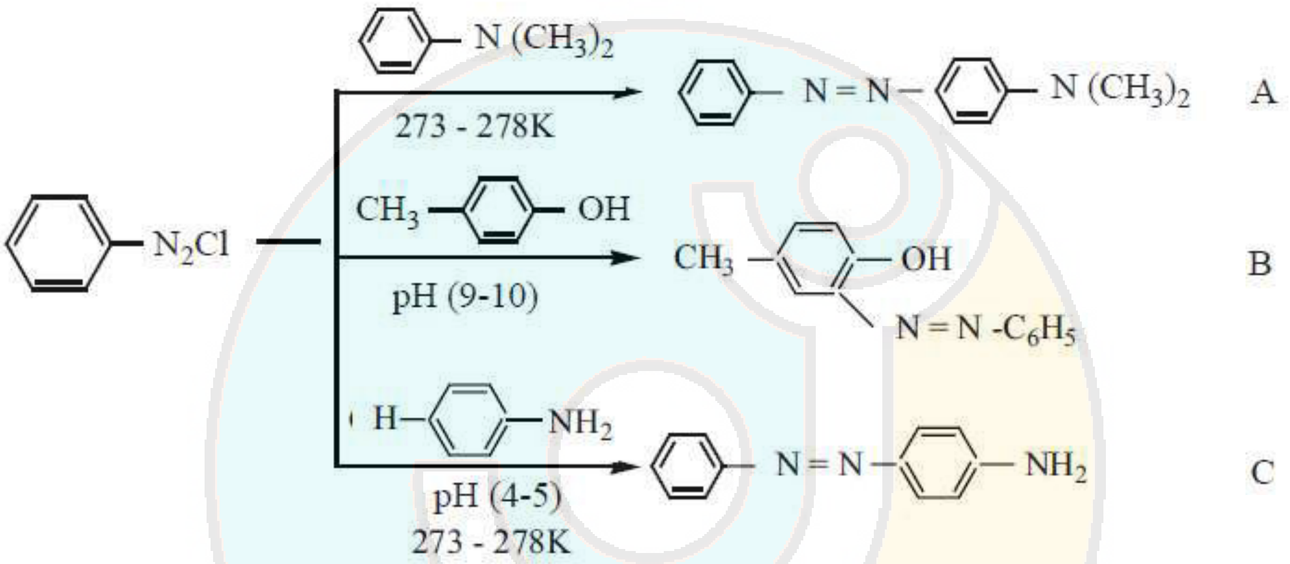


A - Acetanilide **B - p- nitroacetanilide** **C- p- nitro aniline**

vi)



Ans:



A- p-N,N - dimethyl amino azobenzene

B - 2 - phenylazo - 4 -Methyl phenol

C - p - amino azobenzene (Yellow dye)

---

vii) $CH_3\text{-}CH_2\text{-}NC \xrightarrow{HgO} A \xrightarrow{H_2O} B \xrightarrow[\text{ii) } H_2O]{\text{i)}NaNO_2\ /HCl} C$

Ans : $CH_3\text{-}CH_2\text{-}NC \xrightarrow{HgO} CH_3\text{-}CH_2\text{-}N = C = O \xrightarrow{H_2O} CH_3\text{-}CH_2\text{-}NH_2$

$\xrightarrow{\text{i)}NaNO_2\ /HCl} \underset{\text{unstable}}{[C_2H_5N_2Cl]} \xrightarrow{\text{ii) } H_2O} CH_3\text{-}CH_2OH + N_2$

A- Ethyl iso cyanate **B-** Ethyl amine **C-** Ethanol

---

6. **Write short notes on the following**
   - i. Hofmann's bromide reaction
   - ii. Ammonolysis
   - iii. Gabriel phthalimide synthesis
   - iv. Schotten - Baumann reaction
   - v. Carbylamine reaction
   - vi. Mustard oil reaction
   - vii. Coupling reaction
   - viii. Diazotisation
   - ix. Gomberg reaction

i. Hofmann's bromide reaction

When Amides are treated with bromine in the presence of aqueous or ethanolic solution of KOH, primary amines with one carbon atom less than the parent amides are obtained.

$$CH_3\text{-}CONH_2 \xrightarrow{Br_2/KOH} CH_3\text{--}NH_2 + K_2CO_3 + KBr + H_2O$$

ii. Ammonolysis

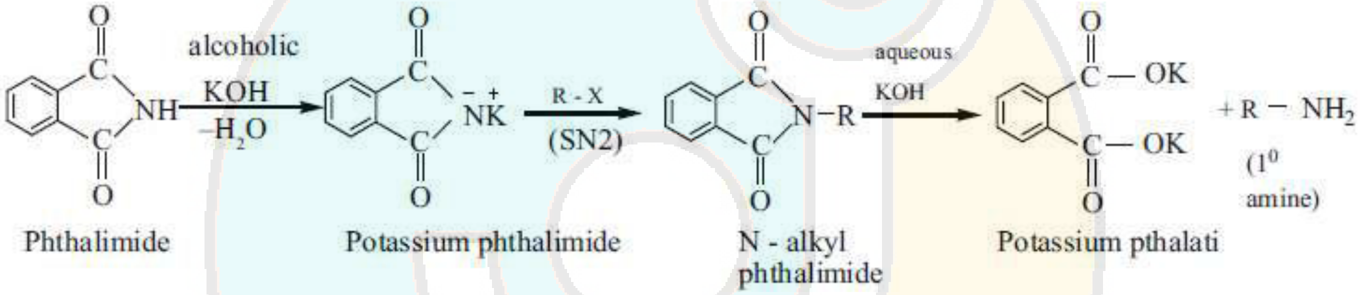
When Alkyl halides (or) benzylhalides are heated with alcoholic ammonia in a sealed tube, mixtures of 1^0, 2^0 and 3^0 amines and quaternary ammonium salts are obtained

$$CH_3\text{-}Br \xrightarrow{NH_3/\Delta} \underset{1^o\ \text{amine}}{CH_3\text{--}NH_2} \xrightarrow{CH_3Br} \underset{2^o\ \text{amine}}{(CH_3)_2\text{-}NH} \xrightarrow{CH_3Br} \underset{3^o\ \text{amine}}{CH_3)_3\text{-}N}$$

$$\xrightarrow{CH_3Br} CH_3)_4\text{-}N^+Br^- \ \textbf{Quarternary ammonium bromide}$$

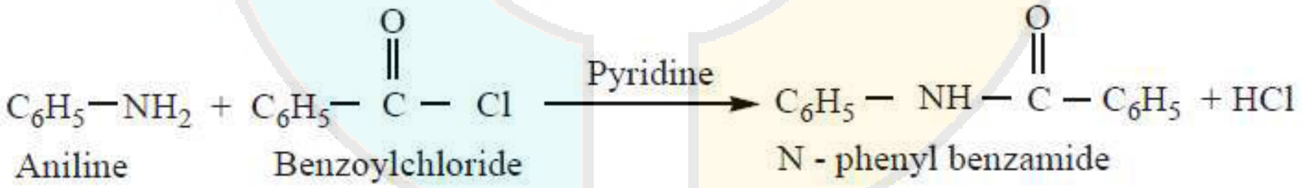
iii. Gabriel phthalimide synthesis

Phthalimide on treatment with ethanolic KOH forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis gives primary amine. Aniline cannot be prepared by this method because the arylhalides do not undergo nucleophilic substitution with the anion formed by phthalimide



iv. Schotten - Baumann reaction

Aniline reacts with benzoylchloride (C_6H_5COCl) in the presence of NaOH to give N-phenyl benzamide. This reaction is known as Schotten - Baumann reaction



$$\underset{\text{Aniline}}{C_6H_5-NH_2} + \underset{\text{Benzoylchloride}}{C_6H_5-\overset{\overset{O}{\|}}{C}-Cl} \xrightarrow{\text{Pyridine}} \underset{\text{N - phenyl benzamide}}{C_6H_5-NH-\overset{\overset{O}{\|}}{C}-C_6H_5} + HCl$$

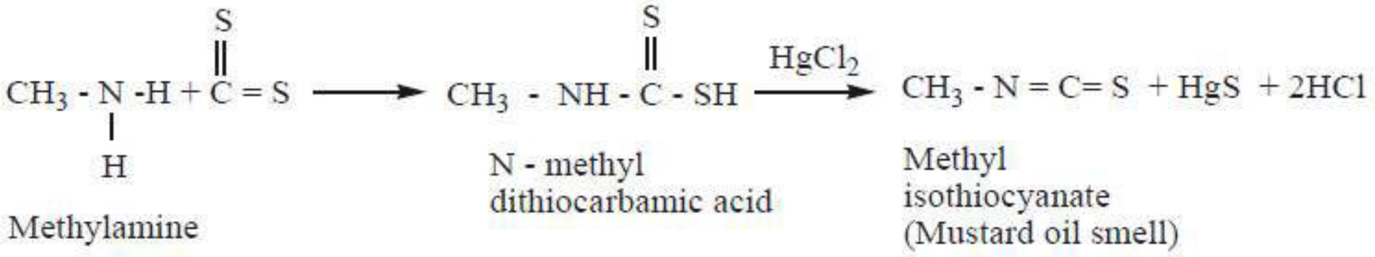
v. Carbylamine reaction

Aliphatic (or) aromatic primary amines react with chloroform and alcoholic KOH to give isocyanides (carbylamines), which has an unpleasant smell. This reaction is known as carbylamines test.
This test used to identify the primary amines

$$C_2H_5\text{-}NH_2 + 3KOH + CHCl_3 \xrightarrow{Br_2/KOH} \underset{\text{carbylamines}}{C_2H_5\text{-}NC} + 3\ KCl + 3H_2O$$

vi. Mustard oil reaction

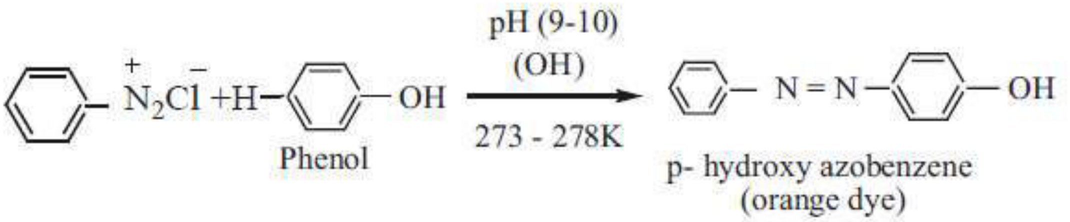
i) When primary amines are treated with carbon disulphide (CS_2), N - alkyldithio carbonic acid is formed which on subsequent treatment with $HgCl_2$,give an alkyl isothiocyanate.



$$\underset{\text{Methylamine}}{CH_3-\underset{\underset{H}{|}}{N}-H} + \overset{\overset{S}{\|}}{C} = S \longrightarrow \underset{\text{N - methyl dithiocarbamic acid}}{CH_3 - NH - \overset{\overset{S}{\|}}{C} - SH} \xrightarrow{HgCl_2} \underset{\text{Methyl isothiocyanate (Mustard oil smell)}}{CH_3 - N = C = S} + HgS + 2HCl$$

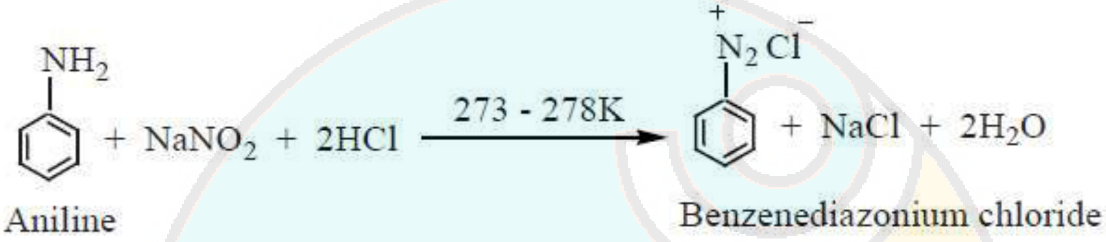
vii. Coupling reaction

Benzene diazonium chloride reacts with electron rich aromatic compounds like phenol, aniline to form brightly coloured azo compounds.



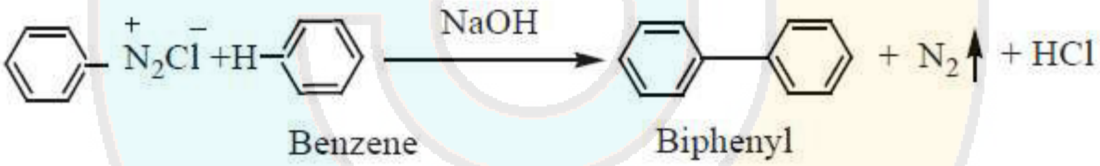
viii. Diazotisation

Aniline reacts with nitrous acid at low temperature (273 - 278 K) to give benzene diazonium chloride which is stable for a short time and slowly decomposes seven at low temperatures.This reaction is known as **diazotization**.



ix. Gomberg reaction

Benzene diazonium chloride reacts with benzene in the presence of sodium hydroxide to give biphenyl. This reaction in known as the Gomberg reaction.



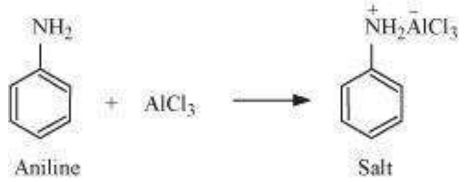
7. How will you distinguish between primary secondary and tertiary alphatic amines.

Reagents	Primary amine	Secondary amine	Tertiary amine
With HNO_2	forms forms alcohol	N-nitroso amine	forms salt.
With $CHCl_3$/KOH	forms carbylamine	No reaction.	No reaction
With CS_2 and $HgCl_2$	alkyl isothiocyanate is formed	No reaction	No reaction
With Diethyl oxalate	dialkyl oxamide, a solid at room temperature is formed.	Forms N,N-dialkyl oxamic ester, a liquid.	No reaction
With acetyl chloride	forms N-alkyl acetamide.	form N,N-dialkyl acetamide	No reaction

8. Account for the following

i. Aniline does not undergo Friedel . Crafts reaction

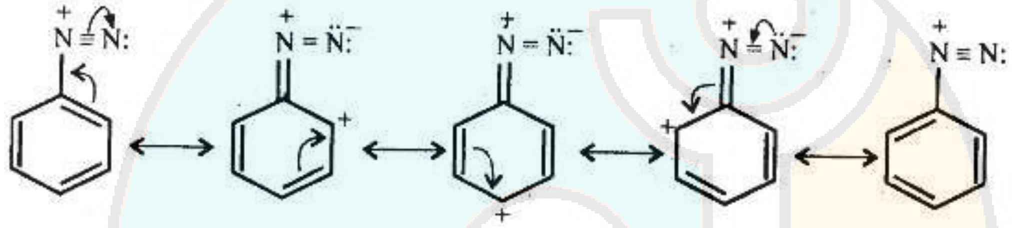
A Friedel-Crafts reaction is carried out in the presence of $AlCl_3$. But $AlCl_3$ is acidic in nature, while aniline is a strong base. Thus, aniline reacts with $AlCl_3$ to form a salt.



Due to the positive charge on the N-atom, electrophilic substitution in the benzene ring is deactivated. Hence, aniline does not undergo the Friedel-Crafts reaction.

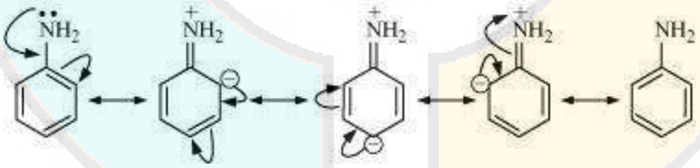
ii. Diazonium salts of aromatic amines are more stable than those of aliphatic amines

In diazonium salt, the structure goes under resonance due to which the dispersal of positive charge is more and we know that higher is the resonance higher is the stability. Therefore diazonium salt of aromatic amines is more stable than those of aliphatic amines.



iii. pKb of aniline is more than that of methylamine

Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate.On the other hand, in case of methylamine (due to the +I effect of methyl group), the electron density on the N-atom is increased. As a result, aniline is less basic than methylamine. Thus, pK_b of aniline is more than that of methylamine.

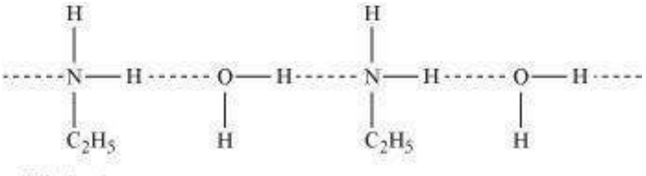


iv. Gabriel phthalimide synthesis is preferred for synthesising primary amines.

Gabriel phthalimide synthesis results in the formation of 1° amine only. 2° or 3° amines are not formed in this synthesis. Thus, a pure 1° amine can be obtained. Therefore, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

v. Ethylamine is soluble in water whereas aniline is not

Ethylamine when added to water forms intermolecular H-bonds with water. And therefore it is soluble in water. But aniline does not form H-bond with water to a very large extent due to the presence of a large hydrophobic -C6H5group. Hence, aniline is insoluble in water.



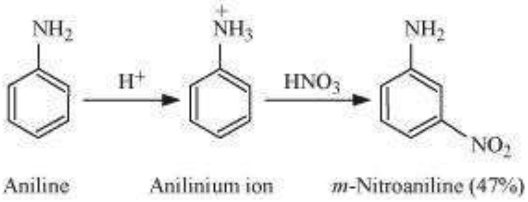
Ethylamine

vi. Amines are more basic than amides

The lone pair of electrons on the amine are more available to accept a proton and act as a base. This is because in amides, the carbonyl (C=O) group is highly electronegative, so has a greater power to draw electrons towards it, making the lone pair of the amide nitrogen less availble to accept a proton.

vii. Although amino group is o - and p- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m- nitroaniline

Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).



For this reason, aniline on nitration gives a substantial amount of m-nitroaniline.

9. Arrange the following

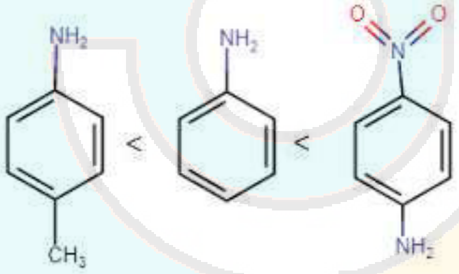
i. In increasing order of solubility in water, $C_6H_5NH_2$,$(C_2H_5)_2NH$,$C_2H_5NH_2$

The more extensive the H-bonding, the higher is the solubility.Thus, $C_2H_5NH_2$ undergoes more extensive H-bonding than $(C_2H_5)_2NH$. Hence, the solubility in water of $C_2H_5NH_2$ is more than that of $(C_2H_5)_2NH$.

$$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$$

ii. In increasing order of basic strength

a) aniline, p-toludine and p-nitroaniline



p-nitroaniline < aniline < p-toludine

In p-toluidine, the presence of electron-donating $-CH_3$ group increases the electron density on the N-atom. Thus, p-toluidine is more basic than aniline. $-NO_2$ group decreases the electron density over the N-atom in p-nitroaniline. Thus, p-nitroaniline is less basic than aniline.

b) In increasing order of basic strength $C_6H_5NH_2$,$C_6H_5NHCH_3$,p-Cl-$C_6H_4NH_2$,

i) Chlorine atom has both - I effect and + R effect so para chloro aniline is less basic than aniline

CH_3- group is electron donating group in so increases electron density in N - atom so, N - Methyl aniline is more basic than aniline

$$p\text{-}Cl\text{-}C_6H_4NH_2 < C_6H_5NH_2 < C_6H_5NHCH_3$$

iii. In decreasing order of basic strength in gas phase

$C_2H_5NH_2$, $(C_2H_5)_2NH$,$(C_2H_5)_3N$ and NH_3

In gas phase there is no hydrogen bonding , therefore stabalisation due to hydrogen bonding is not there. Therfore the only effect to determine the strength is the inductive effect.The +I effect increases with increase in the alkyl group.Therefore the basic strength will be the highest in $(C_2H_5)_3N$ and least in NH_3. Therefore the decreasing order of basic strength in gas phase will be

$$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$$

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iv. In increasing order of boiling point C_6H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

The elcetronegativity of O is more than N. Therefore C_6H_5OH forms hydrogen bonding and because of the hydrogen bonding the alcohols will have higher boiling point than the amines with comparable molecular mass.Now between $(CH_3)_2NH$ and $C_2H_5NH_2$, $C_2H_5NH_2$ has more hydrogen atom attached the Nitrogen.Therfore the extent of hydrogen bonding will be more in primary amines i.e $C_2H_5NH_2$ as compared to sec or ter amines.Therfore $C_2H_5NH_2$ will have higher boiling point as compared to $(CH_3)_2NH$ .Therefore the increasing order of boiling point will be as given below.

Ans: $(CH_3)_2NH < C_2H_5NH_2 < C_6H_5OH$

v. In decreasing order of the pKb values $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and CH_3NH_2

Larger the value of Kb or smaller the value of pKb , stronger is the base.

(i) In $C_2H_5NH_2$, only one $-C_2H_5$ group is present while in $(C_2H_5)_2NH$, two $-C_2H_5$ groups are present. Thus, the +I effect is more in $(C_2H_5)_2NH$ than in $C_2H_5NH_2$. Therefore, the electron density over the N-atom is more in $(C_2H_5)_2NH$ than in $C_2H_5NH_2$. Hence, $(C_2H_5)_2NH$ is more basic than$C_2H_5NH_2$.

ii) In $C_6H_5NHCH_3$ is less basic than $((C_2H_5)_2NH$ and $C_2H_5NH_2$ due to the delocalization of the lone pair in the former two. Further, among $C_6H_5NHCH_3$ the former will be more basic due to the +I effect of $-CH_3$ group. Hence, the order of increasing basicity of the given compounds is as follows:

$C_6H_5NHCH_3 < CH_3NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$

We know that the higher the basic strength, the lower is the pKb values.

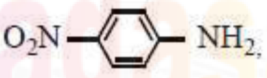
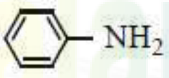
$C_6H_5NHCH_3 > CH_3NH_2 > C_2H_5NH_2 > (C_2H_5)_2NH$

vi. Increasing order of basic strength $C_6H_5NH_2$,$C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

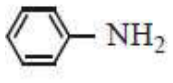
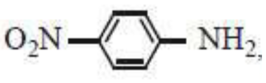
$C_6H_5N(CH_3)_2$ is more basic than $C_6H_5NH_2$ due to the presence of the + I effect of two - CH_3 group in $C_6H_5N(CH_3)_2$ Further CH_3NH_2 contains one - CH_3 group while $(C_2H_5)_2NH$ contains two - C_2H_5 group. Thus, $(C_2H_5)_2NH$ is more basic than CH_3NH_2
Now $C_6H_5N(CH_3)_2$ is less basic than CH_3NH_2 because of the - R effect of - C_6H_5 group.
Hence, the increasing order of the basic strength of the given compounds is as follows

$C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

vii. In decreasing order of basic strength

$CH_3CH_2NH_2$   , $CH_3 - NH_2$.

Aliphatic amines are more basic than aromatic amines.so $CH_3CH_2NH_2$and$CH_3 - NH_2$ are more basic .
$CH_3CH_2NH_2$ is more +I effect than $CH_3 - NH_2$, so $CH_3CH_2NH_2$ more basic than $CH_3 - NH_2$
In case of substituted aniline, electron withdrawing group like - NO_2, they have both - R effect as well as - I effect . as result all nitro amines are weaker bases than aniline .

$CH_3CH_2NH_2 > CH_3 - NH_2 >$  > 

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10. **How will you prepare propan -1- amine from butane nitrile**
i) butane nitrile **ii) propanamide** **ii) 1- nitropropane**

i) Butane nitrile converted into propan -1- amine

$CH_3-CH_2-CH_2CN \xrightarrow{H^+/Hydrolysis} CH_3-CH_2-CH_2CONH_2 \xrightarrow{Br_2/KOH} CH_3-CH_2-CH_2NH_2$

ii) propanamide converted into propan -1- amine Hoffmann's degradation

$CH_3-CH_2-CONH_2 \xrightarrow{LiAlH_4/H_2O} CH_3-CH_2-CH_2NH_2$

iii) 1- nitropropane converted into propan -1- amine

$CH_3-CH_2-CH_2NO_2 \xrightarrow{Sn/HCl} CH_3-CH_2-CH_2NH_2 + 2H_2O$

11. Identify A,B,C and D

$CH_3-NO_2 \xrightarrow[6[H]]{LiAlH_4} CH_3NH_2 \rightarrow \xrightarrow{HNO_2} + CH_3-CH_2-NH-CH_3 \xrightarrow{CH_3-CH_2Br_2}$

$(CH_3-CH_2)_2N-CH_3 \xrightarrow{H_2SO_4} [(CH_3-CH_2)_2NH^+-CH_3]HSO_4^-$

A - Methyl amine **B - N -Metyl ethan-1- amine**
C - N,N-diethylmethylamine **D - Quarternary ammonium hydrogen sulphate**

12. How will you convert diethylamine into
i) N,N-diethylacetamide **ii) N- nitrosodiethylamine**

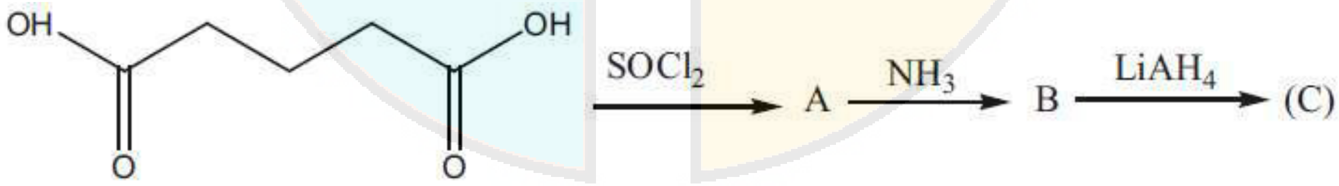
i) Conversion of diethylamine into N,N-diethylacetamide

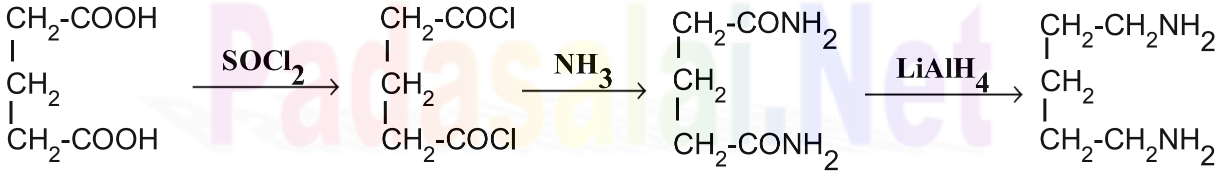
$(CH_3-CH_2)_2N-H + CH_3COCl \xrightarrow{pyridine} (CH_3-CH_2)_2N-CO-CH_3 + HCl$

ii) Conversion of diethylamine into N- nitrosodiethylamine

$(CH_3-CH_2)_2N-H \xrightarrow{HNO_2} (CH_3-CH_2)_2N-N=O$ (N-nitrosodiethylamine)

13. Indentify A,B and C





$$\begin{matrix} CH_2-COOH \\ | \\ CH_2 \\ | \\ CH_2-COOH \end{matrix} \xrightarrow{SOCl_2} \begin{matrix} CH_2-COCl \\ | \\ CH_2 \\ | \\ CH_2-COCl \end{matrix} \xrightarrow{NH_3} \begin{matrix} CH_2-CONH_2 \\ | \\ CH_2 \\ | \\ CH_2-CONH_2 \end{matrix} \xrightarrow{LiAlH_4} \begin{matrix} CH_2-CH_2NH_2 \\ | \\ CH_2 \\ | \\ CH_2-CH_2NH_2 \end{matrix}$$

glutaric acid A B C

A- Glutaryl chloride

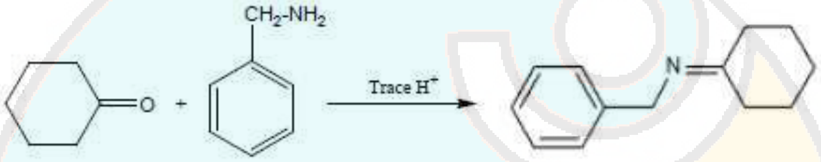
B -Pentanediamide (Glutaramide)

C-1,5 - diaminopentane

14. Indentify A,B,C and D

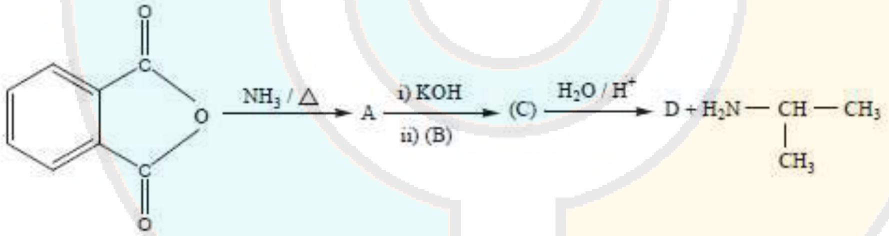
aniline + benzaldehyde → A $\xrightarrow{\text{Conc HNO}_3/\text{ B}}$ C and D

15. Complete the following reaction

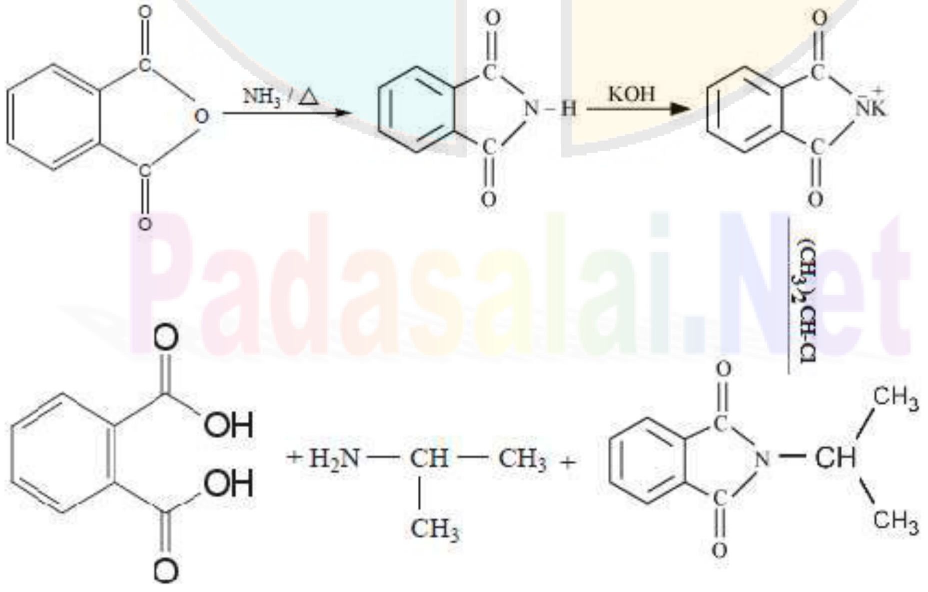


N-benzyl cyclo hexane imine

16. Predict A,B,C and D for the following reaction



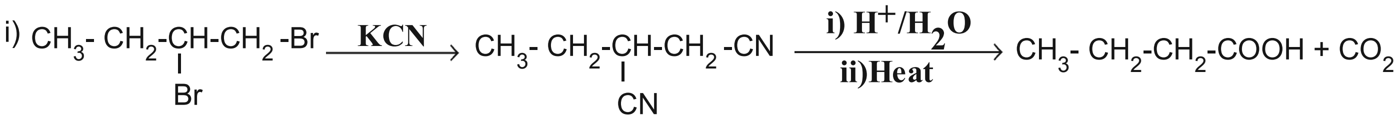
Ans:



A- phthalimide **B - 2 -Chloropropane**

C- N- isopropyl phthalimide **D- phthalic acid**

17. A dibromo derivative (A) on treatment with KCN followed by acid hydrolysis and heating gives a monobasic acid (B) along with liberation of CO_2. (B) on heating with liquid ammoniafollowed by treating with Br_2 /KOH gives (c) which on treating with $NaNO_2$ and HCl at low temperature followed by oxidation gives a monobasic acid (D) having molecular mass 74.Identify A to D.


i) $CH_3-CH_2-\underset{\displaystyle Br}{CH}-CH_2-Br \xrightarrow{KCN} CH_3-CH_2-\underset{\displaystyle CN}{CH}-CH_2-CN \xrightarrow[ii)Heat]{i)\ H^+/H_2O} CH_3-CH_2-CH_2-COOH + CO_2$

ii) $CH_3-CH_2-CH_2-COOH + NH_{3\ (lig)} \xrightarrow{Heat} CH_3-CH_2-CH_2-CONH_2 \xrightarrow{Br_2/KOH} CH_3-CH_2-CH_2-CONH_2$

iii) $CH_3-CH_2-CH_2-CONH_2 \xrightarrow[Low\ T]{NaNO_2/HCl} CH_3-CH_2-CH_2-OH \xrightarrow[2(O)]{K_2Cr_2O_7/H^+} CH_3-CH_2-COOH$

A - 1,2 - diamino butane

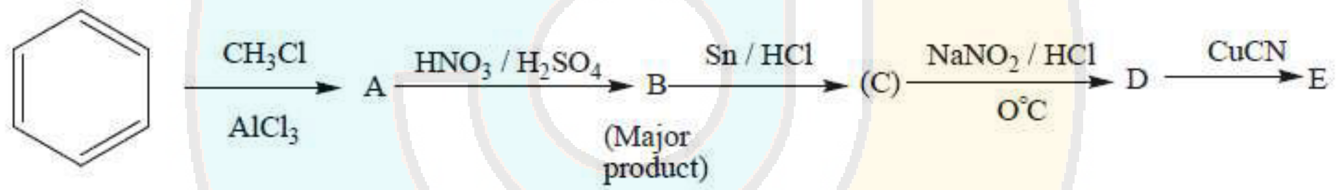
B- 1,2 dicyano butane

C- 1 - amino prpane

D - Propanoic acid

Molecular mass of propanoic acid - 74

18. Indentify A to E in the following frequency of reactions.



Ans:

A - Toluene

B- p- nitro benzene

C- p- toluidine

D - p- toluene diazonium salt

E - p- cyano toluene

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UNIT - 14

BIOMOLECULES

1. What type of linkages hold together monomers of DNA?

Monomer of DNA are held together by phosphodiester linkage.

2. Give the differences between primary and secondary structure of proteins.

Primary structure of proteins:

Proteins are polypeptide chains made up of amino acids connected through peptide bonds.The relative arrangement of the amino acids in the polypeptide chain is called the primary structure of the protein.

Secondary structure of proteins:

The amino acids in the polypeptide chain forms highly regular shapes (sub-structures) through the hydrogen bond between the carbonyl oxygen (-C=O) and the neighbouring amine hydrogen (-NH)of the main chain.α-Helix and β-strands or sheets are two most common substructures formed by proteins.

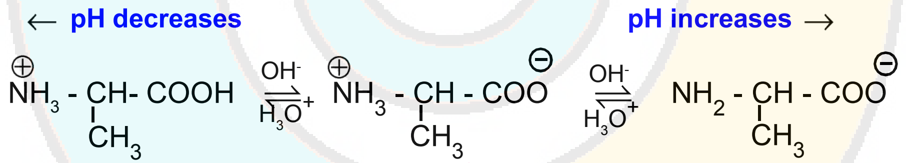
3. Name the Vitamins whose deficiency cause i) rickets ii) scurvy

i) rickets (children) - deficiency of vitamin D

ii) scurvy (bleeding gums) - deficiency of vitamin C

4. Write the Zwitter ion structure of alanine

It contains an amine group and a carboxylic acid group, both attached to the central carbon atom which also carries a methyl group side chain. Under biological conditions, it exists in its zwitterionic form with its amine group protonated (as $-NH_3^+$) and its carboxyl group deprotonated (as $-COO^-$).



$$\overset{\oplus}{N}H_3-\underset{|\atop CH_3}{CH}-COOH \underset{H_3O^+}{\overset{OH^-}{\rightleftharpoons}} \overset{\oplus}{N}H_3-\underset{|\atop CH_3}{CH}-CO\overset{\ominus}{O} \underset{H_3O^+}{\overset{OH^-}{\rightleftharpoons}} NH_2-\underset{|\atop CH_3}{CH}-CO\overset{\ominus}{O}$$

Alanine at pH < 6 (charge = +1)

Zwitterion of Alanine pH = 0 (charge = 0)

Alanine at pH > 6 (charge = -1)

5. Give any three difference between DNA and RNA

DNA	RNA
1. It is mainly present in nucleus, mitochondria and chloroplast	1. It is mainly present in cytoplasm, nucleolus and ribosomes
2. It contains deoxyribose sugar	2. It contains ribose sugar
3. Base pair A = T. G ≡ C	3. Base pair A = U. C≡ G
4. Double stranded molecules	4. Single stranded molecules
5. It's life time is high	5. It is Short lived
6. It is stable and not hydrolysed easily by alkalis	6. It is unstable and hydrolyzed easily by alkaliss
7. It can replicate itself	7. It cannot replicate itself. It is formed from DNA

6. **Write a short note on peptide bond**

The amino acids are linked covalently by peptide bonds. The carboxyl group of the first amino acid react with the amino group of the second amino acid to give an amide linkage between these amino acids. This amide linkage is called **peptide bond**.

7. **Give two difference between Hormones and vitamins**

Vitamin:

1. Vitamins are synthesized in plants and taken by animals cheifle through diet.
2. Chemically these are various compounds like esters, organic acids, etc.
3. Mostly these are coenzymes or a constituents of coenzymes.
4. Vitamins have catalyc action.
5. Their deficiency causes specific deficiency disease(symptom).

Hormone:

1. Hormones are secreted mostly by endrocrine glands and some by neurosecretory cells of animals.
2. These are water soluble amino acids and polypeptides or fat soluble steroids.
3. Mostly these are excitatory, sometimes inhibitory but never act as coenzyme.“
4. Hormones directly influence gene expressions.
5. Deficiency causes metabolic disorder.

8. **Write a note on denaturation of proteins**

Each protein has a unique three-dimensional structure formed by interactions such as disulphide bond, hydrogen bond, hydrophobic and electrostatic interactions. These interactions can bedisturbed when the protein is exposed to a higher temperature, certain chemicals such as urea,alteration of pH, ionic strength etc., It leads to the loss of the three-dimensional structure partially or completely. The process of a protein-losing its higher order structure without losing the primary structure, it called denaturation.

9. **What are reducing and non – reducing sugars?**

Reducing Sugars-

Reducing sugar is a saccharide that is capable of acting as a reducing agent because it has a free aldehyde or ketone group.

The Saccharide which reduces Fehling’s solution , Benedict’s solution & Tollen’s reagent are called reducing sugars.

Example-

All Monosaccharide are reducing sugars like D-Glucose, D-Fructose, Disaccharides -Maltose & Lactose

Non Reducing Sugars-

The Saccharides which do not reduce Fehling’s solution, Benedict’s solution & Tollen’s reagent are called Non reducing sugars.

a) Non reducing sugars do not contain free -CHO group or >C=O group on the carbon adjacent to >C=O group.

b) Cyclic form of non reducing sugars can not be opened into an open chain having free >C=O group.

Example-

All PolySaccharides are non reducing sugars (like starch, cellulose). Sucrose (disaccharide) is also non reducing sugar because anomeric carbon of both the mono saccharides are involved in glyco side or acetal formation.

10. Why carbohydrates are generally optically active.

Not all carbohydrates are optically active. Generally the monosacchrides are optically active. This is because they contain chiral carbon atoms, and chilrality results in optical activity.

11. Classify the following into monosaccharides, oligosaccharides and polysaccharides.

i) Starch ii) fructose iii) sucrose iv) lactose iv) maltose

i) Starch - **polysaccharides.**

ii) fructose - **monosaccharides,**

iii) sucrose - **oligosaccharides(**disaccharide)

iv) lactose **-** **oligosaccharides (**disaccharide)

iv) maltose - **oligosaccharides(**disaccharide)

12. How are vitamins classified

There are 13 universally recognized vitamins - A, B complex which contains B_1, B_2, B_3, B_5, B_6, B_7, B_9 & B_{12}, vitamin C, D, E & K.

All of these 13 universally recognized vitamins are categorized into **2 types** based on their solubility- fat soluble and water soluble.

Fat-soluble vitamins are- Vitamin A, Vitamin D, Vitamin E & Vitamin K. These vitamins are easily stored in fatty tissues & liver.

Water-soluble vitamins like Vitamin B complex & Vitamin C does not stay in the body for long. Be cause of their water solubility, they are easily excreted via urine.

13. What are harmones? Give examples

Hormone is an organic substance (e.g. a peptide or a steroid) that is secreted by one tissue. it limits the blood stream and induces a physiological response (e.g. growth and metabolism) in other tissues. It is an intercellular signalling molecule.

1.Chemically, hormones may be classified as

i) protein (e.g. insulin, epinephrine) ii) steroids (e.g. estrogen, androgen).

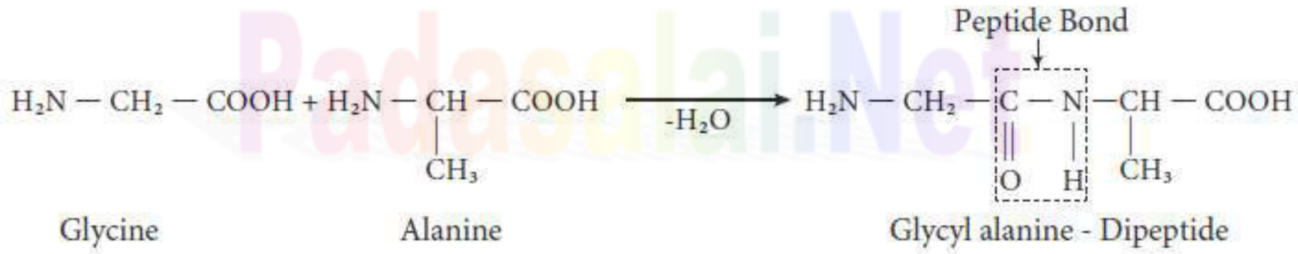
2.Hormones are classified according to the distance over which they act as,

Endocrine hormones - insulin

Paracrine hormones -interleukin-1 (IL-1)

Autocrine hormones -interleukin-2 (IL-2).

14. Write the structure of all possible dipeptides which can be obtained form glycine and alanine



$$H_2N-CH_2-COOH + H_2N-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH \xrightarrow{-H_2O} H_2N-CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-\underset{\displaystyle H}{\underset{|}{N}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$$

15. Define enzymes

There are many biochemical reactions that occur in our living cells. Digestion of food and harvesting the energy from them, and synthesis of necessary molecules required for various cellular functions are examples for such reactions. All these reactions are catalysed by special proteins called enzymes

Enzymes are biocatalysts that catalyse a specific biochemical reaction.

16. Writhe the structure of α-D (+) glucophyranose

α-D (+) glucophyranose

α-D-glucopyranose
(α-D-glucose)

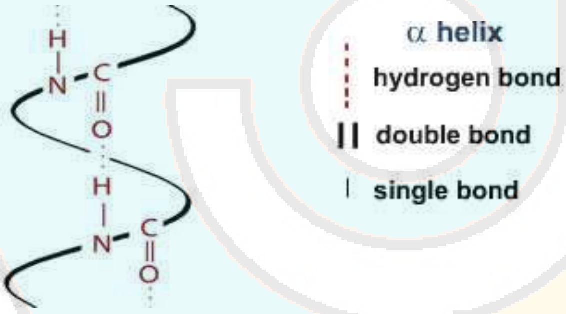
17. What are different types of RNA which are found

RNA molecules are classified according to their structure and function into three major types

i. Ribosomal RNA (rRNA) :	Ribosomes are the sites at which protein synthesis takes place .
ii. Messenger RNA (mRNA):	The function of tRNA is to carry amino acids to the sites of protein synthesis on ribosomes.
iii. Transfer RNA (tRNA) :	mRNA carries genetic information from DNA to the ribosomes for protein synthesis.

18. Write a note on formation of α-helix .

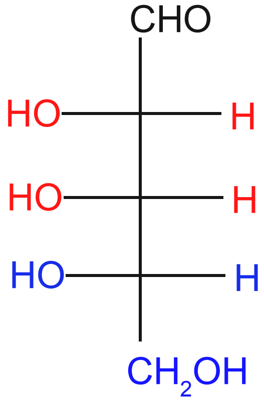
An a-helix is a right-handed coil of amino-acid residues on a polypeptide chain, typically ranging between 4 and 40 residues. This coil is held together by hydrogen bonds between the oxygen of C=O on top coil and the hydrogen of N-H on the bottom coil. Such a hydrogen bond is formed exactly every 4 amino acid residues, and every complete turn of the helix is only 3.6 amino acid residues.



19. What are the functions of lipids in living organism.

1. Lipids are the integral component of cell membrane.They are necessary of structural integrity of the cell.
2. The main function of triglycerides in animals is as an energy reserve. They yield more energy than carbohydrates and proteins.
3. They act as protective coating in aquatic organisms.
4. Lipids of connective tissue give protection to internal organs.
5. Lipids help in the absorption and transport of fat soluble vitamins.
6. They are essential for activation of enzymes such as lipases.
7. Lipids act as emulsifier in fat metabolism.

20. Is the following sugar, D – sugar or L – sugar?



Ans: L – sugar (L-Ribose)

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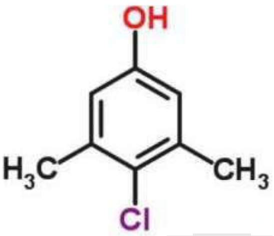
1. **Which chemical is responsible for the antiseptic properties of dettol.**

   The two main constituents of dettol composition for its antiseptic property are Chloroxylenol & Terpineol. But among these two Chloroxylenol plays more important role. It is also known as para-chloro-meta-xylenol, is an antiseptic and disinfectant which is used for skin disinfection and cleaning surgical instruments.



2. **What are antibiotics?**

   Antibiotics are medicines used to treat infections that are caused by bacteria (germs).Antibiotics cannot treat infections caused by viruses (such as colds and the flu).

   Taking antibiotics when you don't need them, like for a cold or flu, is a waste and will not help you get better.

   Penicillins - for example, phenoxymethylpenicillin, flucloxacillin and amoxicillin.

   Cephalosporins - for example, cefaclor, cefadroxil and cefalexin.

   Tetracyclines - for example, tetracycline, doxycycline and lymecycline

3. **Name one substance which can act as both analgesic and antiphyretic**

   Aspirin (Acetyl salicylic acid) is a chemical substance which lowers body temperature and reduces pain as well. Therefore it acts both as analgesic and antipyretic

4. **Write a note on synthetic detergents**

   Synthetic detergents are formulated products containing either sodium salts of alkyl hydrogen sulphates or sodium salts of long chain alkyl benzene sulphonic acids. There are three types of detergents.

   Anionic detergent - Sodium Lauryl sulphate (SDS)

   Cationic detergent - n-hexaadecyltrimethyl ammonium chloride

   Non-ionic detergent - (Pentaerythrityl stearate) 3-hydroxy-2,2-bis(hydroxymethyl)propyl heptanoate

5. **How do antiseptics differ from disinfectants?**

   Antiseptics

   Stop or slow down the growth of microorganisms .Applied to living tissue such as wounds, cuts, blurs and diseased surfaces

   Examples: povidone-iodine,benzalkonium chloride,Dettol

   Disinfectants

   Stop or slow down the growth of microorganisms .Generally used on inanimate objects

   Examples:Chlorine compounds, alcohol

   Chloride in the concentration of 0.2 to 0.4 ppm in aqueous solution and SO2 in very low concentration are disinfectants.,Hydrogen peroxide.

6. **What are food preservatives?**

   Preservatives are capable of inhibiting, retarding or arresting the process of fermentation,

   acidification or other decomposition of food by growth of microorganisms.

   Examples

   Acetic acid is used mainly as a preservative for the preparation of pickles and for preserved vegetables.

   Sodium metasulphite is used as preservatives for fresh vegetables and fruits.

7. **Who do soaps not work in hard water?**

Hard water contains calcium and magnesium ions. When soaps are dissolved in hard water, these ions displace sodium or potassium from their salts and form insoluble calcium or magnesium salts of fatty acids. These insoluble salts separate as scum. This is the reason why soaps do not work in hard water.

8. **What are drugs? How are they classified**

drug is any substance (with the exception of food and water) which, when taken into the body, alters the body’s function either physically and/or psychologically. Drugs may be legal (e.g. alcohol, caffeine and tobacco) or illegal (e.g. cannabis, ecstasy, cocaine and heroin).

Psychoactive drugs affect the central nervous system and alter a person's mood, thinking and behaviour.Psychoactive drugs may be divided into four categories: depressants, stimulants, hallucinogens and 'other'.

Classification of drugs:

i)Classification based on the chemical structure:

In this classification, drugs with a common chemical skeleton are classified into a single group.

For example, ampicillin, amoxicillin, methiceillinetc..

ii) Classification based on Pharmacological effect:

In this classification, the drugs are grouped based on their biological effect that they produce on the recipient.

For example, the medicines that have the ability to kill the pathogenicbacteria are grouped as antibiotics.

Examples:Antibiotic drugs: amoxicillin, ampicillin,cefixime, cefpodoxime, erythromycin, tetracycline etc..

Antihypertensive drugs: propranolol, atenolol, metoprolol succinate, amlodipine etc

iii)Classification based on the target system (drug action):

In this classification, the drugs are grouped based on the biological system/process, that they target in the recipient

For example, the antibiotics streptomycin and erythromycin inhibit the protein synthesis (target process) in bacteria and are classified in a same group. However, their mode of action is different.

iv)Classification based on the site of action (molecular target):

The drug molecule interacts with biomolecules such as enzymes, receptors etc,, which are referred as drug targets. We can classify the drug based on the drug target with which it binds. This classification is highly specific compared to the others. These compounds often have a common mechanism of action, as the target is the same

9. **How the tranquilizers work in body.**

Acts on the central nervous system by blocking the neurotransmitter dopamine in the brain.

Tranquilizers

They are neurologically activedrugs.

Major tranquilizers: Haloperidol,clozapine

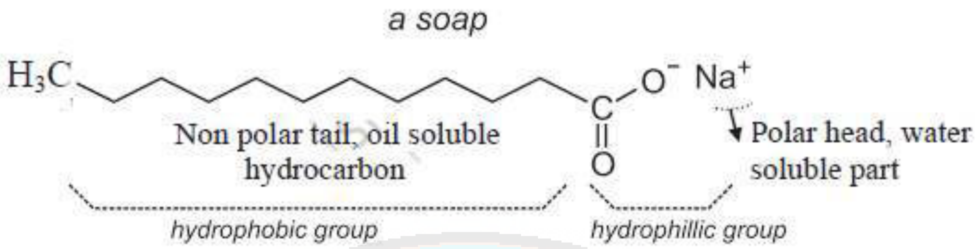
Minor tranquilizers:Diazepam (Valium),alprazolam

10. **Write the structural formula of aspirin.**

11. Explain the mechanism of cleansing action of soaps and detergents

The cleansing action of soap:

To understand how a soap works as a cleansing agent, let us consider sodium palmitate an example of a soap. The cleansing action of soap is directly related to the structure of carboxylate ions (palmitate ion) present in soap. The structure of palmitate exhibit dual polarity. The hydrocarbon portion is non polar and the carboxyl portion is polar.

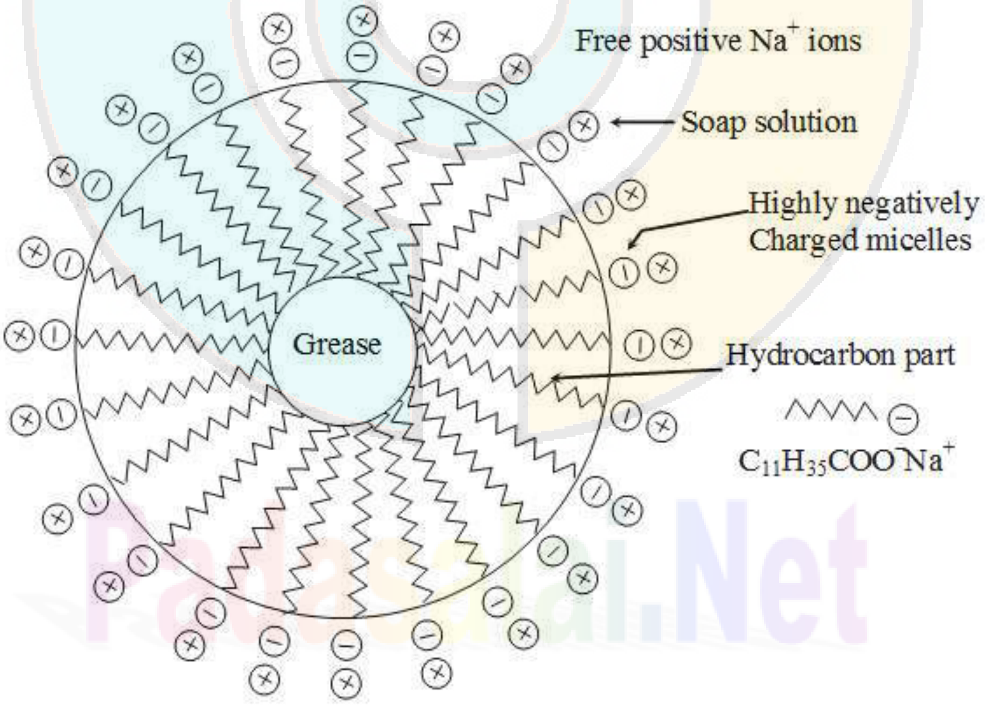


The nonpolar portion is hydrophobic while the polar end is hydrophilic. The hydrophobic hydro carbon portion is soluble in oils and greases, but not in water. The hydrophilic carboxylate group is soluble in water

When thesoap is added to an oily or greasy part of the cloth, the hydrocarbon part of the soap dissolve in the grease, leaving the negatively charged carboxylate end exposed on the grease surface.

Formation of micelles

At the same time the negatively charged carboxylate groups are strongly attracted by water, thus leading to the formation of small droplets called micelles and grease is floated away from the solid object. When the water is rinsed away, the grease goes with it.



Cleansing action of soap. Soap micelle entraps the oily dirt particle

The micelles do not combine into large drops because their surfaces are all negatively charged and repel each other. The cleansing ability of a soap depends upon its tendency to act as a emulsifying agent between water and water insoluble greases.

Detergents: Detergents are superior to soaps as they can be used even in hard water and in acidic conditions. The cleansing action of detergents are similar to the cleansing action of soaps.

12. **Which sweetening agent are used to prepare sweets for a diabetic patient?**

Name a sweetening agent used in the preparation of sweets for a diabetic patient.

Artificial sweetening agents such as

saccharin, alitame, and aspartame

can be used in preparing sweets for diabetic patients**.**

13. **What are narcotic and non . narcotic drugs. Give examples**

Analgesics are two types

I) **Narcotic :** are drugs that are naturally derived from opium (or) produce effects like opium that are highly addictive.

Mode of action: They alleviate pain by reducing local inflammatory responses

Examples: Morphine, codeine

Non-narcotic analgesics are medications used to control pain and inflammation. They are available at drugstores without a prescription or by prescription when given at higher doses

Mode of action: Relive pain and produce sleep. These drugs are addictive. In poisonous

dose,these produces coma and ultimately death.

Examples Tylenol (chemical name: acetaminophen);

non-steroidal anti-inflammatory drugs (NSAIDs) such as aspirin, Motrin, or Advil (chemical name: ibuprofen); and Aleve or Naprosyn (chemical name: naproxen sodium)

14. **What are anti fertility drugs? Give examples.**

Antifertility drugs are chemical substances which suppress the action of hormones that promote pregnancy. Antifertility drugs are made up of derivatives of synthetic progesterone or a combination of derivatives of estrogen and progesterone.

Example :Acetaminophen or paracetamol,Ibuprofen, Asprin.Norethindrone .

15. **Write a note on co.polymer.**

Co-polymers:

A polymer containing two or more different kinds of monomer units is called a copolymer.

For example, SBR rubber(Buna-S) contains styrene and butadiene monomer units. Co-polymers have properties quite different from the homopolymers.

16. **What are bio degradable polymers? Give examples.**

The materials that are readily decomposed by microorganisms in the environment are called biodegradable

examples. examples of aliphatic biodegradable polymers are polyglycolic acid(PGA),

Polyhydroxy butyrate (PHB),

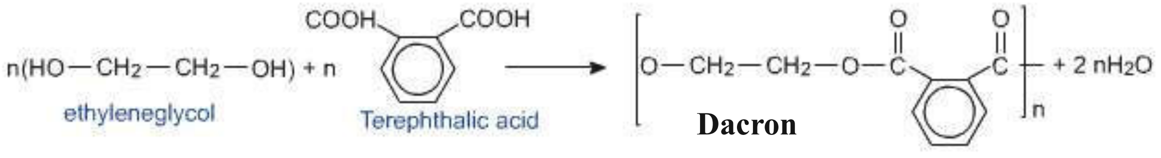
Polyhydroxy butyrates-co-beta hydroxyl valerate(PHBV),

Polycaprolactone(PCL),

Nylon-2-nylon-6

17. **How is terylene prepared?**

The monomers are ethylene glycol and terepathalic acid (or) dimethylterephthalate. When these monomers are mixed and heated at 500K in the presence of zinc acetate and antimony trioxide ca



18.Write a note on vulcanization of rubber

Natural rubber is mixed with 3-5% sulphur and heated at 100-150¢ªC causes cross linking of the cis-1,4-polyisoprene chains through disulphide (-S-S-) bonds.

The physical properties:

The rubber can be altered by controlling the amount of sulphur that is used for vulcanization. In sulphur rubber, made with about 1 to 3% sulphur is soft and stretchy. When 3 to 10% sulphur is used the resultant rubber is somewhat harder but flexible.

19. Classify the following as linear, branched or cross linked polymers

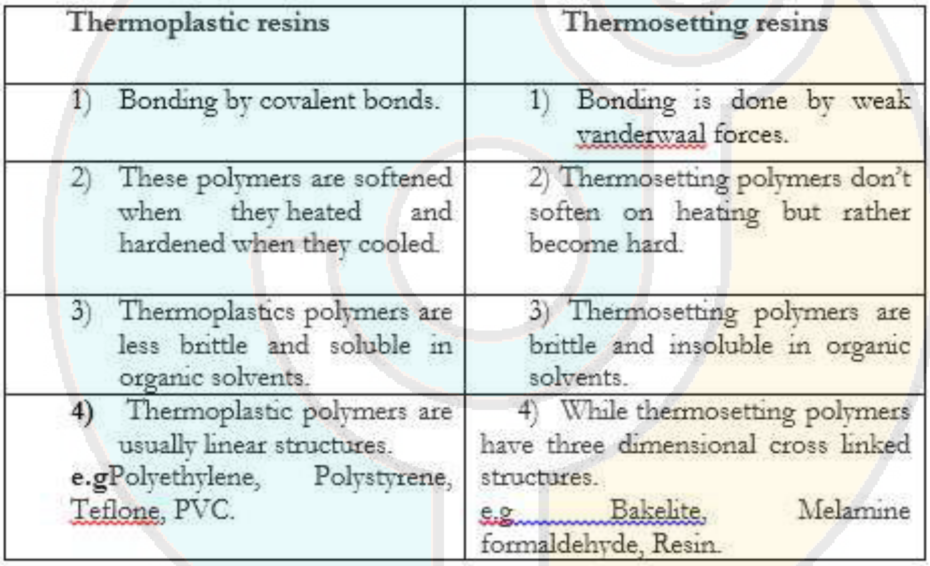
a) Bakelite **b) Nylon** **c) polythene**

Ans **a) Bakelite -** . Cross linked or Network polymers

b) Nylon - Linear polymers

c) polythene - Linear polymers

20. Differentiate thermoplastic and thermosetting.



Thermoplastic resins	Thermosetting resins
1) Bonding by covalent bonds.	1) Bonding is done by weak vanderwaal forces.
2) These polymers are softened when they heated and hardened when they cooled.	2) Thermosetting polymers don't soften on heating but rather become hard.
3) Thermoplastics polymers are less brittle and soluble in organic solvents.	3) Thermosetting polymers are brittle and insoluble in organic solvents.
4) Thermoplastic polymers are usually linear structures. **e.g**Polyethylene, Polystyrene, Teflone, PVC.	4) While thermosetting polymers have three dimensional cross linked structures. e.g Bakelite, Melamine formaldehyde, Resin.

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