PTU QUESTION PAPER CHEMISTRYY, DEC. 2024
SOLVED

SECTION-A

l. Write short notes on:

(f) How does the zeolite process work in softening of hard water?

Ans: Zeolite process(Permutit Process) used for softening of hard water, In this process when hard water containing calcium and magnesium ions passes through a bed of zeolite (a sodium-based mineral), the sodium ions in the zeolite are exchanged with the calcium and magnesium ions in the water, effectively removing the hardness-causing ions and leaving soft water.

(g)What is the hardness of water? Differentiate between temporary and permanent hardness.

Ans: The hardness of water is due to the presence of soluble bicarbonates, chlorides and sulfates of calcium and magnesium. Water which does not give lather with soap is known as hard water.

Temporary Hardness of Water

The presence of magnesium and calcium carbonates in water makes it temporarily hard. In this case, the hardness in water can be removed by boiling the water.

When we boil water, the soluble salts of $Mg(HCO_3)_2$ are converted to $Mg(OH)_2$, which is insoluble, and hence gets precipitated and is removed. After filtration, the water we get is soft water.

Permanent Hardness of Water

When the soluble salts of magnesium and calcium are present in the form of chlorides and sulphides in water, it is knowns as permanent hardness because this hardness cannot be removed by boiling.

We can remove this hardness by treating the water with washing soda. Insoluble carbonates are formed when washing soda reacts with the sulphide and chloride salts of magnesium and calcium, and thus, hard water is converted to soft water.

(h)What is ionization energy, and how does it vary across periods and groups in the periodic table?

Ans: Definition: The energy required to remove the most loosely bound electron from an isolated gaseous atom.

(i)Trend across a period: Ionization energy increases as you move left to right across a period because the nucleus gains more protons, pulling the outermost electrons closer and making them harder to remove.

(ii)Trend down a group: Ionization energy decreases as you move down a group because the added electron shells increase the distance between the nucleus and the outermost electrons, making them easier to remove.

(i)What is optical activity and how it can be used to distinguish between enantiomers?

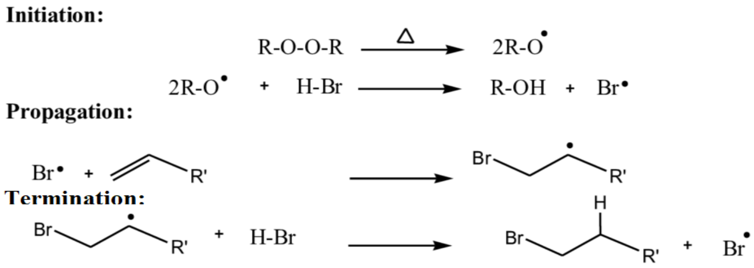
Ans: The property of a compound being able to rotate the plane of polarization of plane-polarized light is called the optical activity. It is used to distinguish between enantiomers because each enantiomer of a pair will rotate the plane of polarized light in opposite directions (one clockwise, the other counterclockwise), allowing for identification based on the direction of rotation.

(j) How does a free radical addition reaction occur?

Ans: A free radical addition reaction occurs when a free radical, a molecule with an unpaired electron, attacks a carbon-carbon double bond, adding itself to one of the carbons and creating a new carbon-centered radical, which then propagates the reaction by abstracting another atom from a reactant molecule

A free-radical addition is an addition reaction which involves free radicals. These reactions can happen due to the free radicals having an unpaired electron in their valence shell, making them highly reactive.

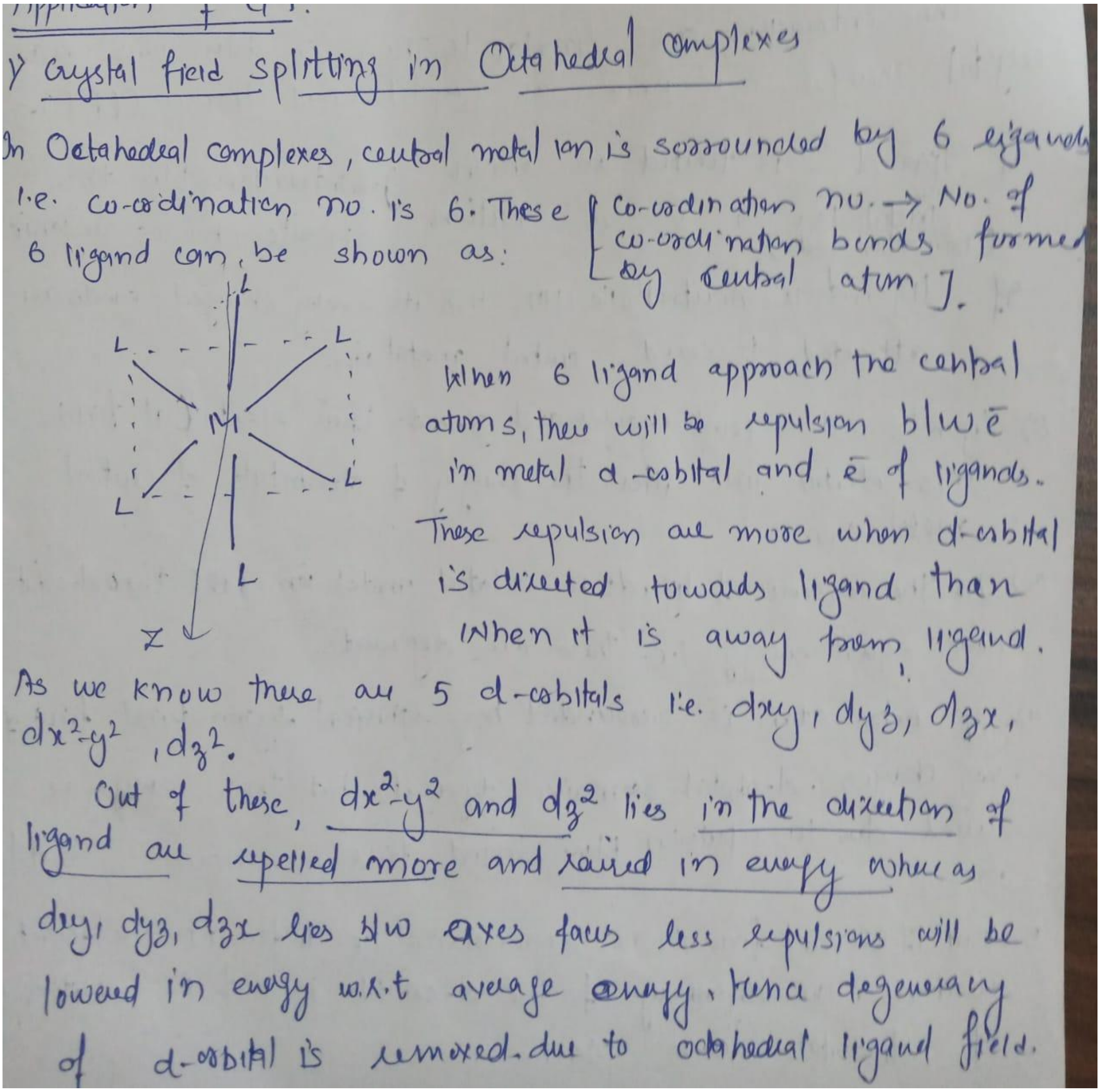
Example: The addition of hydrogen bromide (HBr) to an alkene in the presence of a peroxide is a classic example of a free radical addition reaction, where the peroxide acts as the source of free radicals, leading to an anti-Markovnikov addition product.



SECTION B

2. a) How can you explain the splitting of d-orbitals in an octahedral crystal field?

Ans.



i) Crystal field splitting in Octahedral complexes

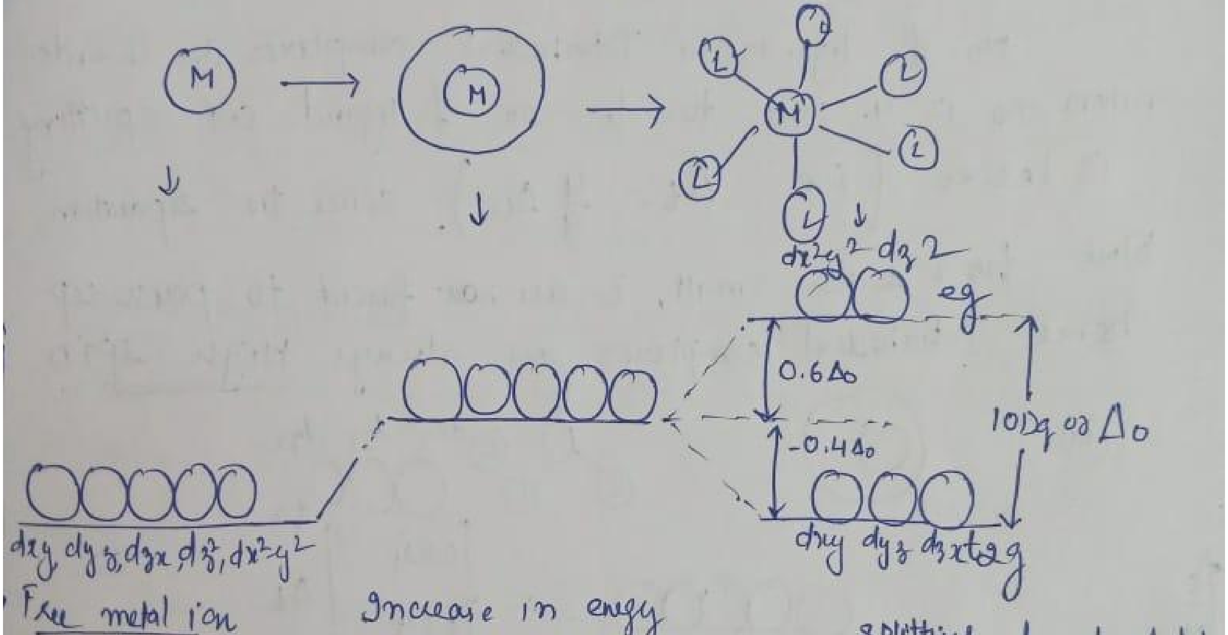
In Octahedral complexes, central metal ion is sorrounded by 6 ligand i.e. co-ordination no. is 6. These 6 ligand can be shown as: [Co-ordination no. → No. of co-ordination bonds formed by central atom].

When 6 ligand approach the central atoms, there will be repulsion b/w $\bar{e}$ in metal d-orbital and $\bar{e}$ of ligands. These repulsion are more when d-orbital is directed towards ligand than when it is away from ligand.

As we know there are 5 d-orbitals i.e. d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2}.

Out of these, $d_{x^2-y^2}$ and d_{z^2} lies in the direction of ligand are repelled more and raised in energy whereas d_{xy}, d_{yz}, d_{zx} lies b/w axes faces less repulsions will be lowered in energy w.r.t average energy, hence degeneracy of d-orbital is removed due to octahedral ligand field.

(5) In octahedral complexes, two sets of d-orbitals are formed ② one set of three orbitals of lower energy i.e. t_{2g} and other set of two orbitals of higher energy i.e. e_g. cf Spitting of octahedral complexes is shown in fig.



Free metal ion

Increase in energy of d-orbitals in the presence of crystal field (symmetrical)

splitting of d-orbital in Octahedral field.

The splitting of degenerate level due to presence of ligand in a definite geometry is called crystal field splitting. It is denoted by Δ_o. [Δ → energy separation, O → octahedral)

In octahedral system, energy of two eg orbitals ↑es by 0.6Δ_o or 6Dq and energy of three t_{2g} orbital ↓es by 0.4Δ_o or 4Dq.

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Electron assignment in d orbitals in octahedral complexes.

Electron filling follows Hund's Rule, Pauli Exclusion & Afbau Principle.

For $d^1 \rightarrow t_{2g}^1\ e_g^0$

$d^2 \rightarrow t_{2g}^2\ e_g^0$

$d^3 \rightarrow t_{2g}^3\ e_g^0$

For $d^4 \rightarrow$ Two possiblities (i) 4th electron can enter t_{2g} and pairing occurs. [Low spin]

(ii) 4th ē can enter e_g and pairing doesn't occur. [High spin]

These two possiblities depends upon (1) $\Delta_o \rightarrow$ magnitute of crystal field splitting (ii) P i.e pairing energy ⇒ energy required for ē pairing. Hence we have two options.

i) If $\Delta_o > P$ i.e field is stronger than pairing energy i.e energy required for pairing less ⇒ pairing takes place electron goes to t_{2g}.

ii) If $\Delta_o < P$ ⇒ energy required for pairing is high for weak field ⟹ pairing doesn't occur ⇒ ē goes to e_g.

Sum up:

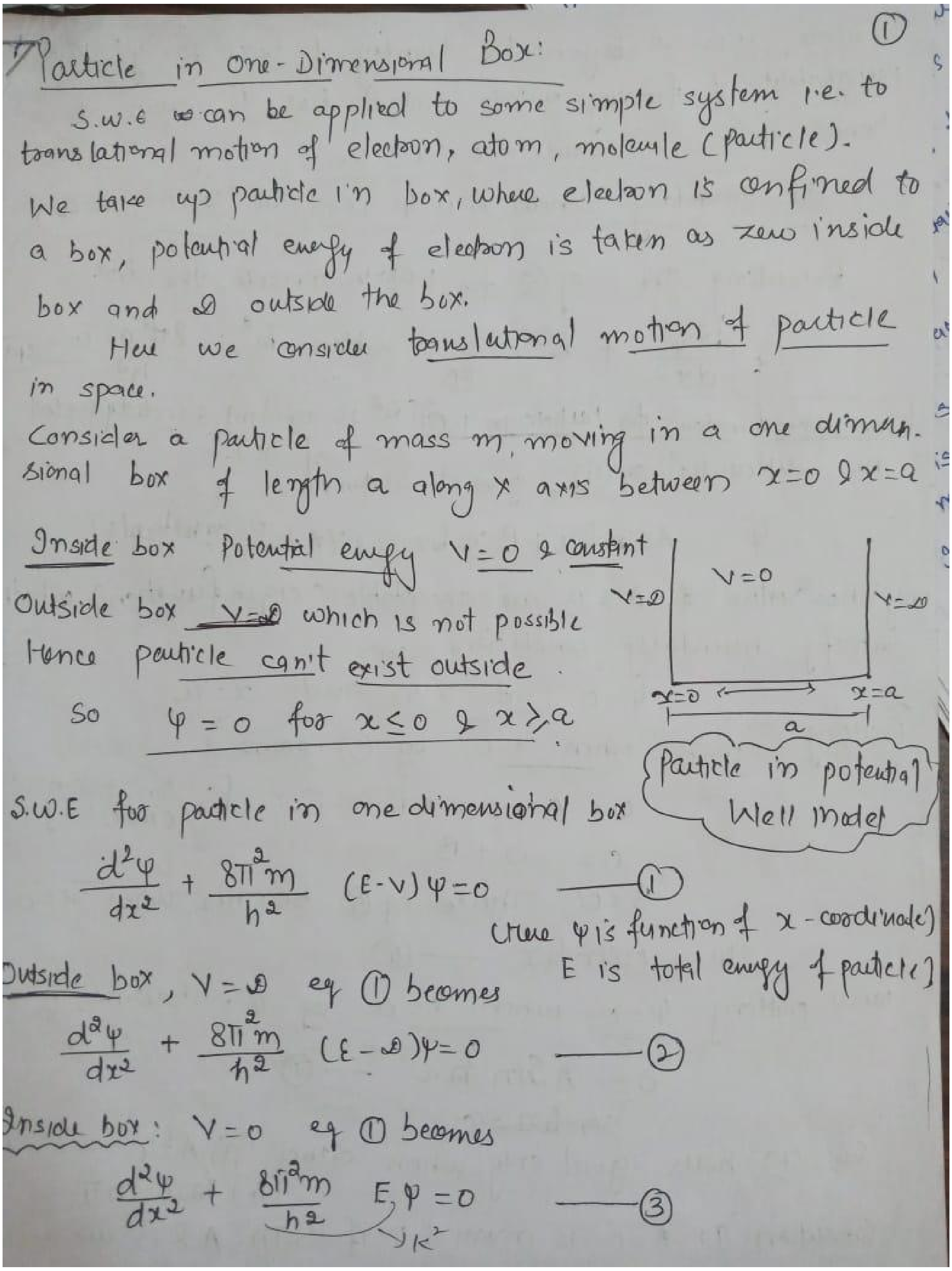
$d^4 \Rightarrow \Delta_o > P \Rightarrow t_{2g}^4\ e_g \Leftrightarrow$ Low spin ⇔ strong field

$d^4\ \ \Delta_o < P \Rightarrow t_{2g}^3\ e_g^1 \Leftrightarrow$ High spin ⇔ Weak field.

Strong field ligands form Low spin complexes

Weak field ligand form High spin complexes.

(b) Give the solution to the Schrodinger equation for a particle in a one-dimensional box.
Ans.



①

Particle in One-Dimensional Box:

S.W.E can be applied to some simple system i.e. to translational motion of electron, atom, molecule (particle).

We take up particle in box, where electron is confined to a box, potential energy of electron is taken as zero inside box and ∞ outside the box.

Here we consider translational motion of particle in space.

Consider a particle of mass m, moving in a one dimensional box of length a along x axis between $x=0$ & $x=a$

Inside box Potential energy $V=0$ & constant

Outside box $V=\infty$ which is not possible

Hence particle can't exist outside

So $\psi=0$ for $x\leq 0$ & $x\geq a$

S.W.E for particle in one dimensional box

$$\frac{d^2\psi}{dx^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0 \quad \text{—— ①}$$

(Here ψ is function of x-coordinate)
E is total energy of particle]

Outside box, $V=\infty$ eq ① becomes

$$\frac{d^2\psi}{dx^2}+\frac{8\pi^2 m}{h^2}(E-\infty)\psi=0 \quad \text{—— ②}$$

Inside box: $V=0$ eq ① becomes

$$\underbrace{\frac{d^2\psi}{dx^2}+\frac{8\pi^2 m}{h^2}E}_{k^2}\psi=0 \quad \text{—— ③}$$

Since V is ∞ beyond the boundary of box. so ψ^2 i.e. probababililty of finding particle outside box is zero. & hence $\psi = 0$ outside $0 \le x \le a$.

The boundary condition is ψ is 0 at $x = 0$, $x = a$

Rewriting the eq ③ for particle inside the box

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad —④ \qquad \text{where } k^2 = \frac{8\pi^2 m.E}{h^2} — (4a)$$

The wave function for Particle in 1-D [k^2 is constant & indedependent of x).

For differential eq ④, general solution is:

$$\psi = A\sin kx + B\cos kx \; —⑤ \; (A \,\&\, B \text{ constants})$$

only Those value of A & B are acceptable (eigen function) which satisfy boundary conditions viz

$$\psi = 0 \quad \text{at} \quad x = 0 \quad \text{and} \quad x = a$$

Putting $\psi = 0$ when $x = 0$ eq ⑤ becomes

$$0 = A\sin 0 + B\cos 0 \qquad \left[\because \begin{matrix}\sin 0 = 0 \\ \cos 0 = 1\end{matrix}\right]$$

$$0 = 0 + B$$

$B = 0$, Thuse eq ⑤ becomes when $x = 0$

$$\psi = A\sin kx \quad —⑥$$

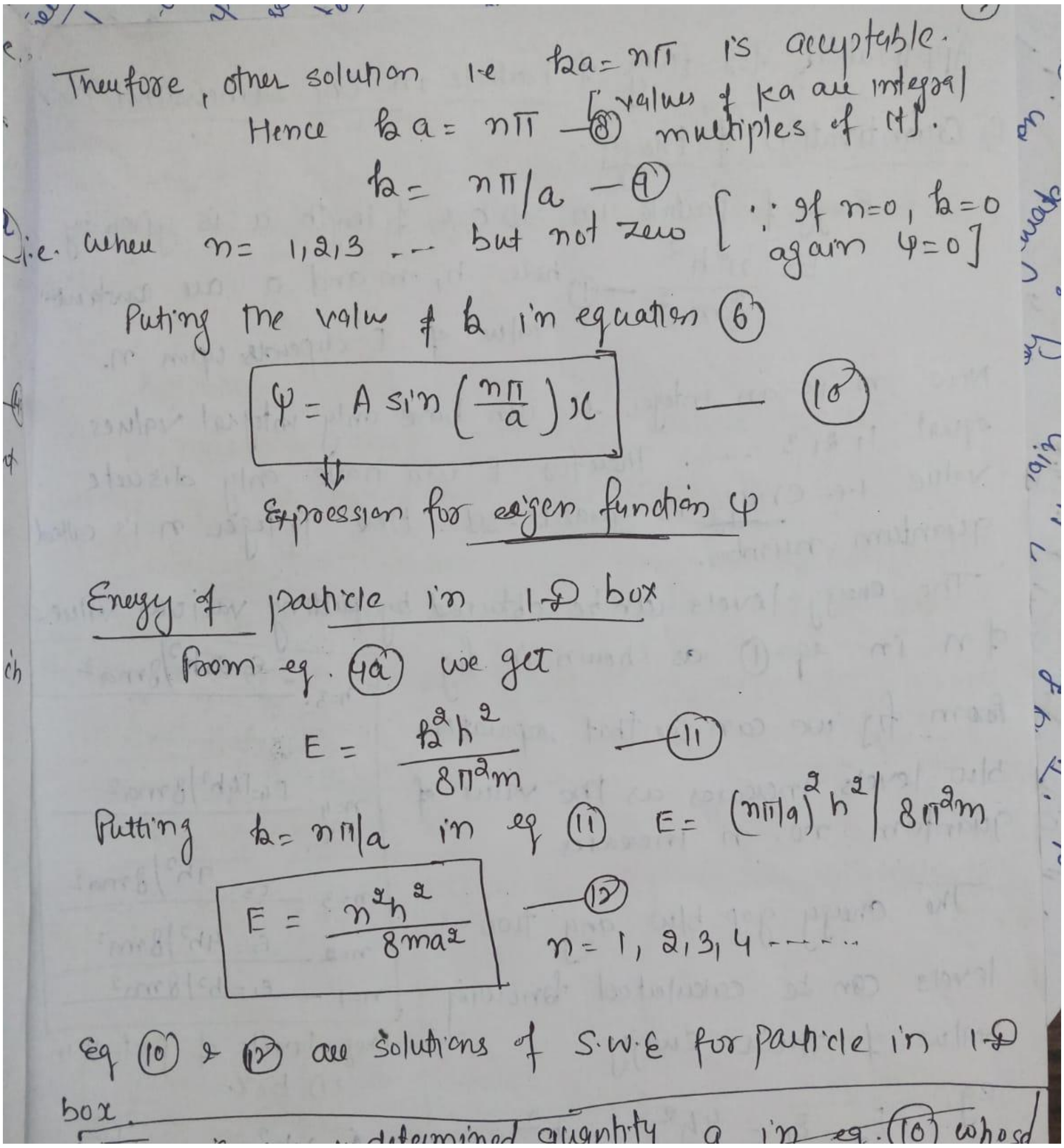
Now putting $\psi = 0$ when $x = a$ eq ⑥ becomes

$$0 = A\sin ka \quad —⑦$$

~~$\sin ka$~~ $= 0$

Eq. ⑦ holds good only when either (i) $A = 0$
(ii) $ka = n\pi$

Condition (i) $A = 0$ is invalid $\because$ if both A & B are zero, then $\psi = 0$ for all value of a between zero & a (i.e.



Therefore, other solution i.e $ka = n\pi$ is acceptable.

Hence $ka = n\pi$ — ⑧ [∵ values of ka are integral multiples of π].

$k = n\pi/a$ — ⑨

i.e. when $n = 1, 2, 3 \ldots$ but not zero [∵ If $n=0$, $k=0$ again $\psi = 0$]

Puting the valu of k in equation ⑥

$$\boxed{\psi = A \sin\left(\frac{n\pi}{a}\right)x} \quad \text{—} \quad (10)$$

⇓

Expression for eigen function ψ

Energy of particle in 1-D box

from eq. (4a) we get

$$E = \frac{k^2 h^2}{8\pi^2 m} \quad \text{—} \quad (11)$$

Putting $k = n\pi/a$ in eq ⑪ $E = (n\pi/a)^2 h^2 / 8\pi^2 m$

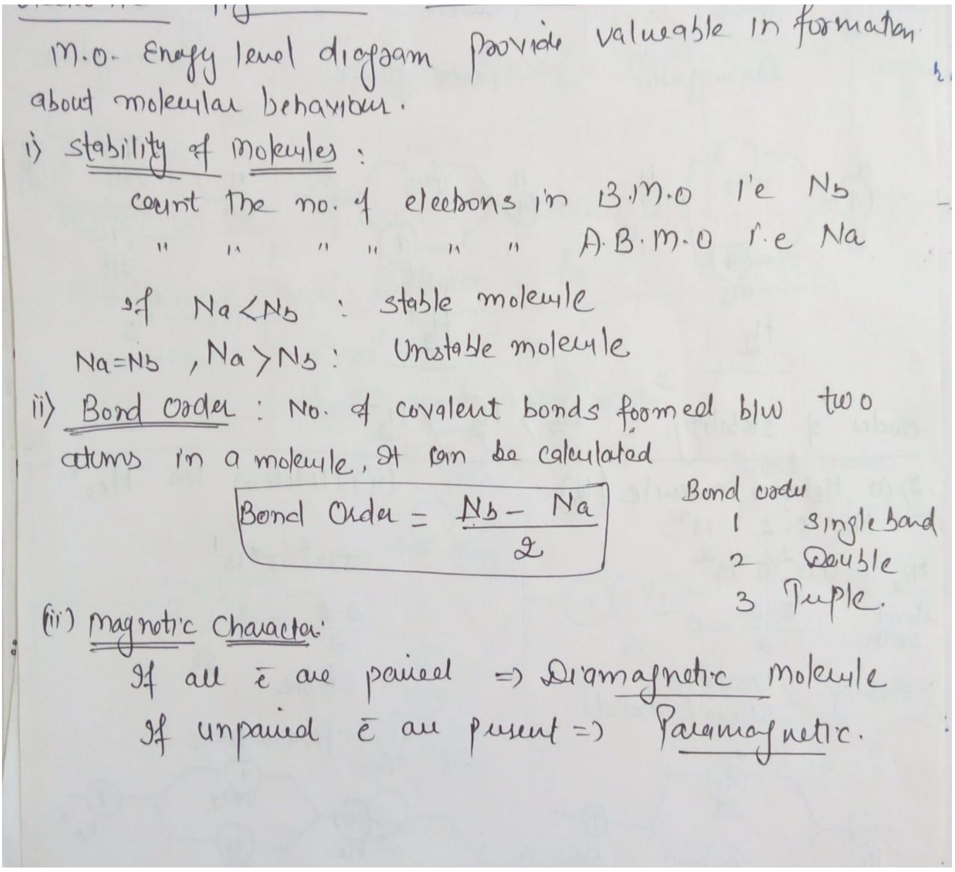
$$\boxed{E = \frac{n^2 h^2}{8ma^2}} \quad \text{—} \quad (12)$$

$n = 1, 2, 3, 4 \ldots\ldots$

eq ⑩ & ⑫ are solutions of S.W.E for particle in 1-D box.

determined quantity a in eq. ⑩ whose

3(a) a) Provide the molecular orbital energy level diagram for nitrogen (N_2). Based on this diagram, determine the bond order, discuss the molecule's stability, and explain whether it is paramagnetic or diamagnetic.



M.O. Energy level diagram provide valueable information about molecular behaviour.

i) stability of molecules :

count the no. of electrons in B.M.O i.e N_b

" " " " " " A.B.M.O i.e N_a

If $N_a < N_b$: stable molecule

$N_a = N_b$, $N_a > N_b$: Unstable molecule

ii) Bond Order : No. of covalent bonds formed b/w two atoms in a molecule. It can be calculated

$$\boxed{\text{Bond Order} = \frac{N_b - N_a}{2}}$$

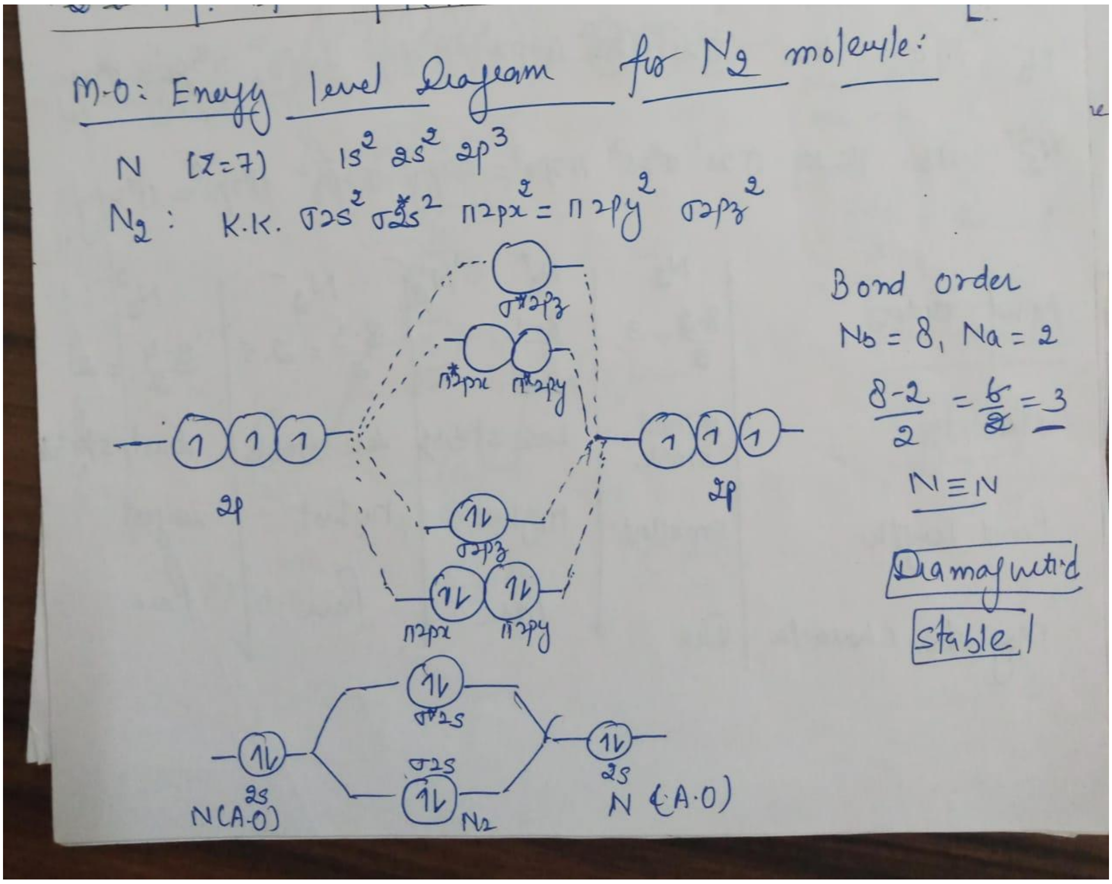
Bond order
1 Single bond
2 Double
3 Triple.

(iii) magnetic Character:

If all ē are paired => Diamagnetic molecule

If unpaired ē are present => Paramagnetic.

Ans.



M.O: Energy level Diagram for N_2 molecule:

N (Z=7) $1s^2\ 2s^2\ 2p^3$

N_2 : K.K. $\sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_x^2 = \pi 2p_y^2\ \sigma 2p_z^2$

Bond order

$N_b = 8$, $N_a = 2$

$\frac{8-2}{2} = \frac{6}{2} = 3$

N≡N

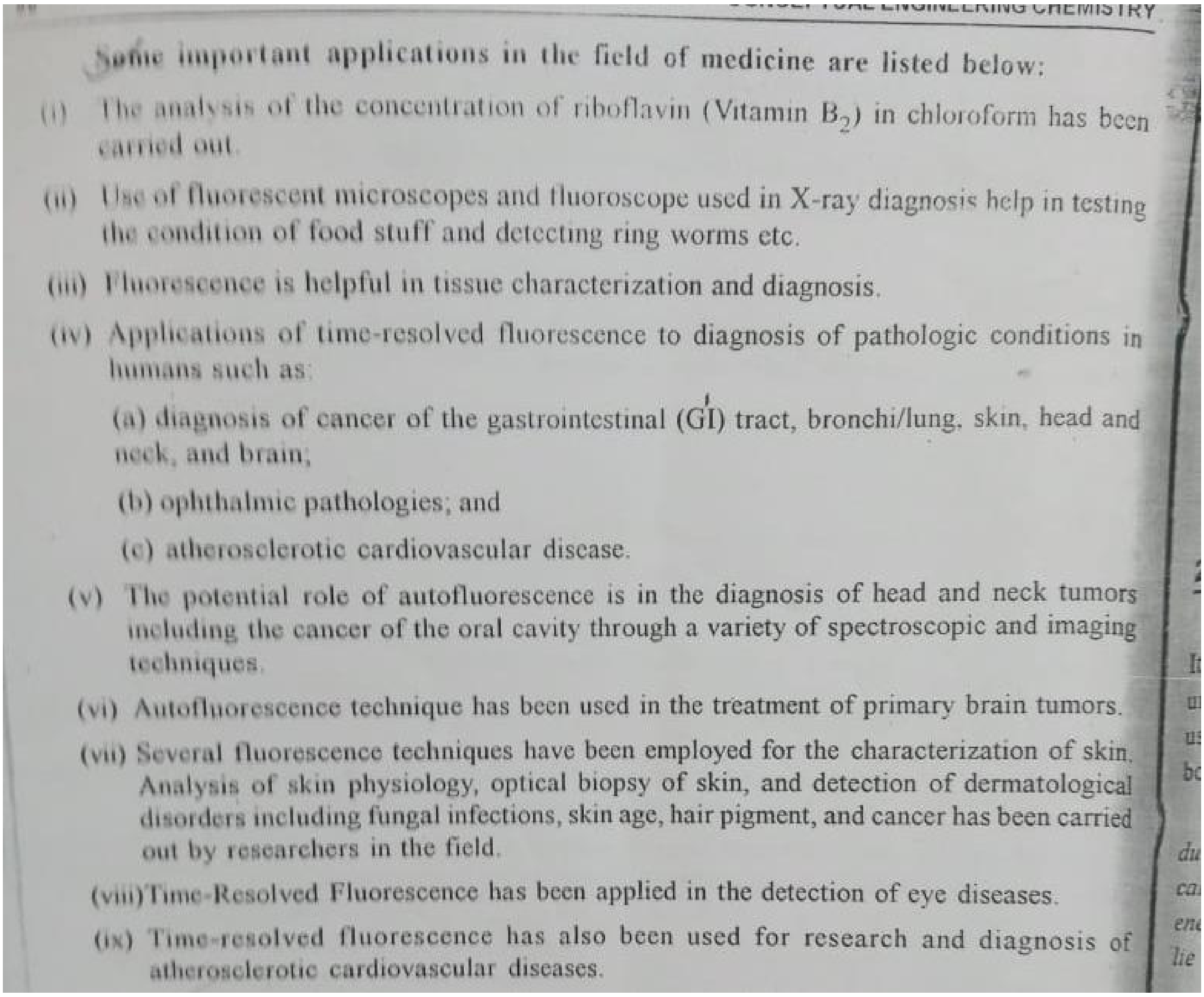
Diamagnetic

stable!

b) What is fluorescence, and how is it used in medical applications?

Ans. Certain substances absorb radiations and get excited I.e. their electron are raised to higher energy levels from lower energy level, the excited molecule immediately remit a part of absorbed radiation at greater wavelength. Such substances which absorb radiations and emit a part of it immediately at greater wavelength within short time (10 sec) are called **fluorescent substances** and this phenomenon is called **Fluorescence.**

Medical applications of fluorescence:



Some important applications in the field of medicine are listed below:

(i) The analysis of the concentration of riboflavin (Vitamin B_2) in chloroform has been carried out.

(ii) Use of fluorescent microscopes and fluoroscope used in X-ray diagnosis help in testing the condition of food stuff and detecting ring worms etc.

(iii) Fluorescence is helpful in tissue characterization and diagnosis.

(iv) Applications of time-resolved fluorescence to diagnosis of pathologic conditions in humans such as:

(a) diagnosis of cancer of the gastrointestinal (GI) tract, bronchi/lung, skin, head and neck, and brain;

(b) ophthalmic pathologies; and

(c) atherosclerotic cardiovascular disease.

(v) The potential role of autofluorescence is in the diagnosis of head and neck tumors including the cancer of the oral cavity through a variety of spectroscopic and imaging techniques.

(vi) Autofluorescence technique has been used in the treatment of primary brain tumors.

(vii) Several fluorescence techniques have been employed for the characterization of skin. Analysis of skin physiology, optical biopsy of skin, and detection of dermatological disorders including fungal infections, skin age, hair pigment, and cancer has been carried out by researchers in the field.

(viii) Time-Resolved Fluorescence has been applied in the detection of eye diseases.

(ix) Time-resolved fluorescence has also been used for research and diagnosis of atherosclerotic cardiovascular diseases.

4 (a) What are the selection rules for vibrational and rotational transitions in diatomic molecules?

Ans. The restrictions imposed on the quantum number during any transitions are called selection rules.

Selection rule for vibrational transitions is **$\Delta V = \pm 1$** where V is vibrational quantum number.

Selection rules for rotational transitions is **$\Delta J = \pm 1$** where J is rotational quantum number.

(b) **List two factors that can affect the wavelength (λ_{max}) and intensity of absorption bands in electronic spectroscopy. Also explain the reason.**

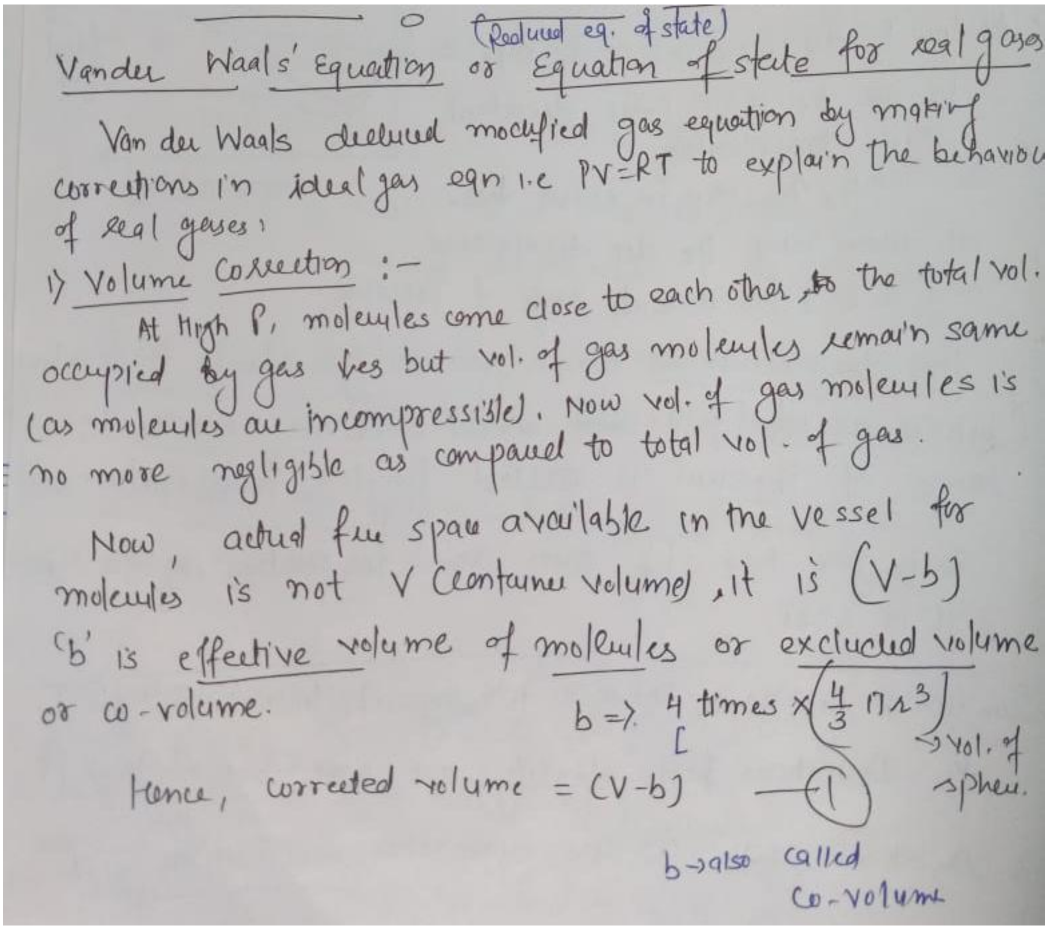
Ans. Two mainly factors that affect wavelength **(λ_{max})** and intensity of absorption bands in electronic spectroscopy are **i)** Conjugation **(ii)** Presence of Auxochrome

Conjugation: Conjugation in a molecule increases the wavelength as well as intensity of light absorbed in UV spectroscopy. This is because conjugation decreases the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).This increase in wavelength is called a bathochromic shift and increase in intensity is called hyperchromic shift. For example, 1-butene has a λ_{max} of 176 nm whereas 1,3-butadiene has a λ_{max} of 292 nm as there are two double bons in conjugation in 1,3-butadiene.

Presence of Auxochrome: Auxochrome is functional group such as -NH_2, -OH, -Cl etc. with non-bonding electrons when attached to chromophore shift wavelength towards longer wavelength i.e. bathochromic shift or red shift and increase the intensity of absorption hyperchromic shift.When an auxochrome attaches to a chromophore, it extends the conjugation of the chromophore. This extended conjugation lowers the energy of the transition, allowing for a longer wavelength transition.

4(a) **What is the van der Waals equation of state, and how does it describe the behavior of real gases?**

Ans.



Vander Waals' Equation or Equation of state for real gases (Reduced eq. of state)

Van der Waals deduced modified gas equation by making corrections in ideal gas eqn i.e $PV = RT$ to explain the behaviour of real gases.

1) **Volume Correction** :-

At High P, molecules come close to each other, the total vol. occupied by gas ↓es but vol. of gas molecules remain same (as molecules are incompressible). Now vol. of gas molecules is no more negligible as compared to total vol. of gas.

Now, actual free space available in the vessel for molecules is not V (container volume), it is $(V-b)$

'b' is effective volume of molecules or excluded volume or co-volume.

$$b \Rightarrow 4 \text{ times} \times \left(\frac{4}{3}\pi r^3\right)$$

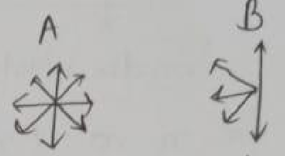
→ vol. of sphere.

Hence, corrected volume $= (V-b)$ —— ①

b → also called co-volume

(i) Pressure Correction :-

At High pressure, molecules come close to each other, Hence intermolecular forces are no more negligible. i.e intermolecular forces develop among the molecule.



Molecule B, at wall faces net inward pull due to intermolecular forces. So the force exerted by molecule striking on the wall ↓es, Hence measured P is less than ideal pressure (i.e when no attraction)

The observed P is less than expected from kinetic theory. Hence a correction term must be added to P to get ideal pressure.

$$\text{Ideal Pressure} = P + p_a$$

p_a -> inward force exerted on molecule which is about to strike on wall.

$p_a \propto$ no. of molecules striking wall.

Hence $p_a \propto d^2$,

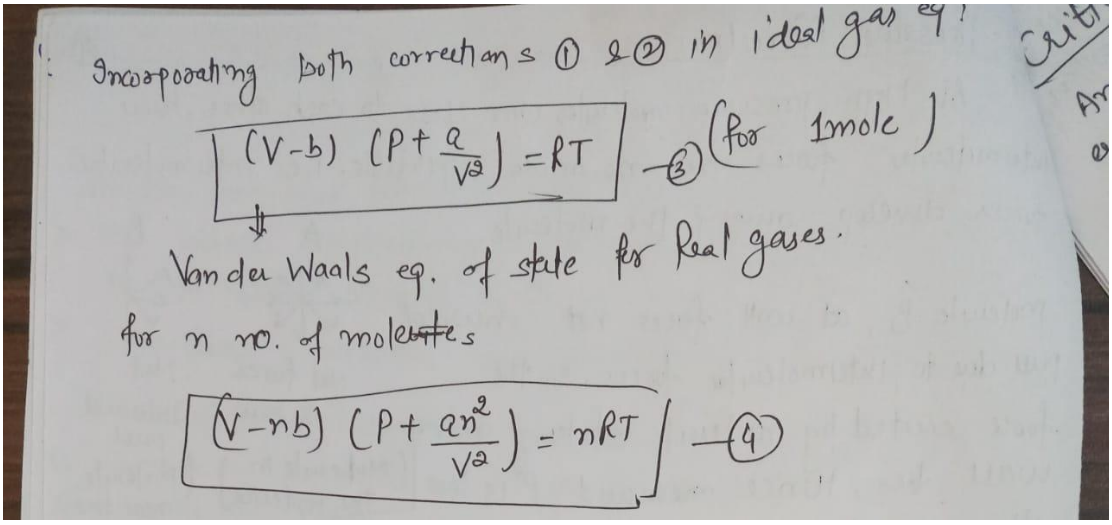
but density $\propto \frac{1}{\text{Vol.}}$

$$p_a \propto \frac{1}{V^2}$$

$$\text{Pic} \quad p_a = \frac{a}{V^2}$$

a -> efficient of proportionality, called co-efficient of attraction.

Hence ideal pressure $= \left(P + \frac{a}{V^2}\right)$ —②



∴ Incorporating both corrections ① & ② in ideal gas eq:

$$\boxed{(V-b)\left(P+\frac{a}{V^2}\right)=RT} \text{ — ③ (for 1mole)}$$

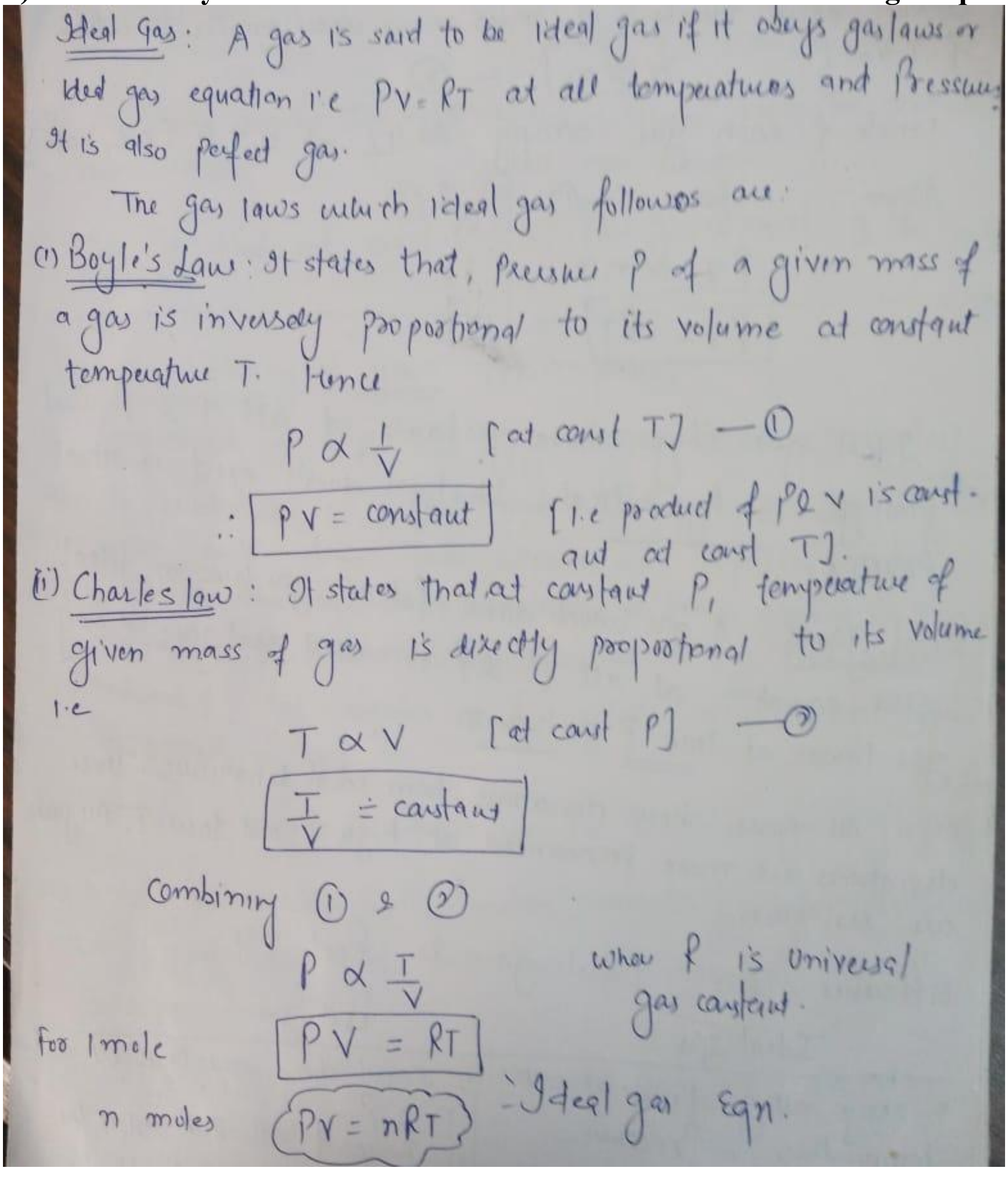
$\Downarrow$

Van der Waals eq. of state for Real gases.

for n no. of molecules

$$\boxed{(V-nb)\left(P+\frac{an^2}{V^2}\right)=nRT} \text{ — ④}$$

b) Describe Boyle's Law and Charles's Law. Also derive the ideal gas equation.



Ideal Gas: A gas is said to be ideal gas if it obeys gas laws or Ideal gas equation i.e PV = RT at all temperatures and Pressure. It is also perfect gas.

The gas laws which ideal gas followes are:

(i) Boyle's Law: It states that, Pressure P of a given mass of a gas is inversely proportional to its volume at constant temperature T. Hence

$$P \propto \frac{1}{V} \quad [\text{at const } T] \text{ — ①}$$

$$\therefore \boxed{PV = \text{constant}}$$ [i.e product of P & V is constant at const T].

(ii) Charles law: It states that at constant P, temperature of given mass of gas is directly proportional to its volume

i.e

$$T \propto V \quad [\text{at const } P] \text{ — ②}$$

$$\boxed{\frac{T}{V} = \text{constant}}$$

Combining ① & ②

$$P \propto \frac{T}{V}$$

where R is Universal gas constant.

for 1mole $\boxed{PV = RT}$

n moles $(PV = nRT)$: Ideal gas Eqn.

Section – C

Q6. (a) What is electrochemical corrosion, and how it differs from dry corrosion.

Wet or electrochemical corrosion occurs mostly under wet or moist conditions through the formation of electrochemical cell.

Mechanism:

(1) existence of separate anodic and cathodic area between which current flows through conducting solution.

(2) oxidation (loss of e's) takes place at anodic area and metal is destroyed. corrosion takes place at anode. $M \rightarrow M^{n+} + ne^-$ (oxidation)

(3) Reduction (gain of e's) takes place at cathode. the electrons from anode are accepted by the electrons such as OH^- or O^{2-} ions dissolved O_2 forming ion

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \text{ (Red)}$$

(4) the metallic ions formed at the anode and non-metallic ions formed at cathode. diffuse through the conducting medium and combine to form corrosion product.

the cathodic reactions accept e's by 2 ways:

(1) Evolution of Hydrogen:- the process of liberation of H_2 in acidic conditions in absence of O_2 H^+ acquire e's with the liberation of H_2 gas at cathode reaction whereas the anodic metal atoms lose their electrons and pass into solution in form of +ve ion.

$$2H_3O^+ + 2e^- \rightarrow 2H_2O + H_2\uparrow$$

neutral / alkaline medium.

$$2H_2O + 2e \rightarrow 2OH + H_2\uparrow \text{ (cathodic)}$$

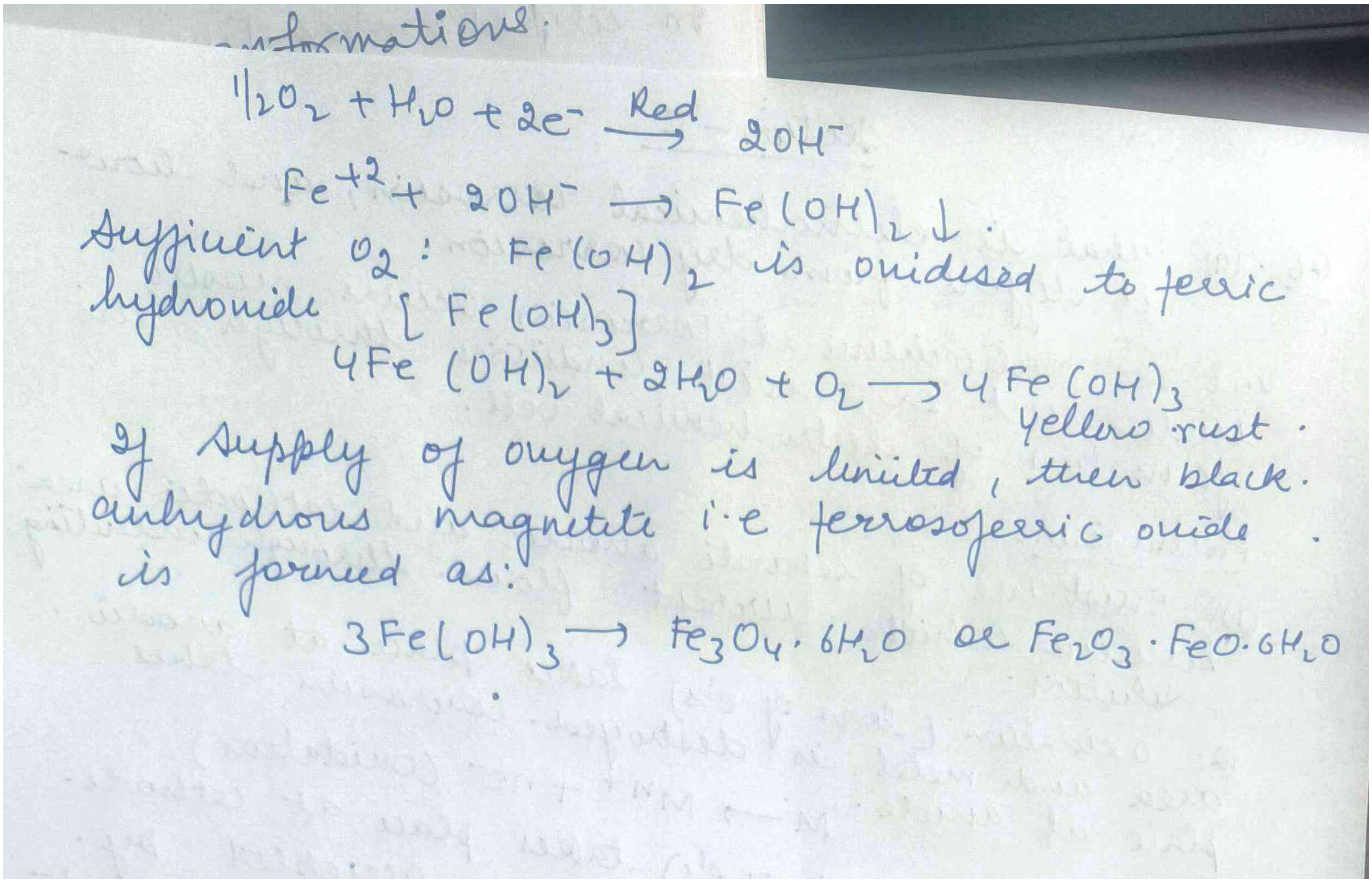
whereas $Fe \rightarrow Fe^{+2} + 2e^-$ (anodic)

$$Fe + 2H^+ \rightarrow Fe^{+2} + H_2$$

(2) Absorption of O_2: it occurs in neutral medium in aqueous solution of NaCl in presence of oxygen.

$$Fe \xrightarrow{\text{oxid}} Fe^{+2} + 2e^-$$

e's are taken by O_2:



formations:

$$\frac{1}{2}O_2 + H_2O + 2e^- \xrightarrow{Red} 2OH^-$$

$$Fe^{+2} + 2OH^- \longrightarrow Fe(OH)_2 \downarrow .$$

Sufficient O_2: $Fe(OH)_2$ is oxidised to ferric hydroxide $[Fe(OH)_3]$

$$4Fe(OH)_2 + 2H_2O + O_2 \longrightarrow \underset{\text{yellow rust}}{4Fe(OH)_3}.$$

If supply of oxygen is limited, then black anhydrous magnetite i.e ferrosoferric oxide is formed as:

$$3Fe(OH)_3 \longrightarrow Fe_3O_4 \cdot 6H_2O \text{ or } Fe_2O_3 \cdot FeO \cdot 6H_2O$$

Comparision of chemical and Electrochemical corrosion.

Chemical corrosion	Electrochemical corrosion.
(1) It occurs in dry condition	1) It occurs in wet condition in the presence of moisture and electrolyte.
(2) It involves the chemical attack of oxygen or other gases.	② It involves electrochemical attack of corrosive Environment on surface of metal.
③ It can occur at homogenous and heterogenous metal surfaces.	③ It occurs only on heterogenous metal surface
④ It is uniform in nature throughout the surface of metal	④ It is not uniform. If the area of anode is small, pitting corrosion takes place.
⑤ It is a slow process taking place by chemical reaction of atmospheric gases.	⑤ It is a fast electrochemical process. It proceeds through the cells.
⑥ corrosion products accumulate at the place where corrosion occurs ie at anode.	⑥ Corrosion products accumulate between the area of anode and cathode.
⑦ Its mechanism is explained on the basis of absorption	⑦ Its mechanism is explained on the basis of Electrochemical Reactions.

(b) What is the relationship between free energy and electromotive force (emf) of a cell?

The relationship between free energy and emf of a cell is derived by: the equation.

$$\Delta G^\circ = - nFE^\circ.$$

where ΔG° = standard Gibbs free energy change.

n = no. of moles of electrons transferred in redox Reaction

F = faraday's constant (F = 968485 C mol-1).

E° = standard cell potential or EMF.

This equation is derived from the fact that work done in an electrochemical cell is equal to free energy change. The negative sign indicates that the process is spontaneous when the EMF of cell is positive.

7 (a) Explain the concept of Hard and Soft Acids and Bases (HSAB) and give examples of each.

Hard and soft acid and Bases explains the stability of metal complexes and mechanism of their reaction.

Pearson classified Lewis acid and Lewis bases as hard and soft acid and bases.

Pearson gave a qualitative correlation between Lewis Acids and Bases. by dividing them into 2 categories hard and soft as:

Class (a) metals which are small and has. less polarizable and form stable complexes. with ligands having donor atom of 1st group. 15, 16, 17 (N, O, F)

ligands: are small and not very polarizable. so metals are hard Acids and ligands are soft bases for class (a)

Class (b) metals having large size; more polarizable and form most stable complexes. with ligands having donor atom of lower member of grp (15 (P) 16 (S) and 17 (Cl) ligands have same properties.

Egs of class (a) Acids: Alkali metals / Alkaline earth metals 1st row of transition metal in higher oxidation state. Fe^{+3}, Co^{+3}.

egs of class (b) lighter transition elements in low oxidation state and heavier transition elements (Cu^{+}, Ag^{+}, Hg^{+})

HSAB principle: for predicting the stability of complexes formed between hard and soft Acid and bases.

Hard Acid prefer to bind with hard bases. and soft acids prefer to bind with soft bases to give stable complex compounds.

3rd class: whose characteristics are intermediate between hard and soft acid / bases are called boderline Acid / Bases.

Application of HSAB principle

(1) AgI_2^- is stable and AgF_2^- is unstable.

AgI_2^- is stable due to soft - soft interaction. AgF_2^- is unstable due to soft - hard interactions.

$$\underset{\text{soft}}{AgI} + \underset{\text{soft}}{I^-} \longrightarrow \underset{(S-S)}{AgI_2^-} \text{ (stable)}$$

$$\underset{\text{(soft)}}{AgF} + \underset{\text{(hard)}}{F^-} \longrightarrow \underset{\text{(Soft - hard)}}{AgF_2^-} \text{ unstable.}$$

(2) complexes of all ligands are soft and all ligands hard are made stable.

eg ① $Co[(CN)_5I]^{3-}$ and $[Co(NH_3)_5F]^{+2}$ are more stable.

② $[Co(CN)_5F]^{-3}$ and $[Co(NH_3)_5I]^{+2}$ are less stable.

7 (b) Explain electron affinity and its trend across period and groups of periodic table giving suitable examples.

Electron gain enthalpy is:
the energy released when electron is added to an isolated gaseous atom to form the gaseous negative ion.
or electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form an anion as:

$A(g) + e^-(g) \longrightarrow A^-(g) \quad \Delta H = \Delta_{eg} H.$

unit = KJ / mole.

the electron gain process can be exothermic and endo thermic for many elements, energy is released when an electron is added to the atom and electron gain enthalpy is negative.
eg: elements of group 17 have very high negative electron gain enthalpy values because they have strong tendency to accept an electron to acquire noble gas configurations.

② noble gases have large positive electron gain enthalpies because they have no tendency to accept electrons. when they gain an electron, it enters the next higher principal quantum number leading to unstable electronic configuration.

Factors on which electron gain enthalpy depends:

(1) Nuclear charge: The ΔHeg value becomes more negative as the nuclear charge increases due to greater attraction for incoming electron.

(2) Size of atom: with the increase in size of atom, the distance between

and incoming electron increases and this results in lesser attraction ∴ so ΔH_{eg} value becomes less -ve with increase in size of the atom

③ Electronic Configuration:
The elements having stable electronic configuration of half filled and completely filled valence sub shells show very small tendency to accept additional electron and thus electron gain enthalpy are less negative.

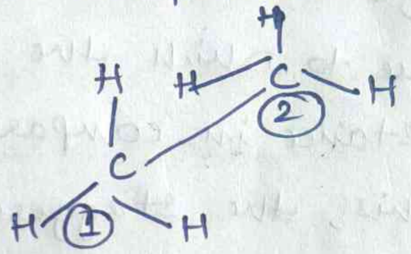
Periodic Trend.
(a) Variation down a group: on moving down a group, the size and nuclear charge increases but the effect of increase in atomic size is much more than that of nuclear charge and thus the additional electron feels less attraction by large atom. So ΔH_{eg} becomes less negative. eg: decrease of ΔH_{eg} in going from chlorine to bromine and to I_2.

(b) Variation along a period: on moving across a period, the size of atom decreases and nuclear charge increases. Both these factors result into greater attraction for the incoming electron ∴ ΔH_{eg} becomes more negative in a period from left to right.

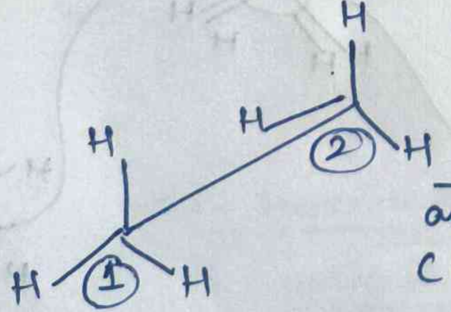
Q : 8 a) Perform a conformational analysis of ethane and illustrate the potential energy diagram for its various conformations.

Ans:- The single covalent bond b/w two carbon atoms is formed by the overlap of sp^3 hybrid orbitals along their internuclear axis. That's why the single covalent bond is cylindrically symmetrical and can freely rotate on its axis. The various spatial arrangements of groups which arises due to free rotation of C – C bond are called conformations and the phenomenon is called conformational isomerism.

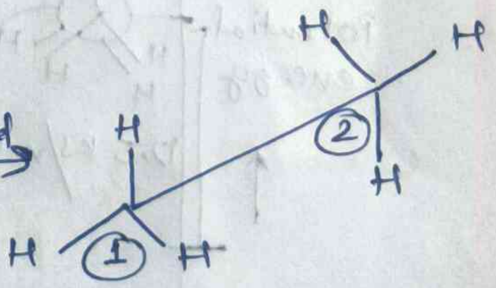
conformations of ethane :-



In ethane various conformations arises due to free rotation of $C_1 - C_2$. Out of various conformations - the two most important conformations of ethane are -



keeping C-1 fixed and rotating the C - 2 by 60°



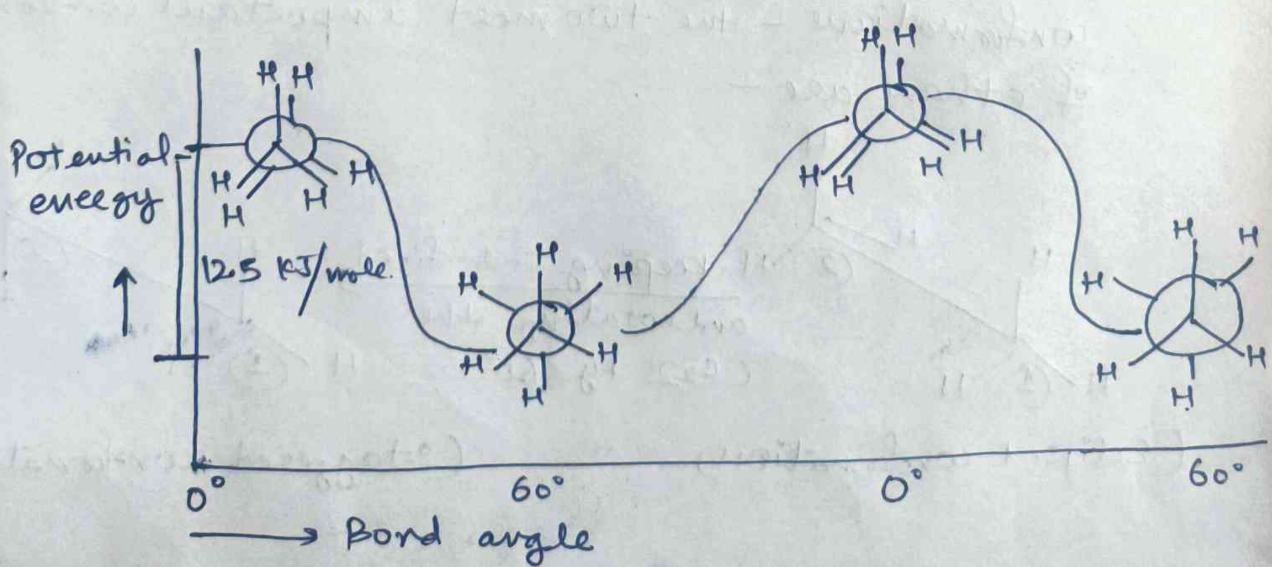
(Eclipsed conformation) (Staggered conformation)

- **Eclipsed conformation** – (less stable, more crowded)

In eclipsed conformation, the three H-atoms tetrahedrally bonded to C_1 are completely parallel to three H-atoms on C_2 (bond angle is 0°) which creates steric hindrance due to repulsions b/w the parallel electronic clouds. The repulsions leads to increase in the energy of eclipsed conformation.

- **Staggered conformation** – (more stable, less crowded)

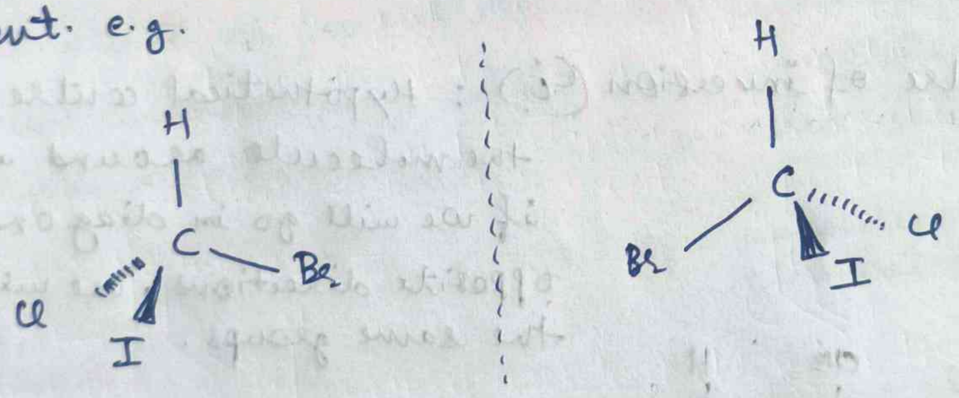
In staggered conformation, the bond angle b/w $C_1 - C_2$ is 60° due to which the H's present on C_1 and C_2 are at a distance in comparison to eclipsed conformation. Due to this, the staggered conformation is less crowded as well as less energetic and more stable in comparison to eclipsed conformation. The staggered conformation is 12.5 KJ/mol less energetic in comparison to eclipsed conformation.



Potential energy diagram of conformations of ethane
(Relative stabilities of eclipsed and staggered conformations)

Q:8) (b) What is chirality and explain why certain molecules are chiral?

Ans:- Chirality is the property of a molecule in which a molecule has non-superimposable mirror images. Or, in other words, a molecule or ion is said to be chiral if it is non superimposable on its mirror image. This pair of isomers is called as enantiomers. Enantiomers are optically active compounds which have the capability of rotating the angle of plane polarized light. If the one isomer of the enantiomeric pair can rotate the angle of plane polarized light to the right side (dextrorotatory), the other enantiomer will rotate the angle of plane polarized light to the left side to equal extent. e.g.



Non-superimposable mirror images (enantiomers)

optically active chiral molecules

(They will rotate the angle of plane polarized light to equal amount in opposite directions)

Plane polarized light to right direction: dextrorotatory

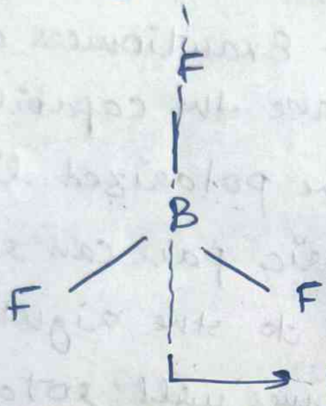
Plane polarized light to left direction: laevorotatory

– conditions for a molecule to be chiral :
(why certain molecules are chiral in nature ?)

For a molecule to be chiral, a molecule must be asymmetric in nature. It must not have

(i) Plane of symmetry : hypothetical plane which can (or σ plane of symmetry) divide the molecule into two equal halves (mirror images)

e.g.

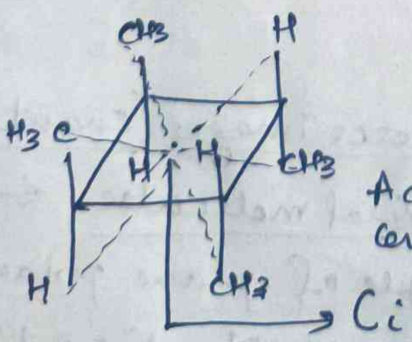


→ plane of symmetry. (σ plane)

Achiral molecule
(as it has plane of symmetry)

(ii) centre of inversion (Ci) : hypothetical centre in the molecule around which if we will go in diagonally opposite directions, we will find the same groups.

e.g.

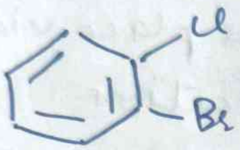


Achiral molecule (as it has centre of inversion Ci)

* So, if a molecule lacks both elements of symmetry (plane of symmetry and centre of inversion) – the molecule will be chiral in nature.

But if any of the above mentioned symmetry elements is present in the molecule the molecule will be symmetric and achiral in nature. eg.

→ Plane of symmetry present
Achiral

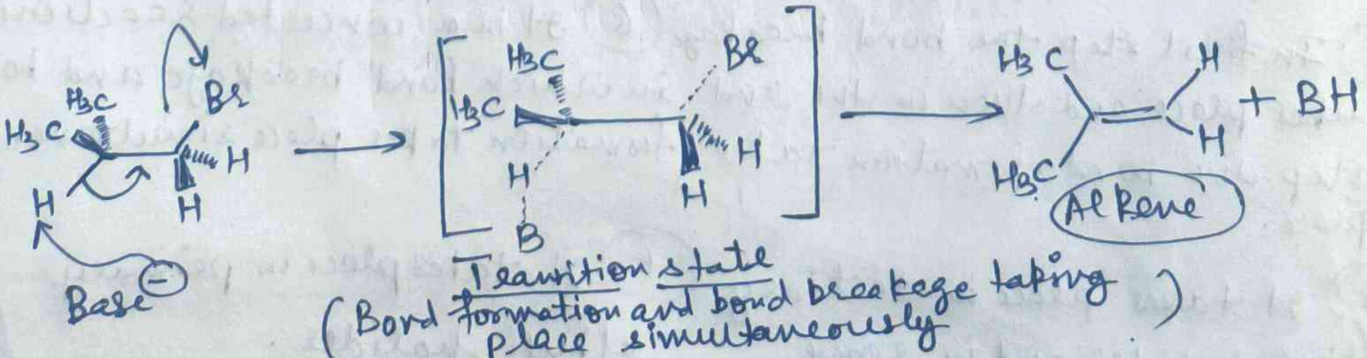


→ No element of symmetry present
chiral.

Q: 9) (a) What are the differences between E1 and E2 elimination reaction?

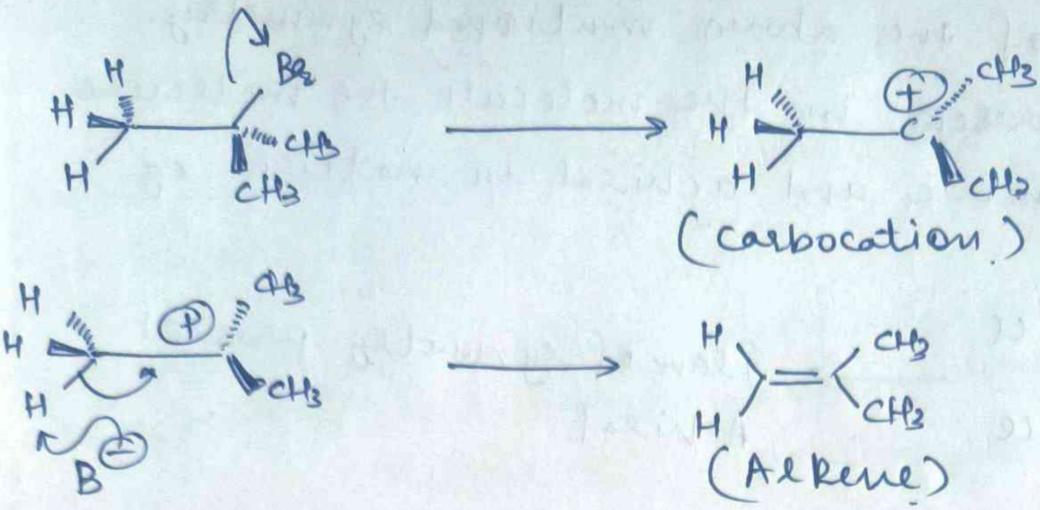
→ An elimination reaction is a type of organic reaction where atoms or group of atoms are removed from molecule without any addition. The elimination reactions are of two types based on their mechanism:-

Elimination → E1: two step: unimolecular elimination.
Elimination → E2: one step - bimolecular elimination



Transition state
(Bond formation and bond breakage taking place simultaneously)

E2 elimination: single step reaction.



E1 elimination: Two step reaction takes place via the formation of carbocation.

E1 elimination	E2 elimination
① It obeys first order kinetics.	① It obeys second order kinetics.
② It takes place in two steps.	② It takes place in one step.
③ It takes place via the formation of carbocation intermediate.	③ No carbocation intermediate formation (there is formation of high energy transition state)
④ It is independent of strength and concentration of base.	④ It depends upon the strength and concentration of base.
⑤ Rate of reaction depends only on the concentration of alkyl halide. $r \propto (R-X)$	⑤ Rate of reaction depends ~~only~~ on the concentration of base as well as alkyl halide. $r \propto [B][R-X]$
⑥ In first step the bond breakage takes place and then in the 2nd step the bond formation takes place.	⑥ It is a concerted reaction in which bond breakage and bond formation takes place simultaneously.
⑦ It takes place in tertiary alkyl halides and in some secondary alkyl halides.	⑦ It takes place in primary alkyl halides.

Q-9) (b) What is Makonikov's rule and how does it apply to addition reactions?

→ Addition reactions are shown by unsaturated molecules having multiple bonds e.g. alkenes and alkynes.

$H_2C = CH_2 + \overset{+}{H}\overset{-}{X} \longrightarrow H_3C - CH_2 - X$

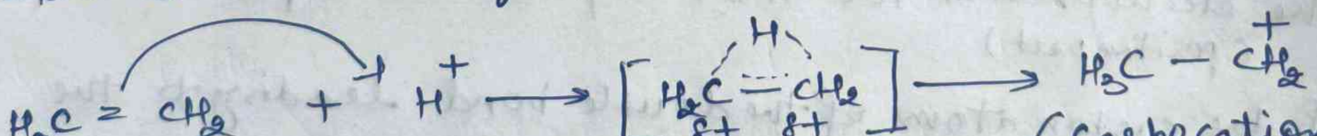
(Addition of HX to alkene double bond)

The addition reactions can be differentiated on the basis of their mechanism – electrophilic addition reaction
nucleophilic addition reaction
free radical addition reaction.

electrophilic addition reaction-

The electrophilic addition reaction takes place in two steps.

(i) In first step the E^+ approaches the reactant (alkene) for the formation of three membered TS transition state which rearranges to carbocation.



$H_2C = CH_2 + \overset{+}{H} \longrightarrow \left[\underset{\delta+}{H_2C} \overset{H}{=} \underset{\delta+}{CH_2} \right] \longrightarrow H_3C - \overset{+}{C}H_2$

(carbocation)

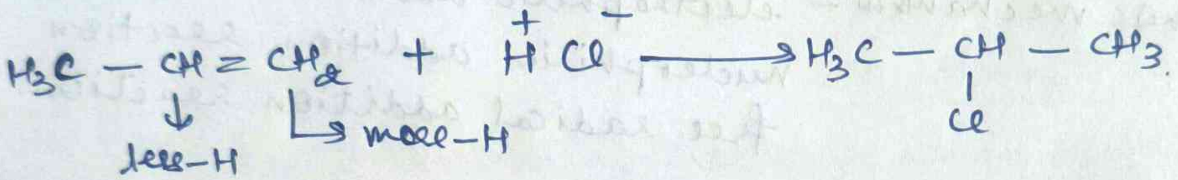
(ii) In 2nd step the nucleophile attacks the carbocation for the formation of addition product.

$H_3C - \overset{+}{C}H_2 + \overset{\ominus}{X} \longrightarrow H_3C - CH_2 - X$

(Addition product)

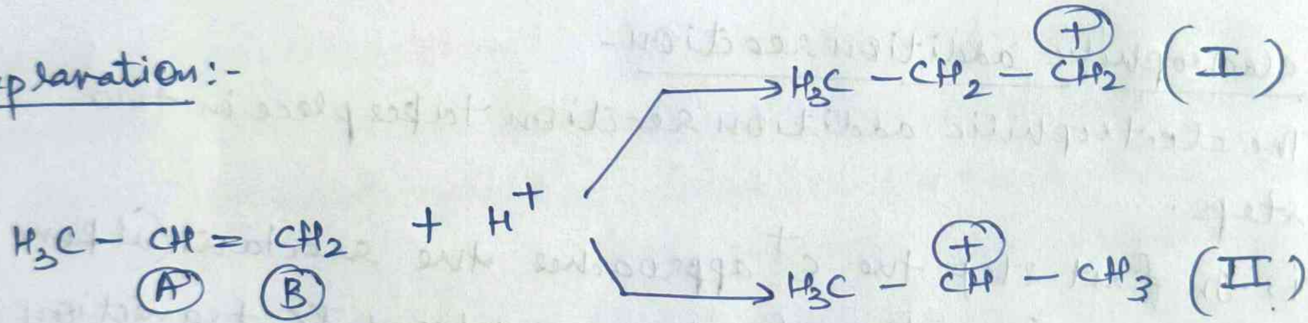
⑧

Markovikov's rule:- It was given for the ~~addition of~~ electrophilic addition reactions to unsymmetrical alkenes. It states that the electron rich part of the reagent (negative part) will add to the carbon atom having lesser no. of H-atoms and the electron deficient part (positive part) of the reagent will add to the carbon atom with more no. of H-atoms.

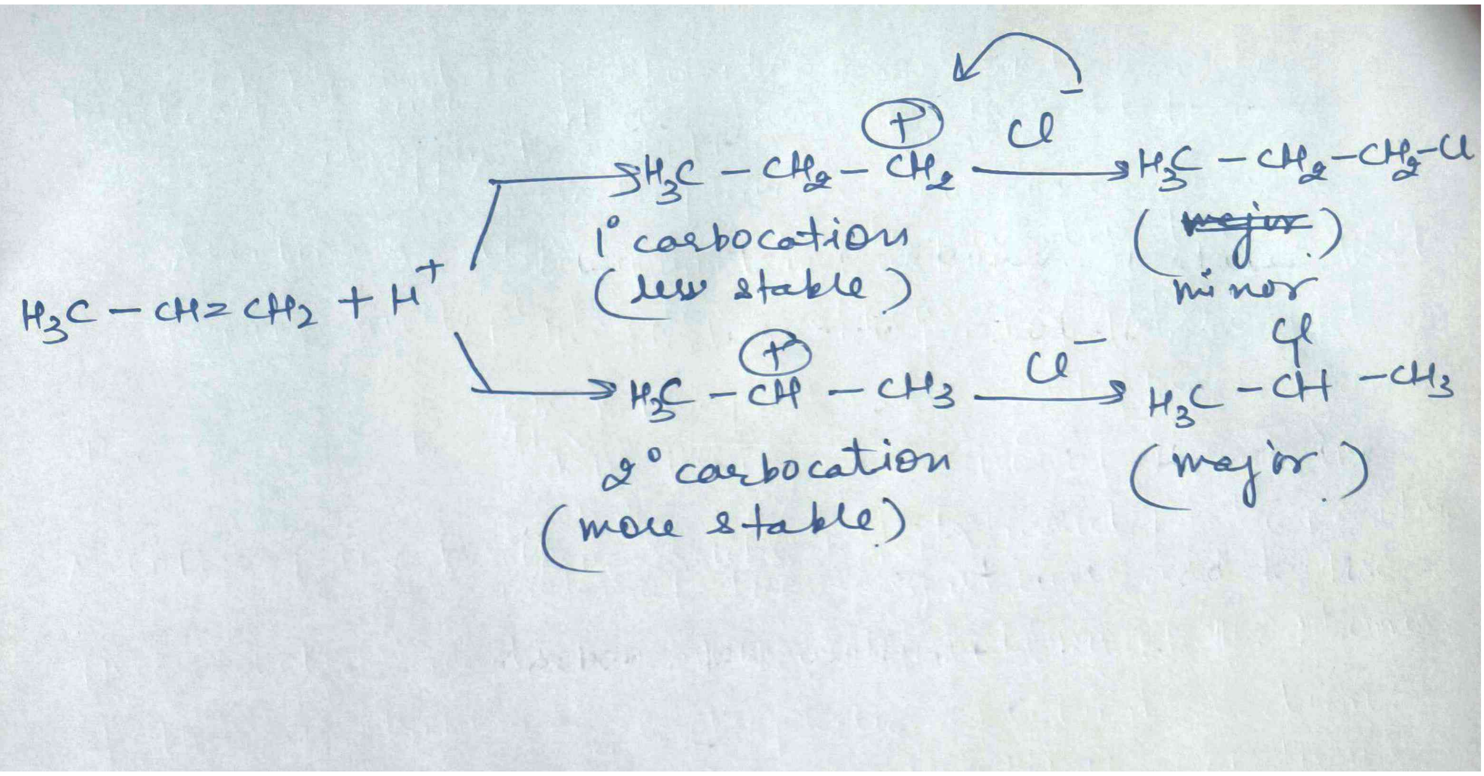


$H_3C-CH=CH_2 + \overset{+}{H}\overset{-}{Cl} \longrightarrow H_3C-\underset{Cl}{CH}-CH_3$

Explanation:-



The electrophile (positive part) in the first step can add upto ~~both~~ any of the carbon atoms of the double bond leading to the formation of two different carbocations. If H^+ adds upto the carbon atoms with lesser no. of H-atoms it will lead to formation of carbocation I whereas if the H^+ will add up to the carbon atom with more no. of H-atoms it will lead to the formation of carbocation II. The carbocation II (2° carbocation) is more stable than carbocation I (1° carbocation). Due to which major product comes from carbocation II.


H3C – CH = CH2 + H+
H3C – CH2 – CH2 +
1° carbocation
(less stable)
Cl−
H3C – CH2 – CH2 – Cl
(~~major~~)
minor
H3C – CH – CH3 +
2° carbocation
(more stable)
Cl−
Cl
H3C – CH – CH3
(major)