

B. Tech All Branches (Sem-1)

Chemistry - I

Subject code: BTCH -101-18

M. Code: 75343.

[Sem-1 (2020-21)]

(1)

(a) What do you understand by radial and angular wave-functions. How will you represent the complete wave function in terms of radial and angular wave function? Also write the relationship between Cartesian (x, y, z) coordinates and polar coordinates.

Solution: For an atomic system containing one electron (eg H_1 , He^+ etc). The wavefunction ψ is a solution of Schrodinger equation. It describes the behaviour of an electron in a region of space called an atomic orbital (ψ - phi). Each wave-function has two parts: the radial part which changes with distance from the nucleus and an angular part whose changes correspond to different shapes.

$$\psi_{xyz} = \psi_{\text{radial}}(r) \psi_{\text{angular}}(\varphi, \theta)$$

$$= R_{nl}(r) Y_{lm}(\varphi, \theta)$$

Radial wave-function:

The radial wavefunctions are of the general form:

$$R(r) = N p(r) e^{-kr}$$

where

N is a positive normalizing constant

$p(r)$ is a polynomial in r

$k =$ positive constant.

The exponential factor is always positive so the nodes and sign of $R(r)$ depends on the behaviour of

$p(r)$. Because the exponential factor has a negative sign in the exponent $R(r)$ will approach 0 as n goes to infinity.

ψ^2 quantifies the probability of the electron being at a particular point. Probability distribution $P(r)$ is the probability that the electron will be at any point that is r distance from the nucleus. For any type of orbital since $\Psi_{n,0,0}$ is separable into radial and angular components that are each approximately normalised and a sphere of radius r has area proportional to r^2 , we have;

$$P(r) = r^2 R^2(r)$$

(2) Angular wavefunction:

The angular wave function $Y(\theta, \phi)$ does much to give an orbital its distinctive shape.

$Y(\theta, \phi)$ is typically normalised so the integral of $Y^2(\theta, \phi)$ over

the unit sphere is equal to one. In this case, $\psi^2(\theta, \phi)$ serves as a probability function. It can be interpreted as the probability that the electron will be found on the ray emitting from the origin that is at angles (θ, ϕ) from the axes. The probability function can also be interpreted as the probability distribution of electron being at position (θ, ϕ) on a sphere of radius r , given that it is r distance from the nucleus.

→ The angular wave functions for a H_2 atom $\psi_{lm}(\theta, \phi)$ are also the wavefunction solutions to Schrodinger's equation for a rigid rotator consisting of two bodies, eg: diatomic molecule.

Representation of a complete wave-function:

Because the atomic orbitals are described with time independent potential V , Schrodinger equation can be solved using separation of variables, so any wave-function has the form:

$$\bar{\Psi}(r, \theta, \phi) = R(r) Y(\theta, \phi)$$

where $R(r)$ = radial wave function
 $Y(\theta, \phi)$ = angular wave function

$$Y(\theta, \phi) = \Theta(\theta) \Phi(\phi)$$

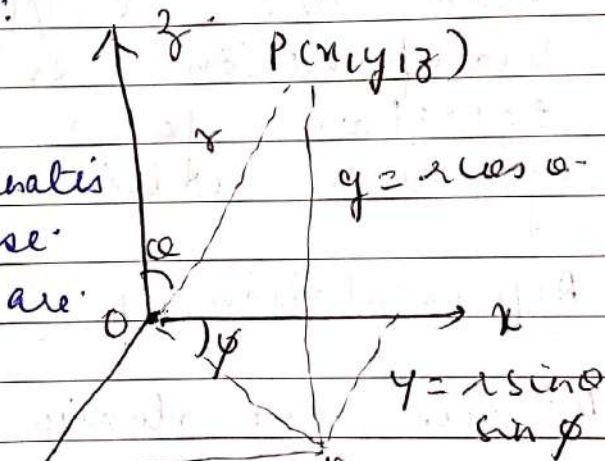
Each set of quantum numbers (n, l, m) describes a different wave-function. The radial wave function is only dependent on n and l , while the angular wave function is only dependent on l and m ; so a particular orbital solution can be written as:

$$\psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r) Y_{l,m}(\theta, \phi)$$

[complete wave-function]

Relationship between Cartesian and polar coordinates:

If (x, y, z) are the Cartesian coordinates of the point whose polar coordinates are (r, θ, ϕ) are:



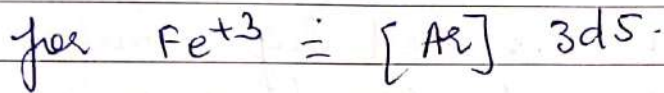
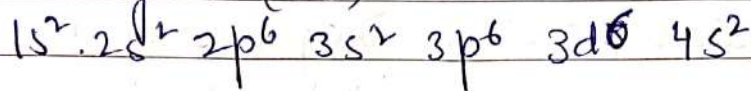
$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned}$$

(b) Calculate the spin magnetic moment for Fe^{+3} and Ni^{+2} ions. Which ion should exhibit larger magnetic moment?

Solu. The spin magnetic moment for:

(a) Fe^{+3} . = Electronic configuration.

of Fe (26) is:



Number of unpaired electron = 5

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

$$\mu = \sqrt{5 \times (5+2)}$$

$$= \sqrt{35} = 5.91 \text{ BM}$$

$\therefore \mu = 5.91 \text{ BM} \approx 6 \text{ BM}$. (approx)

(b) Ni^{+2}

Electronic configuration of $\text{Ni}^{+2} = [\text{Ar}] 3d^8 4s^0$.

No. of unpaired electrons = 2

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

$$= \sqrt{2 \times (2+2)}$$

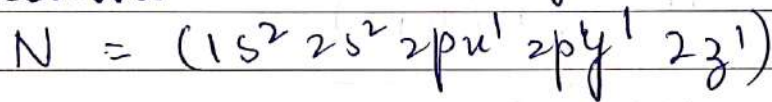
$$= \sqrt{2 \times 4} = \sqrt{8} = 2.83 \text{ BM}$$

Fe^{+3} has larger magnetic moment than Ni^{+2}

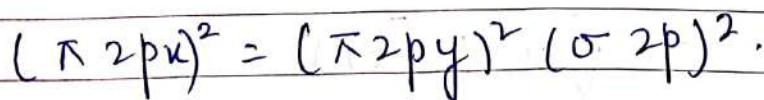
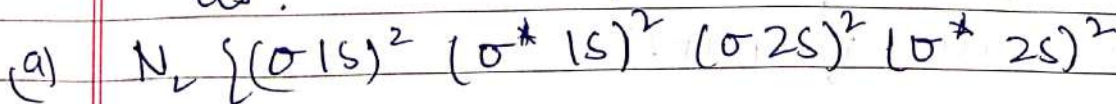
2) (a) Nitrogen molecule (N_2) is diamagnetic while oxygen molecule (O_2) is paramagnetic. Explain on the basis of molecular orbital theory and also draw their molecular orbital energy level diagrams.

Solu. Molecular orbital Diagram of N_2 molecule.

→ N_2 molecule is formed by combination of atomic orbitals of two nitrogen atoms each having seven electrons.



∴ No. of electrons in N_2 molecule = 14
 → These 14 electrons are filled in various molecular orbital in increasing order of their energies (Aufbau principle) and on the basis of Hund's rule and Pauli's exclusion principle i.e. 2 electrons of M.O must have opposite spins)
 so electronic configuration of N_2 molecule is:



(b) Bond order:

$$B.O \text{ for } N_2 \text{ molecule} = \frac{1}{2} [N_b - N_a]$$

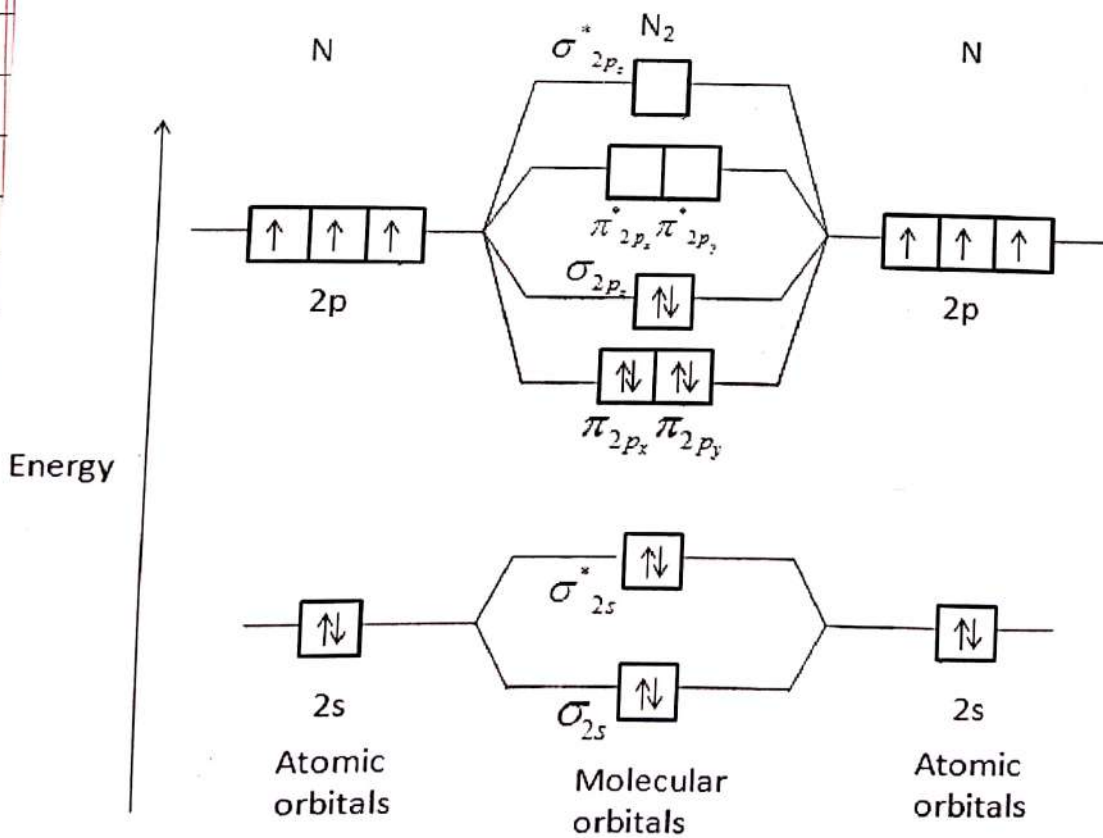
$$= \frac{1}{2} [8 - 2] = 3.$$

∴ 2 N atoms in N₂ molecule are linked by 3 covalent bonds. i.e. a triple bond (N≡N)

(3) Bond dissociation energy of N₂ molecule is 941.0 kJ/mole, which is more than oxygen ∴ N₂ molecule is highly stable.

(4) Bond length of N₂ = 109 pm.

(5) N₂ molecule is diamagnetic due to absence of unpaired electrons.

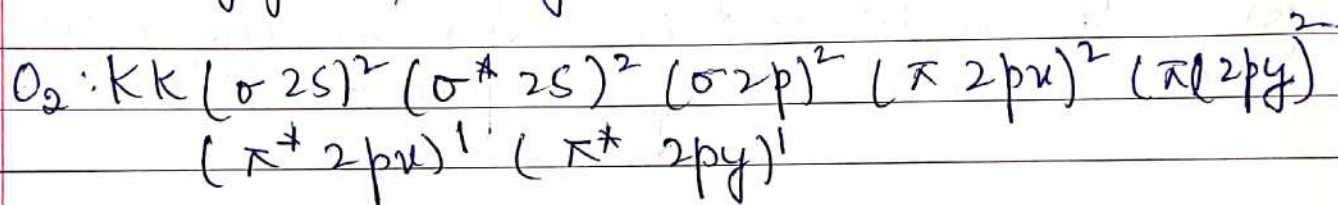


Molecular orbital Diagram of Nitrogen molecule paired e = diamagnetic

→ Molecular orbital diagram of oxygen molecule
 $O_8 : 1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

Each oxygen atom has eight electron \therefore there are 16 electrons in O_2 molecule. Due to the combination of atomic orbitals of 2 atoms, 10 Molecular orbitals are formed. These are filled in the increasing order of their energies (Aufbau principle)

The configuration of O_2 is:



Last two molecular orbital are half-filled due to Hund's rule.

\therefore from the above configuration we have;

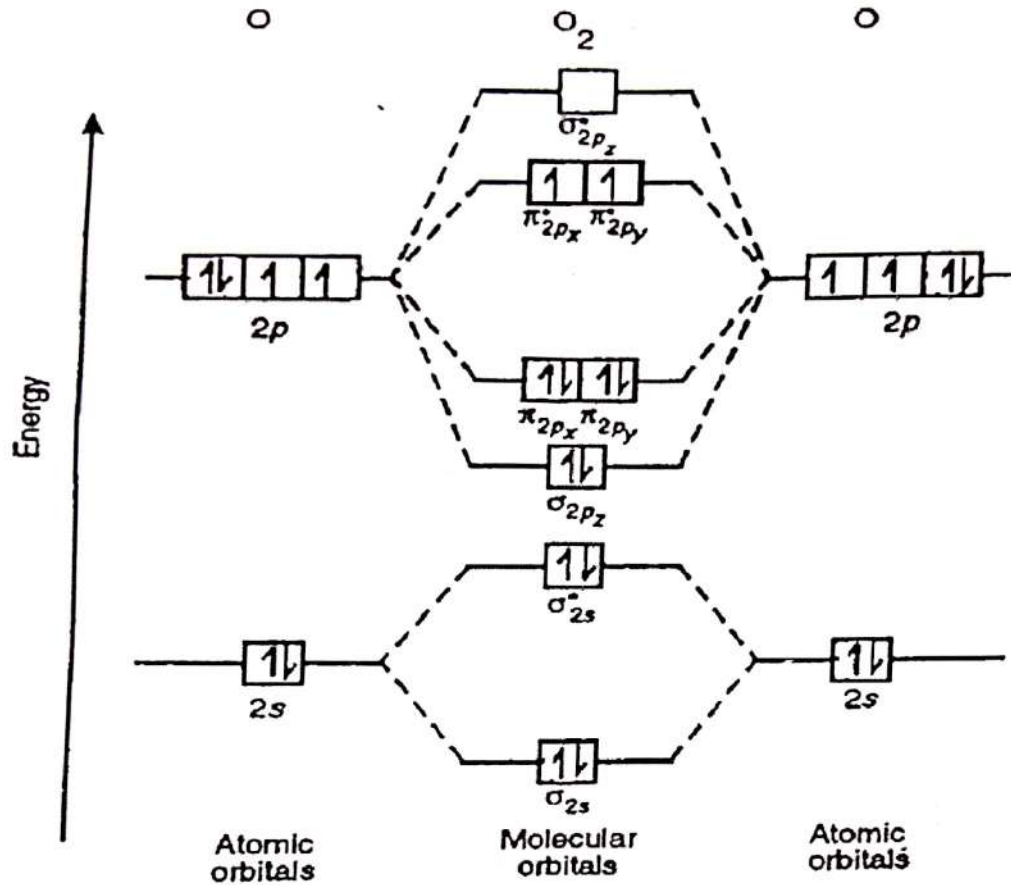
$$N_b = 10 \quad N_a = 6$$

$$\therefore \text{Bond order} = \frac{1}{2} (N_b - N_a) = \frac{1}{2} (10 - 4) = 3$$

Hence, there is triple bond in oxygen molecule.

Due to the presence of two unpaired electron. It is paramagnetic in nature.

Bond dissociation energy of O_2 is 490 kJ/mole and bond length is 121 pm. This is more than that of N_2 .



Molecular orbital Diagram of.

Oxygen.

unpaired electrons = paramagnetic.

(b) Explain the crystal field splitting in octahedral complexes. why the crystal field splitting in octahedral complexes is greater than that of the tetrahedral complexes.

Soln: Crystal field splitting in octahedral complexes. (C.N=6)

→ In such a complex, the metal ion (M^{n+}) is located at the center of octahedron. is surrounded by six ligands.

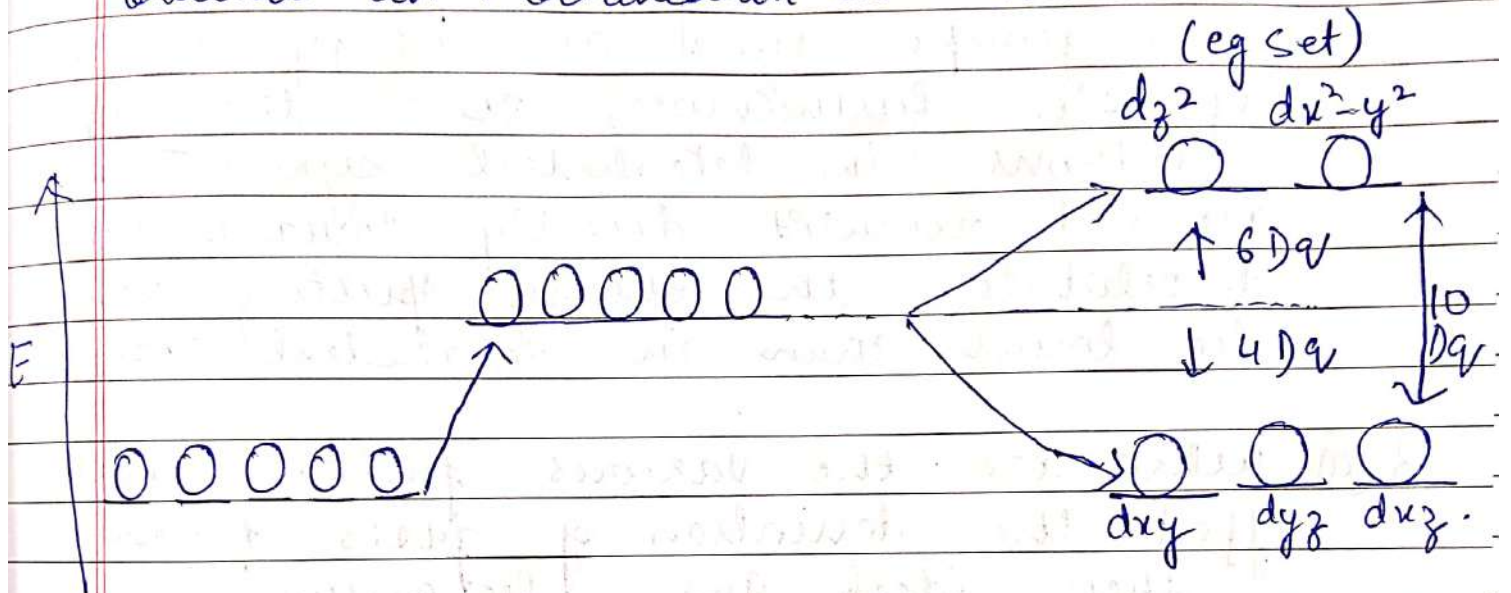
The six ligands in the octahedral field attack the metal ion along the six corners of the octahedron. The set of d-orbital, d_{z^2} and $d_{x^2-y^2}$ lie along the corners of the octahedron and hence they would experience greater repulsion from the attacking ligands than that of other set of d-orbitals d_{xy} , d_{yz} , d_{xz} orbitals.

The result is that, the set of d-orbitals d_{z^2} and $d_{x^2-y^2}$ are raised in higher energy than that of d-orbitals d_{xy} , d_{yz} and d_{xz} orbitals because it lie in between the axis of octahedron

thus set of five d-orbitals is split into two, consisting of three orbitals d_{xy} , d_{yz} and d_{xz} of lower energy

and other consisting of d_{z^2} and $d_{x^2-y^2}$ orbitals of high energy.

The resulting crystal field splitting of d-orbital in octahedron is shown as:



Splitting of d-orbital in octahedral complexes

→ The symbol 'eg' and 't_{2g}' = symbol for symmetry of two set of d-orbital.

The energy difference between two sets eg and t_{2g} of d-orbitals is called crystal field splitting. The magnitude of splitting is denoted by Δ_0 and Dq .

The decrease in energy due to preferential occupation of stable t_{2g} orbital is called CFSE. It can be calculated by:

$$CFSE = n(eg) (0.6 \Delta_0) - n(t_{2g}) (10.4 \Delta_0)$$

Why tetrahedral splitting is less than octahedral splitting?

In tetrahedral crystal field splitting, the d-orbitals again split into two groups, with an energy difference of Δ_{tet} . Furthermore, since the ligand electrons in tetrahedral symmetry are not oriented directly towards the d-orbitals, the energy splitting will be lower than in octahedral case.

3(a) What are the various factors that affect the deviation of gases from their ideal gas behaviour? Explain with reasons.

The real gases obey ideal gas equation $PV = nRT$ only if the pressure is low and the temperature is high. However, if the pressure is high or the temperature is low, the real gases show marked deviations from ideal behaviour.

The causes of deviation from ideal behaviour due to the following two assumptions of kinetic theory of gases.

(i) The volume occupied by gas molecules is negligibly small as compared to the volume occupied by gas =

(a) The force of attraction between gas molecules are negligible.

Reason 1: The first assumption is valid only at low pressure and high temperature, when the volume occupied by gas molecules is negligible as compared to the total volume of the gas. But at low temperature or at high pressure, the molecules being incompressible the volumes of molecules are no more negligible as compared to the total volume of gas.

Reason 2: The second assumption is not valid when the pressure is high and temperature is low. But at high pressure or low temperature when the total volume of gas is small, the force of attraction becomes appreciable and cannot be ignored.

b) How is Potential Energy surface (PES) used to describe the energy of a system? Classify the potential energy surfaces for chemical reaction? Also explain the PES for H_3^+ system.

Definition: A potential energy surface describes the energy of a system particularly a collection of atoms in terms of position of atoms. The surface might

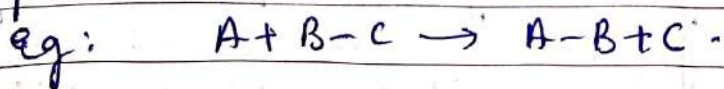
define the energy as a function of one or more coordinates. If there is only one coordinate, the surface is called a potential energy curve or energy profile.

For a system with two degrees of freedom (eg two bond lengths) the value of the energy is a function of two coordinates with respect to position.

In mathematics, the geometry of a set of atoms is described by a vector \vec{r} whose elements represent the atoms' positions. The vector \vec{r} could be the set of Cartesian coordinates of atoms, or could also be a set of interatomic distances and angles. When \vec{r} is given, the energy as a function of position $E(\vec{r})$ is the value of $E(\vec{r})$ for all r of interest. E gives the height of energy diagram.

(b) Classification of Potential Energy System:

Potential energy surfaces for chemical reaction can be classified as attractive or repulsive by comparing the extensions of bond lengths in activated complex relative to those of reactant and product.



The bond length extension for newly formed A-B bond is:

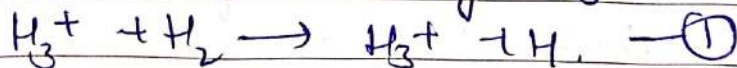
$$R^{\ddagger}_{AB} = R_{AB} - R^{\circ}_{AB}$$

Eg: the reaction: $K + Br_2 \rightarrow K-Br + Br$ in which the initial long range attraction of reactant leads to an activated complex resembling $K^{\ddagger} \cdots Br \cdots Br$. The vibrationally excited population of product molecule is detected by infrared chemiluminescence. This endothermic reaction is classified as 'attractive'.

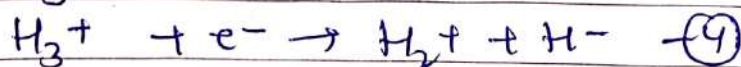
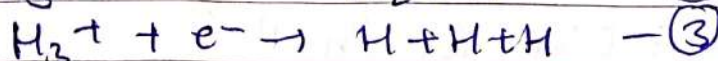
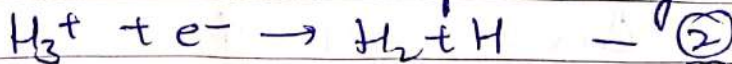
In contrast, the potential energy surface for the reaction $H + Cl_2 \rightarrow HCl + Cl$ is repulsive because $R^{\ddagger}_{HCl} < R^{\ddagger}_{ClCl}$ and the transition state is reached when the products are separating. For this reaction in which the atom H is lighter than Cl_2 and HCl, the reaction energy is released as translational K.E. of products.

Potential Energy Surface for H_3^+ system.

The formation reaction of H_3^+ ion is:



It is achieved in following 3 steps:

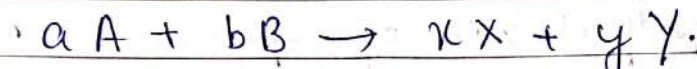


All the above 4 reactions are very fast and fragile equilibrium between them determines the amount of H_3^+ in interstellar spaces.

4(a) Derive the Nernst equation for the single electrode potential. Also give its various applications.

Derivation of Nernst equation for electrode potential and cell-EMF:

For a reversible cell rxn is:



free energy change of this rxn is:

$$\Delta G = \Delta G^\circ + RT \ln \frac{P}{R}.$$

$$\text{or } \Delta G = \Delta G^\circ + RT \ln \frac{(X)^x (Y)^y}{(A)^a (B)^b} \quad \text{--- (1)}$$

$$T = 298 \text{ K}, \quad R = 8.314 \text{ J/mol}.$$

transference of 1 mole of electrons = 1F.

$E =$ EMF of cell, the electrical energy produced in cell = nFE

$$1F = 96500 \text{ C}.$$

Electrical energy produced is equal to decrease in free energy ($-\Delta G$)

$$-\Delta G = nFE \quad \text{--- (2)}$$

$$-\Delta G^\circ = nFE^\circ \quad \text{--- (3)}$$

Substitute ΔG and ΔG° from (2) & (3) in (1)

$$-nFE = -nFE^\circ + RT \ln \frac{P}{R}.$$

$$E = E^\circ + \frac{1}{-nF} RT \ln \frac{P}{R}.$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{P}{R}.$$

$$E = E^{\circ} - \frac{2.303 RT}{nF} \log \frac{P}{R}$$

$$T = 25^{\circ}\text{C} \text{ or } 298 \text{ K } (25 + 273)$$

$$R = 8.314 \quad F = 96500$$

$$\therefore E = E^{\circ} - \frac{0.0591}{n} \log \frac{P}{R}$$

$$\text{or } E = E^{\circ} + \frac{0.0591}{n} \log \frac{R}{P}$$

Application of Nernst Equation:-

(a) Calculation of emf of cell:
Eg $\text{Zn} | \text{Zn}^{2+} || \text{Cu}^{2+} | \text{Cu}$.

Equation $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Cu} + \text{Zn}^{2+}$
on Applying Nernst equation.

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Cu}] [\text{Zn}^{2+}]}{[\text{Zn}] [\text{Cu}^{2+}]}$$

no of electrons $n=2$

activity of solid = 1 (unity)

$$E = E^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

(b) Calculation of single Electrode Potential.

Oxidation Reaction: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^{-}$

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Zn}]}{[\text{Zn}^{2+}]}$$

activity of solid = 1 (unity)

$$E = E^{\circ} - \frac{RT}{nF} \ln \left[\frac{1}{z_{n+2}} \right]$$

$$E = E^{\circ} + \frac{RT}{nF} \ln [z_{n+2}]$$

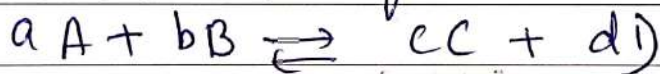
$$E = E^{\circ} - \frac{2.303 RT}{nF} \log [z_{n+2}] \quad \text{or}$$

$$E = E^{\circ} + \frac{0.0591}{n} \log [z_{n+2}]$$

③ Calculation of Equilibrium Constant:

At Equilibrium, concentration of two metal ions, potential difference = zero and Emf of cell = zero.

Reaction at Equilibrium.



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

On Applying Nernst Equation.

$$E_{\text{cell}} = E^{\circ} - \frac{0.0591}{n} \log K_c.$$

$$0 = E^{\circ} - \frac{0.0591}{n} \log K_c.$$

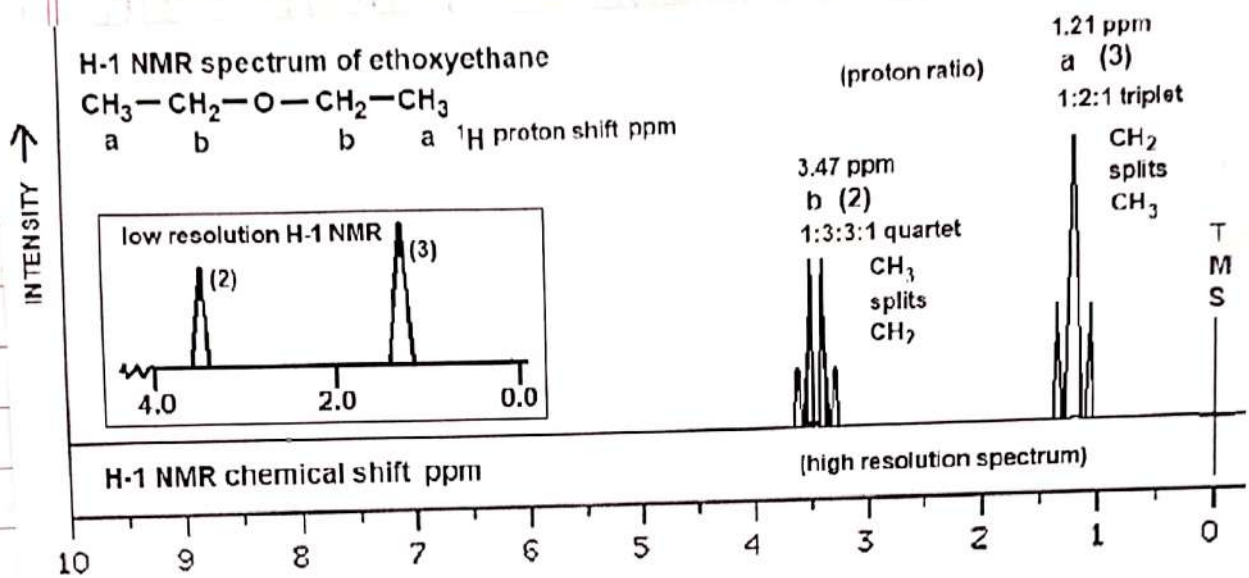
$$\text{or } E^{\circ} = \frac{0.0591}{n} \log K_c.$$

(b) Differentiate between ion-exchange process and zeolite process for water softening.

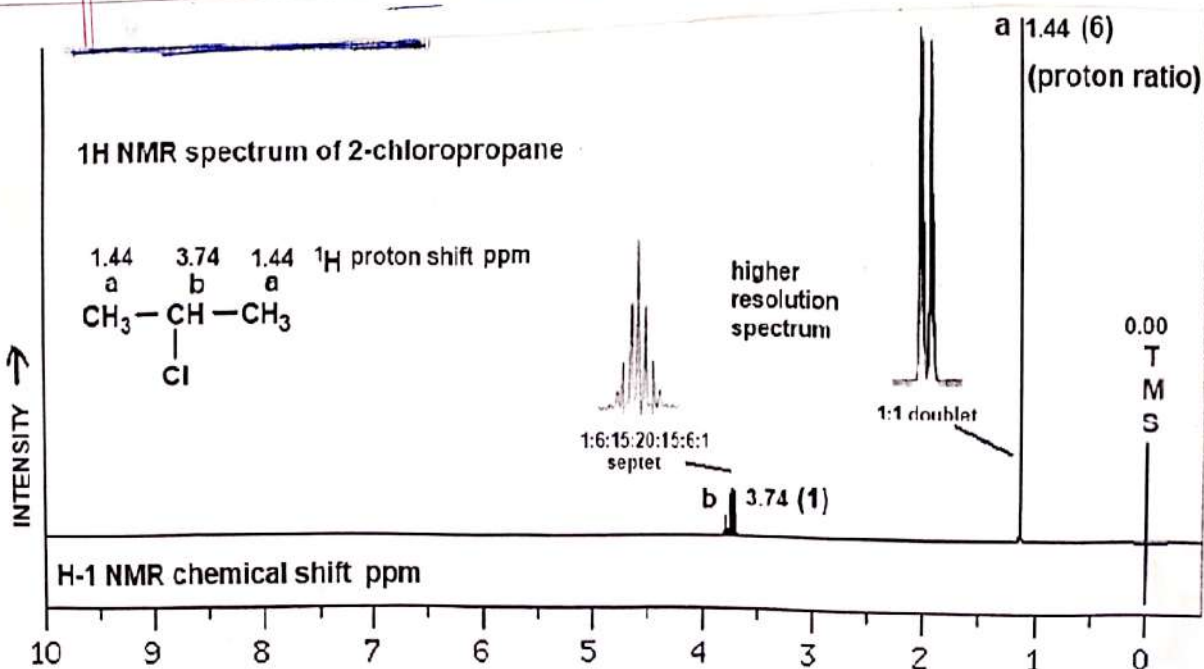
	<u>Zeolite Process</u>	<u>Ion-Exchange Process</u>
<u>Definition</u>	A process of softening hard water by ion-exchange using chemical compound zeolite.	A water softening process in which cations or anions are used in order to soften water.
<u>Ions</u>	It involves sodium ions that can exchange with calcium and magnesium ions in hard water.	It involves sodium ions, hydrogen ions, chloride and hydroxyl ions that can exchange with Ca and Mg ions in hard H ₂ O.
<u>Exchangers</u>	It has a cylinder containing zeolite bed.	It has cation and anion exchangers.
<u>Classification</u>	This is a hard water softening process.	These processes involve softening, dealkalization and demineralization.

5(a) Draw the expected ^1H NMR spectra of diethyl ether and 2-chloropropane.

^1H NMR spectra of diethyl ether:



^1H NMR spectra of 2-chloropropane.



- (b) How can you identify the alkane, alkene and alkyne on the basis of Infra Red (IR) spectroscopy? Explain.

Identification of alkane, Alkene and Alkynes on basis of IR spectroscopy.

(a) Alkanes:

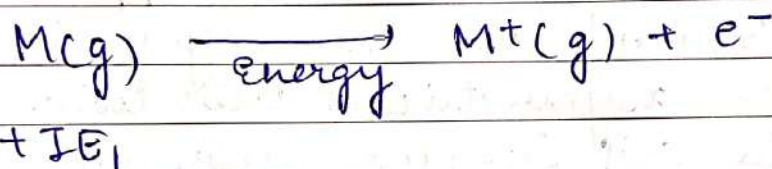
The alkanes are detected from C-H stretching and C-H deformation absorptions. Two C-H stretching absorption bands appear just below 3000 cm^{-1} one for symmetrical and other for asymmetrical vibrational frequencies. The various C-H bending vibrations in alkanes appear in the region $1485-1340\text{ cm}^{-1}$. Vibrational absorptions for C-H bonds are different from C-C bonds due to large mass difference. C-C linkages are characteristic and appear as weak bands in region $1300-1800\text{ cm}^{-1}$.

- (2) Alkenes: In alkenes C-H stretching absorption band appears in region $3100-3000\text{ cm}^{-1}$. Conjugation of double bond with aromatic ring show C=C stretching near 1625 cm^{-1} . For cis alkene C-H around 970 cm^{-1} and for trans alkene at about 710 cm^{-1} .

- (3) Alkynes: In acetylene, a strong band for $\text{C}\equiv\text{C}-\text{H}$ stretching appears at about 3300 cm^{-1} and a weak $\text{C}\equiv\text{C}$ stretching occurs at 2200 cm^{-1} . C-H bending occur at $650-610\text{ cm}^{-1}$.

6(a) How do the ionisation energies of the element vary as we move along a period and down a group? Explain with reasons.

Ionisation Energy: the minimum amount of energy required to remove most loosely bound electron from an isolated atom in gaseous state of an element and convert it into gaseous monovalent positive ion.



Variation of Ionisation Enthalpy in Periodic Table:

(1) In Group: Ionisation enthalpy decreases from top to bottom.

Eg: Li Na K Rb Cs
520 496 419 403 374

—————>
I.P. inc.

Reason:

① On moving down the group atomic size increases as new energy shell is added. ∴ force of attraction towards valence electrons decreases. ∴ I.P. value decrease.

② With increase in atomic No., the number of inner shell increases, so screening effect also increases. So force of attraction reduces.

∴ Value of IP decreases.

As nuclear charge increases, force of attraction increases ∴ IP should increase but combined effect of increase in size and screening effect overcome the effect of increased nuclear charge.

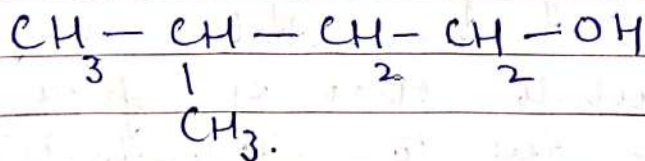
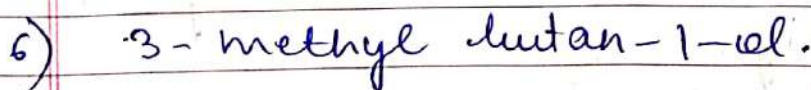
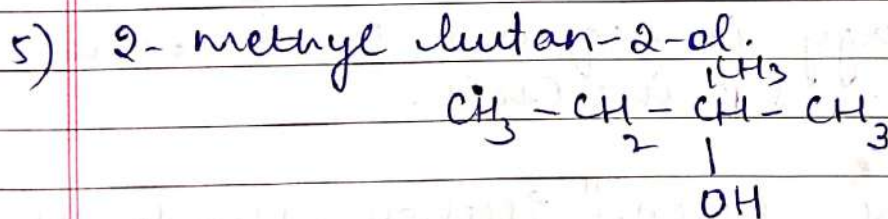
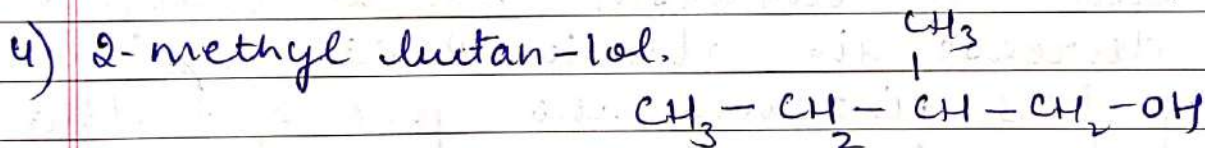
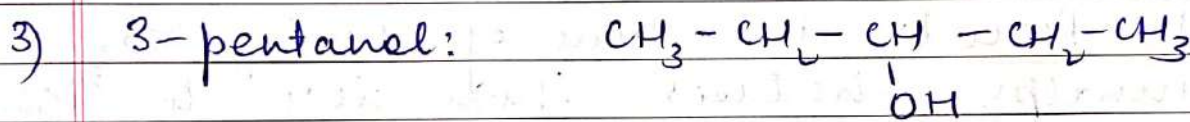
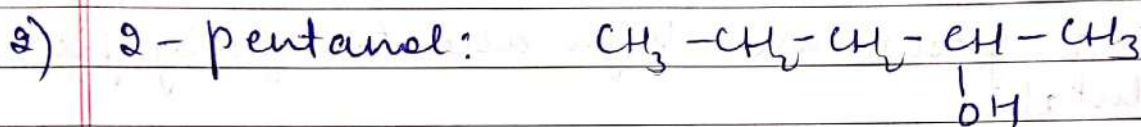
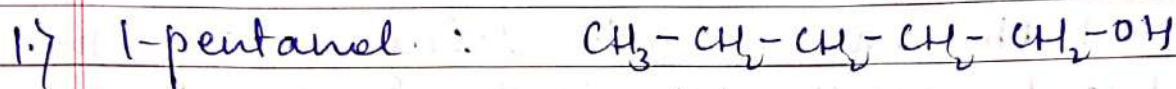
∴ IP decreases in group from top to bottom. Tl has higher IE than In, and Pb has higher value than Sn. due to lanthanide contraction. IP of inert gases are high due to fully filled orbital.

(2) In Period the value of ionization enthalpy increases from left to right due to increased nuclear charge & decrease in atomic radii. As distance of electrons increases the force of attraction towards nucleus. so more and more energy is required to remove electrons ∴ IP increases.

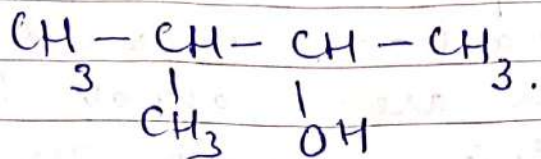
(b) Explain the reason: "Electron affinity of N is almost zero while that of F is very high?"
Electron affinity of nitrogen is almost zero because it has stable half-filled p-orbital while that of fluorine is very high due to incompletely filled p-orbital. ∴ nitrogen will not easily accept an electron, hence its electron affinity is almost zero.

7(a) There are eight alcohols with the formula $C_5H_{12}O$. Name them and tell which are chiral and also identify the stereocenters.

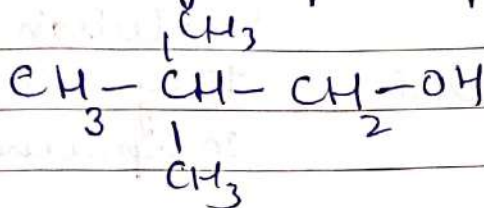
The eight alcohols with formula $C_5H_{12}O$ are:



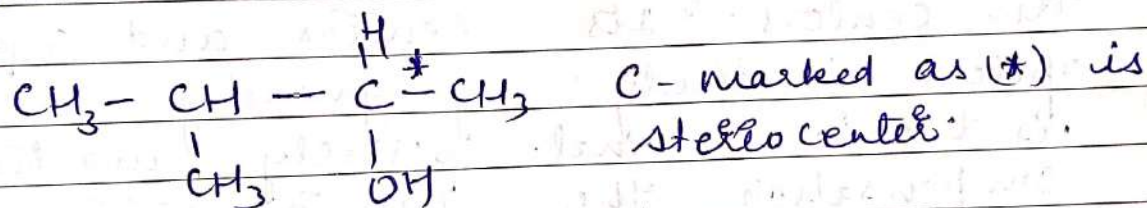
7) 3-methyl pentan-2-ol.



8) 2,2-dimethyl propan-2-ol.



Out of above 8 isomeric alcohol only one, 3-methyl pentan-2-ol, is chiral. Rest all are achiral.



(b) Differentiate between meso compounds and racemic mixture giving suitable examples.

	<u>Racemic Mixture</u>	<u>Meso-Compound</u>
1)	It is a mixture of organic compounds known as enantiomers.	1) A meso compound is a molecule having more than one identical stereocenter and superimposable mirror image.
2)	It contains non-identical isomers.	It contains identical mirror image.
3)	Optically inactive due.	Optically inactive due.

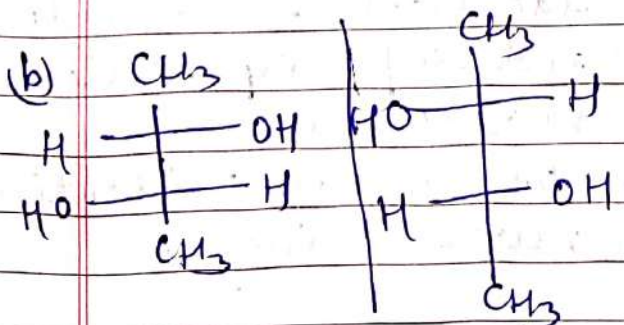
to external compensation

- (4) It can be separated into two enantiomers which are optically active

- (5) They have chiral compounds.

- (6) ~~so~~ It is formed from one or more than two asymmetric centers. Its optical inactivity is due to external compensation. The separation of a racemic mixture into D & L form is called resolution.

- (7) eg: (+) and (-) lactic acid forms.
(a) (\pm) lactic acid.

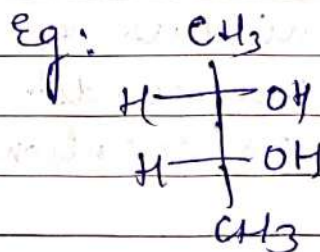


internal compensation.

- (4) It is a single compound which cannot be separated into an optically active compound by resolution process.

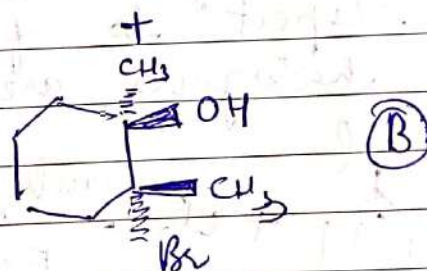
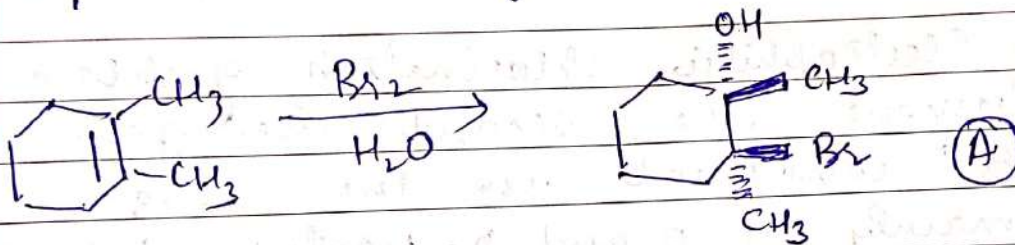
They are achiral compounds.

Meso-form is a compound with two or more chiral centers and a plane of symmetry. It is optically inactive due to internal compensation.

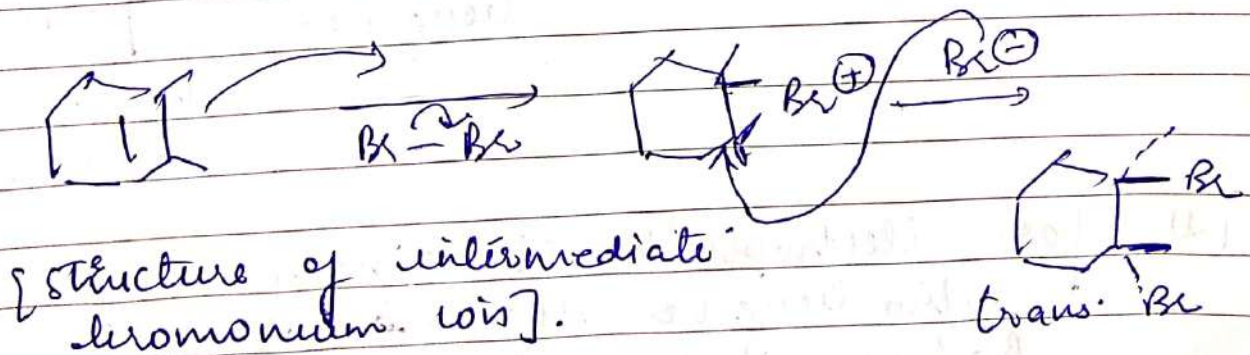


8) (a) What product would you expect to obtain from the addition of Br_2 to 1,2-dimethylcyclohexene? Show the stereochemistry of product. Also give the structure of the intermediate bromonium ion formed.

Soluⁿ When 1,2-dimethylcyclohexene is reacted with bromine and water, two addition products are formed A & B.



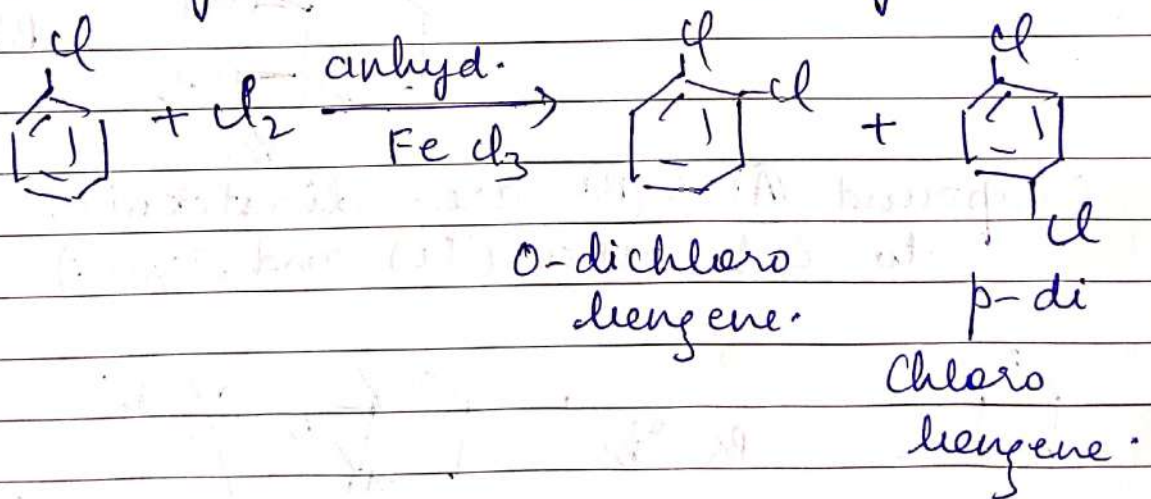
Compound (A) & (B) are diastereoisomers to each other (cis and trans)



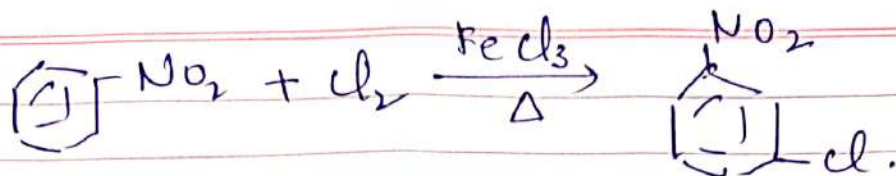
(b) The orientation of electrophilic aromatic substitution on a monosubstituted benzene ring is usually controlled by the group which is already on the ring. Name and draw the structures of major product of electrophilic chlorination of these substances:

(i) Chlorobenzene (ii) Nitrobenzene

(i) For electrophilic chlorination of chlorobenzene the second halogen gets introduced in the ring mainly at o and p-positions with respect to first halogen because halogens are o,p-directing groups.



(2) For electrophilic chlorination of nitrobenzene the second halogen is introduced at meta position because NO_2 -group is deactivating and meta directing.



m-chloronitro benzene.