

B. Tech. CSE / ECE (sem 1, 2)
Chemistry - I.

Subject code: BTCH-101-18

M. Code: 75343.

Date of Exam: 10-02-22

Time: 2 hrs.

Max. Marks: 60

- Q1. Explain quantum mechanical expression for the motion of a particle in a 1-D box. Also give important results from the treatment.

Definition of particle in a 1-D box:

Consider a particle which moves along X-axis between $x=0$, $x=a$ inside a box. particles bounces back and forth between the walls of box which are rigid.

The particle does not lose energy when it collides with the walls, so that the total energy remains constant.

According to quantum mechanics:

$V(\text{of particle}) = \infty$ on both sides of box.

$(V \text{ of particle}) = 0$ inside box.

since particle cannot possess infinite amount of energy it cannot exist out of box.

\therefore wave function ψ is zero.
for $x \leq 0$ and $x \geq a$.

②

with lion, Schrodinger wave of eqⁿ for one-dimension:

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2m}{h^2} (E-V)\psi = 0$$

where ψ = function of x coordinate only.

Outside lion $V=0$ for outside the lion eq (1) becomes.

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

E is negligible in comparison to E eq (2) reduces to.

$$\frac{d^2\psi}{dx^2} = \infty \psi = 0$$

$$\text{or } \frac{d^2\psi}{dx^2} = \infty \psi$$

$$\text{or } \psi = \frac{1}{\infty} \frac{d^2\psi}{dx^2} = 0 \quad \text{--- (3)}$$

This proves that outside the lion $\psi=0$ which mean particle cannot go outside the lion.

for the particle within the lion. $V=0$ \therefore Schrodinger wave equation becomes:

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} E\psi = 0 \quad \text{--- (4)}$$

\rightarrow for a given state of system, energy E is constant.

$$\therefore \frac{8\pi^2m}{h^2} E = k^2 \quad \text{--- (5)}$$

where $k^2 = \text{constant}$, independent of x .
 then eqⁿ (4) becomes.

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \text{--- (6)}$$

This differential eqⁿ can have solution as:

$$\psi = A \sin kx + B \cos kx \quad \text{--- (7)}$$

A, B are constant.

Depending upon the value of A, B and k, ψ can have many values. But all values are not acceptable. Only those values are acceptable which satisfy boundary condition. i.e.

$$\psi = 0, \text{ at } x=0, x=a$$

putting $\psi = 0$, when $x=0$ eq (7) becomes as:

$$0 = A \sin 0 + B \cos 0$$

$$= 0 + B [\sin 0 = 0, \cos 0 = 1]$$

$$B = 0$$

Thus when $x=0$, eq (7) becomes $B=0$

$$\psi = A \sin kx \quad \text{--- (8)}$$

putting $\psi = 0$, when $x=a$ eq (8) becomes

$$0 = A \sin ka$$

$$\text{or } \sin ka = 0 \quad \text{--- (9)}$$

This equation is valid when the values of ka are integral multiple.

$$\text{i.e. } ka = n\pi \quad \text{--- (10)}$$

$n = \text{integral}, n = 0, 1, 2, 3, \dots$

If $n=0, k=0$ and $\psi=0$, for any value between 0 and a (i.e. within box) because particle is always assumed to be present in a box.

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from eq (10)

$$k = n\pi/a$$

sub this in eq (8) we get.

$$\psi = A \sin\left(\frac{n\pi}{a}x\right) \rightarrow (9)$$

This gives the expression for eigen function ψ

The expression for eigen value of energy can be obtained as:

from eq (5)

$$\frac{8\pi^2 m}{h^2} E = k^2$$

$$\therefore E = \frac{k^2 h^2}{8\pi^2 m} \rightarrow (10)$$

Substituting the value of k from eq (10) we get.

$$E = \frac{(n\pi)^2 h^2}{a^2 \cdot 8\pi^2 m}$$

$$\text{or } E = \frac{n^2 h^2}{8ma^2} \quad n = 1, 2, 3, 4, \dots$$

$$\psi = A \sin\left(\frac{n\pi x}{a}\right) \text{ and } (a)$$

$$E = \frac{h^2 h^2}{8ma^2} \rightarrow (b)$$

are the solution of Schrodinger's wave equation for particle in one dimensional box.

Important result (Application of particle in one lion)

(1) Quantization of energy

$$E = \frac{n^2 h^2}{8ma^2}$$

$$n = 1, 2, 3, \dots$$

(Integral values)

$\therefore E$ associated with motion of particle in a lion = discrete value. (energy is quantized). Integer $n =$ q. No. of particle.

\rightarrow If $n = 1, 2, 3, \dots$ discrete energy for particle of mass m in a lion of length (a) lion.

$$\begin{array}{ll} E_4 = 16h^2 / 8ma^2 & n=4 \\ E_3 = 9h^2 / 8ma^2 & n=3 \\ E_2 = 4h^2 / 8ma^2 & n=2 \\ E_1 = h^2 / 8ma^2 & n=1 \end{array}$$

as n increases separation between energy level increases, energy level (E) depends on " a ", as a increases, space for particle increases, quanta of energy becomes small, energy level come close to each other, the energy difference between any two successive energy level is not a constant value and can be calculated as:

$$\begin{array}{l} E_2 - E_1 = 3h^2 / 8ma \\ E_3 - E_4 = 5h^2 / 8ma \end{array}$$

(2) Existence of zero point energy

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minimum value of $n=1$, \therefore energy level of $n=1$ is minimum and can be shown as:

$$E_1 = h^2 / 8ma^2$$

This means:

When the particle is present in potential box, the energy of lowest level ($n=1$) is called zero point energy. \therefore if particle shows to and fro vibrations then the energy of their lowest allowed state is greater than zero.

= zero point energy exists.

3) quantized wave functions are orthogonal to each other.

Consider two wave function where $n=l$ and $n=m$.

when $n \neq m$ then

$$\psi_l = \sqrt{\frac{2}{a}} \sin\left(\frac{l\pi x}{a}\right) \quad \text{--- (1)}$$

$$\psi_m = \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi x}{a}\right) \quad \text{--- (2)}$$

If $l \neq m$, then probability of finding the particle with limit $x=0$ and $x=a$ is.

$$\int_0^a \psi_l \psi_m dx.$$

putting the value of ψ_l and ψ_m we get

$$\int_0^a \psi_l \psi_m dx = \frac{1}{2} \int_0^a 2 \sin\left(\frac{l\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx$$

$$= \frac{1}{2} \int_0^a \left[\cos\left(\frac{(l-m)\pi x}{a}\right) - \cos\left(\frac{(l+m)\pi x}{a}\right) \right] dx$$

$$= \frac{1}{2} \int_0^a \left[\frac{a}{\pi(l-m)} \sin\left(\frac{(l-m)\pi x}{a}\right) - \frac{a}{\pi(l+m)} \sin\left(\frac{(l+m)\pi x}{a}\right) \right] dx$$

because l and $m = \text{integer}$.

so $\sin 0 = 0$ $\sin(l-m)\pi = 0$

$\sin(l+m)\pi = 0$

\therefore right hand side of equation becomes equal to zero.

means:

$$\int_0^a \psi_l \psi_m dx = 0$$

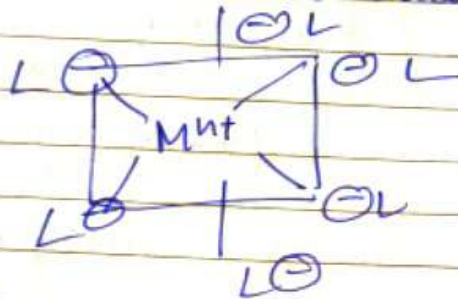
This condition shows that two wave function are orthogonal to each other.

- (b) Describe and compare the splitting of d -orbital under the influence of octahedral and tetrahedral ligand. Calculate CFSE value for d^8 low spin octahedral and d^8 high spin octahedral system.

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Ans: splitting of d-orbitals in octahedral complexes:

Let us consider an octahedral complex $[ML_6]^{n+}$ in which the central metal ion is placed at the center of octahedron and is surrounded by six ligands which reside at six corners of the octahedron as shown below.



The electrons in d-orbital of the metal cation are repelled by negative point charge or by the negative end of the dipole of ligands.

This repulsion increases the energy of all the d-orbitals of the ligands. If all the ligands are

approaching the metal cation are at an equal distance from each d-orbital (i.e. ligand field is spherically symmetrical) the energy of each of the five d-orbitals increases by the same amount. i.e. all the d-orbitals remain degenerate, although they have higher energy.

As the lobes of $d_{x^2-y^2}$ and d_{z^2} orbitals point directly towards the ligands, an electron in either of these orbitals is nearer to the electron pairs of the ligand than if it was in d_{xy} , d_{yz} , d_{zx} orbitals with lobes pointing between the ligands.

Thus the repulsion between the ligands and $d_{x^2-y^2}$ and d_{z^2} orbitals are greater than the repulsions between the ligands and d_{xy} , d_{yz} , d_{zx} orbitals so the energies of $d_{x^2-y^2}$ and d_{z^2} orbitals are higher than the energies of d_{xy} , d_{yz} , d_{zx} orbitals. \therefore the ligands coming closer, removes the degeneracy of the 5-d-orbitals. Splitting them into two sets of degenerate orbitals:

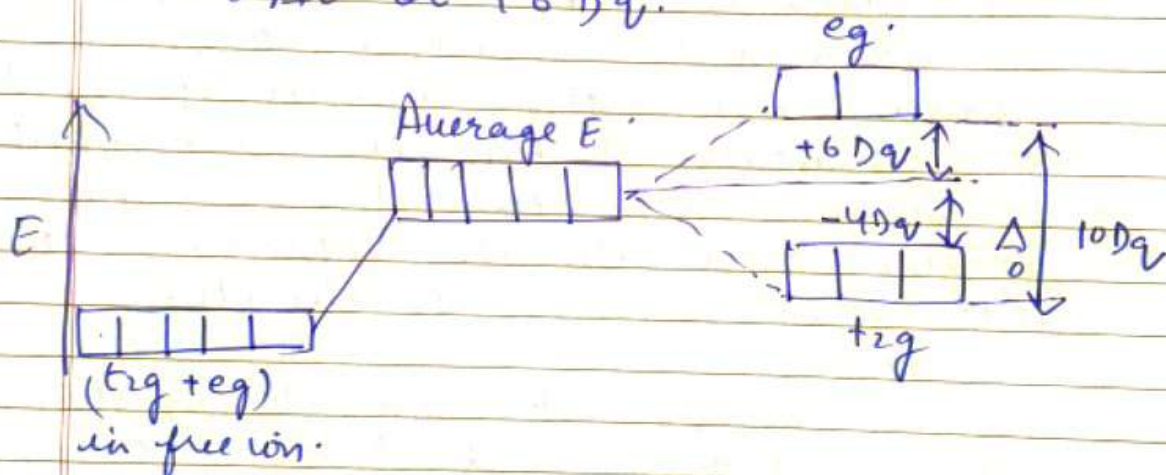
lower energy set consists of d_{xy} , d_{yz} and d_{zx} and higher energy set comprises the $d_{x^2-y^2}$ and d_{z^2}

The three lower energy orbitals are called t_{2g} while the two higher energy orbitals are called e_g .

Thus an energy difference exists between two sets of orbitals. This energy difference is called Crystal field splitting energy (CFSE)

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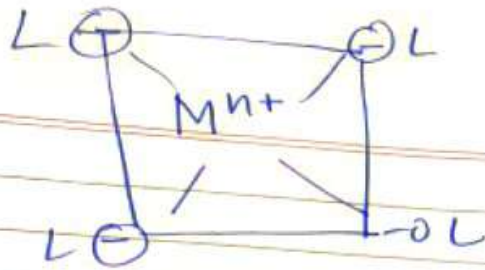
represented by Δ_0 which measures the crystal field strength of ligands. The energy gap between t_{2g} and e_g set is also denoted by $10 Dq$. As energy of t_{2g} orbital is $4 Dq$ less than degenerate d-orbital and e_g orbital is $6 Dq$ above the degenerate d-orbital. Thus t_{2g} set loses an energy equal to $-0.4 \Delta_0$ or $-4 Dq$ while e_g set gain an energy equal to $+0.6 \Delta_0$ or $+6 Dq$.



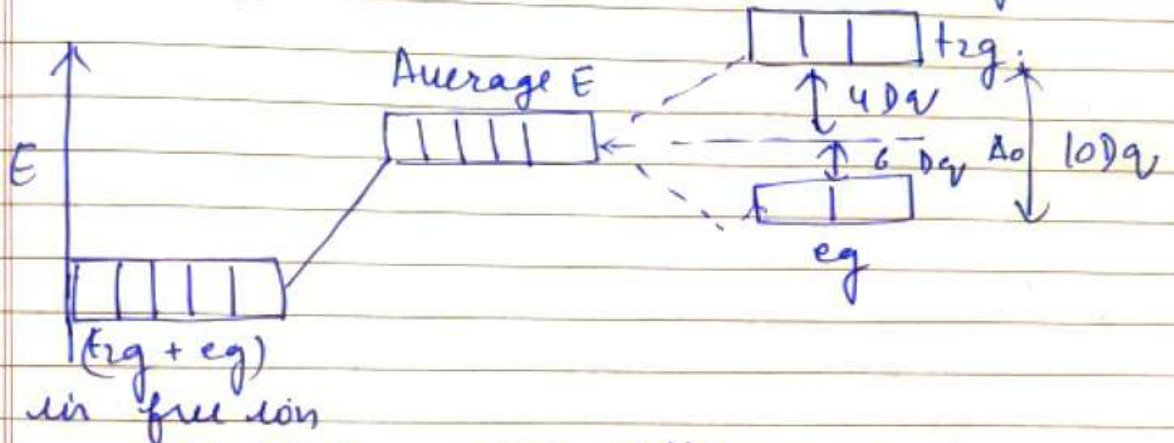
Splitting of d-orbitals in octahedral complexes.

(2) Crystal field splitting in tetrahedral complexes.

The tetrahedral arrangement of four ligands surrounding the metal ion M^{n+} is shown as:



→ The three orbitals i.e. t_{2g} orbitals are close to approaching ligands. The t_{2g} electron suffer more repulsion than e_g electron. The energy of t_{2g} orbitals increases more than e_g orbital.



Crystal field splitting of d-orbitals in a tetrahedral complex.

The energy gap between two sets of orbitals is designated as Δ_t .

Δ_t is less than Δ_o .

$$\Delta_t = \frac{4}{9} \Delta_o$$

Compare Octahedral and tetrahedral complexes:

| <u>Tetrahedral complex</u> | <u>Octahedral complex</u> |
|--|--|
| → They are unoccupied empty space. present in substances having tetrahedral crystal. | They are unoccupied empty space. present in substances having octahedral system. |

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- | | |
|--|---|
| * tetrahedral can be found in substances having tetrahedral arrangement in crystal | * octahedral can be found in substances having octahedral arrangement in crystal. |
| * The coordination no is four. | Coordination no. is six. |
| * e_g is of lower energy, t_{2g} is of higher energy | t_{2g} is of higher energy and e_g is of lower energy. |
| * t_{2g} is raised by $+4Dq$ energy and e_g is lowered by $+6Dq$ | t_{2g} is lowered by $-4Dq$ and e_g is raised by $+6Dq$. |

CFSE value for d^8 ion:

(a) low spin state (strong ligand field)

Configuration: $t_{2g}^6 e_g^1$

$$(-4 \times 6 + 0.6) = -12.01 - 12Dq$$

(b) high spin state (weak ligand field)

Configuration: $t_{2g}^6 e_g^2$

$$(-4 \times 6 + 2 \times 0.6) = -12.01 - 12Dq$$

2(a) Discuss the role of doping in band structure of solids.

Role of Doping on band structure:

The process of deliberately adding the impurity in a semi-conductor so as to increase its conductivity is called doping. The impurity atoms are called dopants and the semi-conductor containing the impurity atoms is called doped or an impurity or extrinsic semi-conductor.

The impurity is added to increase the no. of electrons or holes in the semi-conductor. Since the semi conductor generally belong to fourth group of periodic table, the impurities which are added are elements belonging to 3rd or 5th group of periodic table they are commonly boron, gallium, indium, and aluminium (trivalent) from 3rd group and phosphorous, antimony, and arsenic (pentavalent) from 5th group.

Depending upon the type of impurities added, intrinsic type of semiconductors are classified as:

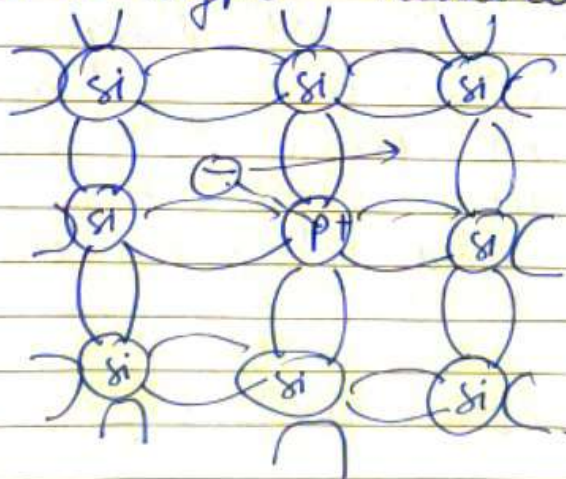
(i) N-type semi-conductor:

* These semiconductor contains a small quantity of a pentavalent element impurity (like phosphorous, arsenic or antimony)

* Doping atom forms four covalent bonds with the surrounding four atoms of intrinsic semiconductor (germanium, silicon) with the help of its four valence e^s.

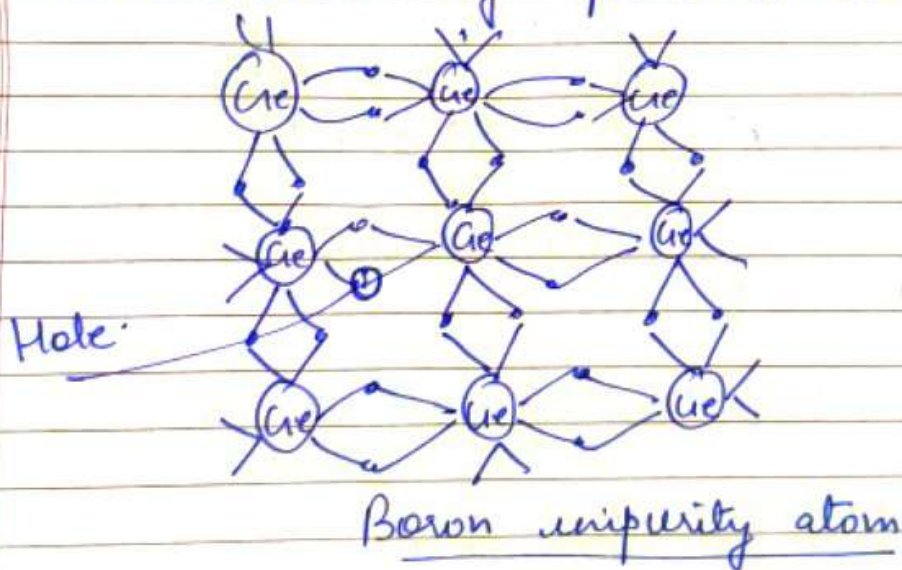
* The 5th excess electron remains loosely bound to the donor atom itself, it is easily excited from the valence band to conduction band on applying electric field.

* Thus conduction is due to movement of extra electron in an n-type semiconductor.



(2) p-type semiconductor:

- * They contain a small quantity of a trivalent element (like boron, aluminium)
- * the three valence electron present in the trivalent impurity forms three covalent bonds with the surrounding three of the four atoms. so that one bond in one of the four surrounding atom is left incomplete.
- * This give rise to positive hole.
- * on applying an electric field, a hole travels to an adjacent atom by acquiring an electron and establishes a new covalent bond by breaking an existing covalent bond in the adjacent atom.
- * Hence conductivity in p-type semiconductor is due to the movement of positive hole.



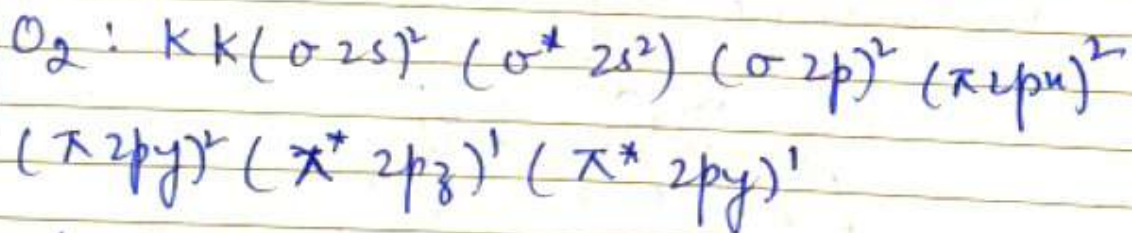
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2(b) On the basis of MO theory, compare the relative stability of the following species and indicate their magnetic properties.
 O_2 , O_2^- ; superoxide and peroxide-

Ans On the basis of M.O theory:
oxygen molecule, O_2 :

O_2 : $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$
 each oxygen atom has eight electrons. There are six electrons in O_2 molecule. Due to combination of atomic orbital of 2 atoms, 10 M.O are formed. These are filled in the increasing order of their energies (aufbau prin)

Configuration of O_2 is:

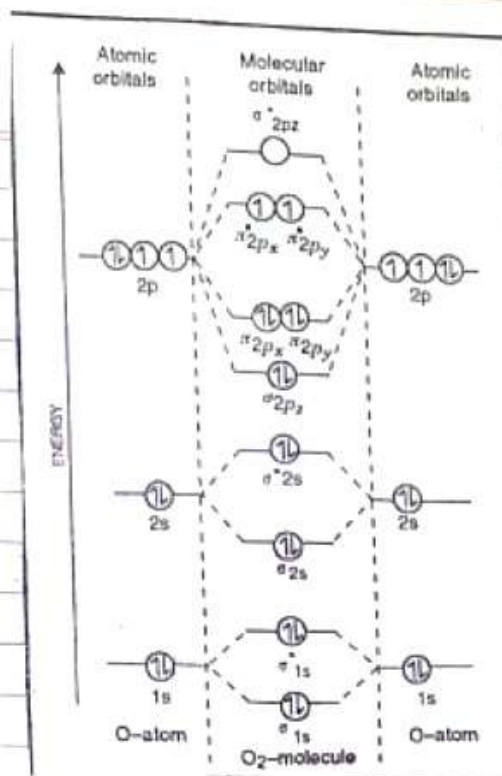


Last 2 MO are half filled:

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

$$\therefore \text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 6) = 2$$

Bond dissociation energy of $O_2 = 490 \text{ kJ/mol}$
 and its bond length = 121 pm.

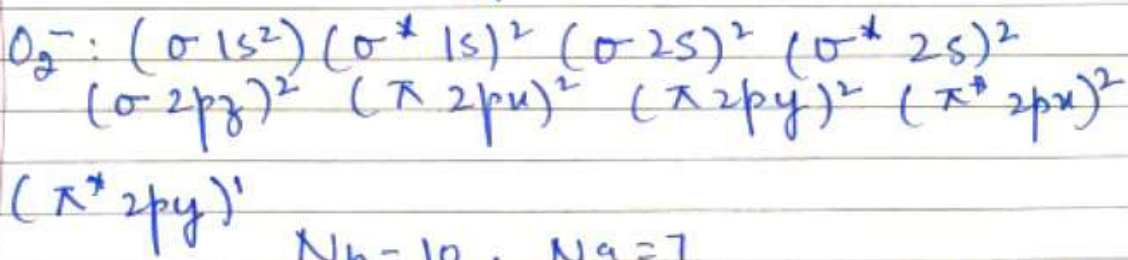


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M.O diagram of oxygen

(2) O_2^- ion (superoxide ion)
 $O_2 + e^- \rightarrow O_2^-$

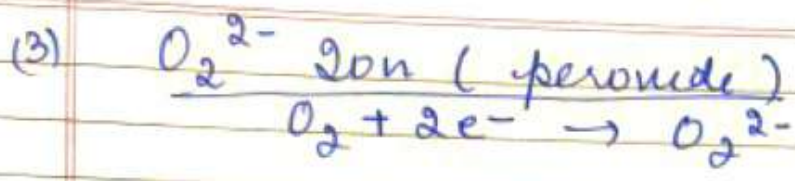
This ion has one electron more than the electrons in oxygen molecule. There are 17 e⁻s in O_2^- and its electronic configuration is:



$N_b = 10, N_a = 7$

$\therefore \text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 7) = 1.5$

Due to presence of one unpaired e⁻. O_2^- ion is paramagnetic.



O_2^{2-} ion has 2 electrons more than O_2 molecule. Its electronic config:

$$O_2^{2-} : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2$$

$$(\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^* 2p_x)^2 (\pi^* 2p_y)^2$$

$N_b = 10, N_a = 8$

\therefore bond order of $O_2^{2-} = \frac{1}{2}(10-8) = 1$
 ion = diamagnetic, due to absence of unpaired e's.

Relative stabilities of $O_2, O_2^{\cdot-}$ and O_2^{2-} as calculated above the bond order of these species are 2, 1.5, 1

The bond dissociation energies are directly proportional to bond order
 \therefore bond dissociation energies are in order:

$$O_2 > O_2^{\cdot-} > O_2^{2-}$$

The stabilities of species are directly proportional to bond order \therefore their bond lengths will be in order:

$$O_2^{2-} > O_2^{\cdot-} > O_2$$

3(a) What is the essential condition for a molecule to be IR active? find the normal modes of vibrations for a molecule of CO_2 . Explain UV-transition.

Molecule IR Active Conditions:

Solu(a) Electric dipole moment of molecule must change when the atoms are displaced relative to one another or when molecule vibrates. Such vibrations are IR active. Molecule need ^{not} to have a permanent dipole moment. But change during vibration is required. Molecule may even have zero dipole moment but during vibration it must change the dipole moment. Heteronuclear diatomic molecule show the change in dipole moment and are IR active.

the normal mode of vibration for a molecule of CO_2 .

In linear molecule of CO_2

$N = 3$, so $3N = 3 \times 3 = 9$.

total degree of freedom = $3N = 9$.

translational degree = 3.

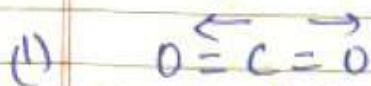
of freedom

Rotational degree of freedom = 2

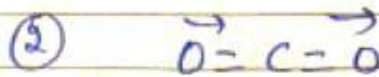
\therefore vibrational degree of freedom = $9 - (3+2) = 4$

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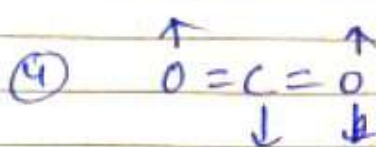
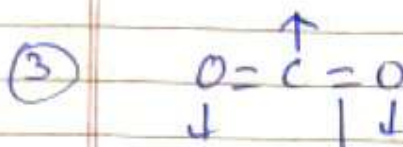
∴ for CO_2 fundamental bands = 4



Symmetric stretching
(IR inactive = 1340)



Asymmetric stretching
 $\nu = 2350$



bending vibration

$\nu = 666$ (degenerate motion)

∴ only 3 fundamental bands actually appear.

Explain UV-transitions:

Electronic transitions:- when a molecule is excited by absorption of energy (UV or visible light) its electrons are promoted from a bonding to antibonding orbital.

The three kind of electrons responsible for electronic transitions are:

- (1) sigma (σ) molecule in saturated molecules
- (2) pi (π) electrons in unsaturated molecules
- (3) Non-bonding (n) electrons in non-bonded elements.

There are four types of electronic transitions:-

(1) $\sigma \rightarrow \sigma^*$ transition:

In this transition, the electrons in a molecule move from the ground state to a higher energy state anti-bonding (σ^*) orbital. This transition takes place due to the E.M.R that get absorbed. The highest quantity of energy is needed to undergo this transition. It is seen in methane molecule due to the presence of only C-H bonds.

(2) $n \rightarrow \sigma^*$ transition:

In this transition the electrons from a non-bonding orbital (n) move to an anti-bonding (σ^*) orbital. The lowest quantity of energy is needed to undergo this transition. Halogens and elements like sulphur, oxygen and nitrogen display this transition.

(3) $n \rightarrow \pi^*$ transition:

In this transition the electrons from a non-bonding orbital (n) move to an anti-bonding (π^*) orbital. Compounds having double bond between hetero atom $C=O$, $C=S$, $N=O$ show these transitions which occur as weak absorption band (R-band).

Eg. Carbonyl group of $C=O$ exhibits an absorption of low intensity at 285 nm.

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(4) $\pi \rightarrow \pi^*$ transition:

The transition in which π 's is excited to an antibonding π^* orbitals are called $\pi \rightarrow \pi^*$ orbitals.

higher energy requirements than $n \rightarrow \pi^*$ absorption.

absorption takes place outside the ordinary UV region for simple molecules containing isolated unsaturation.

but intensity of absorption is high absorption band is called π -band.

Eg: $\pi \rightarrow \pi^*$ for simple aldehydes or ketones produce an absorption of high intensity at 180 nm.

3(b) what type of nuclei show NMR spectra? How shielded and deshielded protons are represented on TMS scale. ? give high resolution HNMR spectrum of ethanol.

Ans 3(b) in NMR spectra; like electrons, particle of nucleus (Neutron + proton) also spin on their own axis. Like electron each proton and neutron is assigned a spin q ; No $= \frac{1}{2}$

The spin quantum no. of nucleus can have values 0, $\frac{1}{2}$, 1, $1\frac{1}{2}$, 2 etc depending upon the no. of neutron and proton having parallel

or anti-parallel spins.

The spin quantum no. of nucleus is represented as I :

(1) for nuclei in which

proton + neutron = even
(even) (even) (even)

$\therefore I = 0$, eg: He_2^4 , C_6^{12} , O_8^{16} , S_{16}^{32}

(2) for nuclei in which

proton + neutron = even (sum)
(odd) (odd)

$\therefore I = 1, 2, 3$ eg: D_1^2 , N_7^{14}

(3) for nuclei in which sum of proton and neutron is odd.

$P + N = (\text{sum}) \text{ odd}$.

$I =$ always odd integral multiple of $1/2$

Eg: $I = 1/2, 3/2, 5/2$ etc.

$I = 1/2$ for H_1^1 and F_9^{19} .

$I = 3/2$ for Na_{11}^{23}

$I = 5/2$ for Cl_{17}^{37}

here: no. of proton + no. of neutron
(odd) | (even) | odd.
even.

Spinning of various particles in nucleus leads to net spinning of nucleus about an axis. \therefore nucleus is charged particle. When this charged particle spins about its own axis.

when $I \neq 0$, i.e. $I > 0$ then such nuclei show NMR spectra.

Shielded and deshielded protons are represented on TMS scale as:

Chemical shift is the position of a NMR absorption. It depends on:

- (1) electron density in the vicinity of an hydrogen atom this is affecting by the molecular structure.
- (2) chemical shifts are reported on the horizontal axis of the spectrum (the δ scale in ppm) from the reference (TMS)

TMS is added to the solution and arbitrarily assigned a chemical shift of 0. All other signals are reported relative to that position.

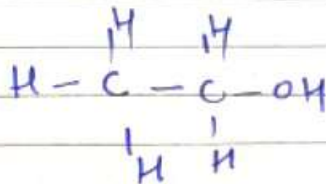
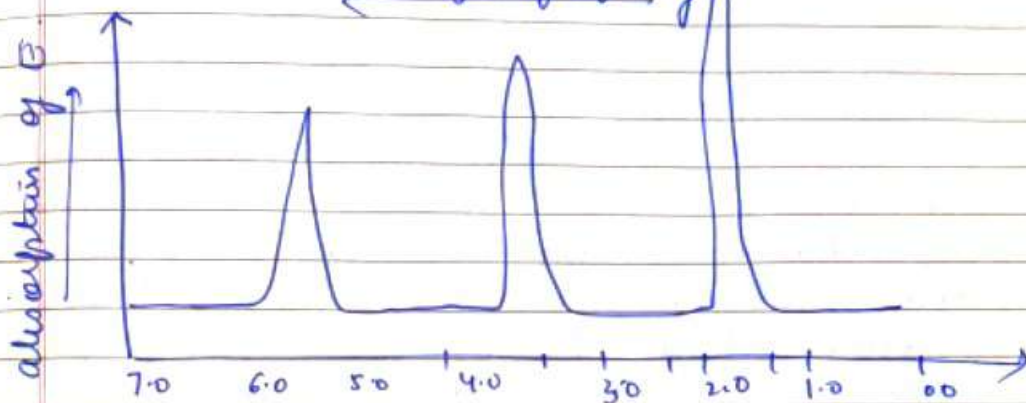
Since electron density is the determining factor in the chemical shifts observed, dipole in the molecule will have an effect in donating or removing electrons from the vicinity of a given proton. This effect is described as:

* Shielded: more e's in proton's vicinity (dipole effect minimum)

* Deshielded: less electron in proton vicinity (dipole effect is increased)

The result is that shielded proton absorb radiation at higher field while deshielded proton will absorb at lower field frequency.

High resolution HNMR spectrum of ethanol:



4(a) What are the reasons of the deviation of real gases from ideal behaviour? How they modified in Vander Waals' equation?

Ans 4(b) The causes of deviation of real gases from ideal behaviour is due to:

- (1) There is no intermolecular force of attraction within gaseous molecules. (at high pressure and low temperature) there is appreciable intermolecular

- (2) force of attraction.
the actual volume of the molecule is negligible as compared to total volume of gas (at high pressure), the gaseous molecule occupy minimum volume which is not negligible.

They are modified in Vander-vaals' equation: as:

- (a) Volume correction in Vander-vaals' Equation:-

As particles have a definite volume, the volume available for their movement is $(V-b)$ where b is the effective volume of the molecules which is equal to 4 times the actual volume of molecule at rest. The effective volume (b) is also called Co-volume or excluded volume.

Let us consider two molecules approaching each other. Let δ and r represent the diameter and the radius of each molecule. The molecule cannot approach more closely than the distance δ . It is because the molecules are impenetrable. So within a sphere of radius δ ($= 2r$), no volume will be occupied by this pair of molecules.

Thus,

the excluded volume per pair of molecules = $\frac{4}{3} \pi (2r)^3 = 8 \left(\frac{4}{3} \pi r^3 \right)$

so excluded volume for a single molecule = $\frac{8}{2} \left(\frac{4}{3} \pi r^3 \right) = 4 V_m$
where V_m is the volume occupied by a single molecule.

Thus the excluded volume (b) for a mole of gas is given as:

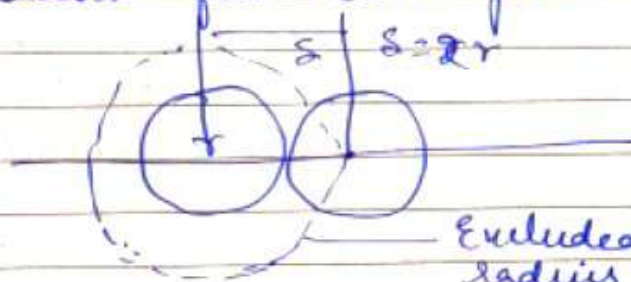
$$b = 4 \left[\frac{4}{3} \pi r^3 \right] \times N = 4 V_m N$$

where N

Being the Avogadro's number

\therefore corrected volume = $(V - b)$

b = volume to be excluded which is 4 times the actual volume of the molecule and it is characteristic constant for each gas.



Excluded volume of radius $S = 2r$.

(2) Pressure correction:

Consider particles A and B in gas the net force of intermolecular attraction on particle A in interior of gas is nil because it is surrounded by molecules which are equally distributed in opposite direction. \therefore attraction cancel mutually.

(26)

molecule B experiences a inward force of attraction or pull due to interior molecules. So due to this inward pull, the measured pressure P is less than the ideal pressure -
 i.e. when no attraction were there. The observed pressure is thus less than that would be expected. This will tend to make PV less than RT and so will tend to cause a negative or under perfect deviation. Thus a correction term P_a should be added to P to get ideal pressure.

Ideal pressure = $P + P_a$.

(a) The inward force P_a exerted on molecule about to strike the walls of the vessel is proportional to the no. of molecules striking the wall at any given instant which is proportional to the density of gas.

(b) The no. of molecules in the interior which are attracting the striking molecules, which is also proportional to the density of gas.

$$\therefore P_a \propto d^2$$

but density $d \propto 1/\text{Volume}$.

$$\therefore P_a \propto 1/V^2$$

$$\therefore P_a = a/V^2$$

a = proportionality constant called coefficient of attraction

Hence, ideal pressure = $(P + a/V^2)$
 Incorporating the volume correction and attraction correction in the gas equation we get,

$$(V-b) \left(P + \frac{a}{V^2} \right) = RT$$

4(b) Write a detailed note on potential energy surface. Also discuss its application.

Ans (4b) A potential energy surface describes the energy of a system particularly a collection of atoms in terms of the position of the 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 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.

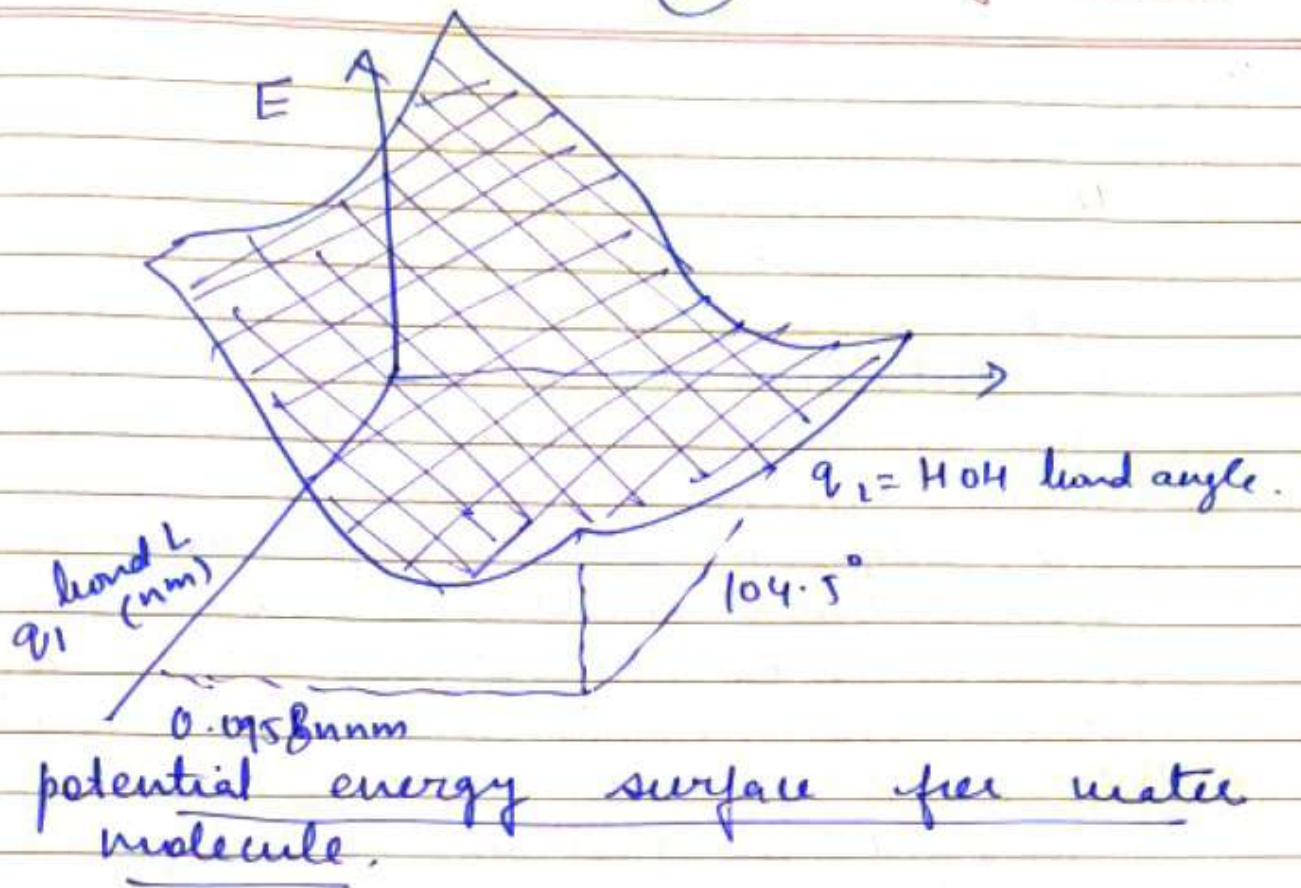
The potential surface concept finds application in many fields such as chemistry and physics. It can be used to theoretically explore properties of structure.

composed of atoms for eg, finding the minimum energy, shape of a molecule. or calculating the rate of a chemical reaction.

Application:

A potential energy surface is a tool for finding the analysis of molecular shape and chemical kinetics for a reaction. Once the necessary points are evaluated on a PES, the points can be classified according to the first and second derivatives of the energy w.r.t. position.

These correspond to the gradient and the curvature of the curve. Stationary points (or points with zero gradient) have physical meaning i.e. energy minima correspond to physically stable chemical species and saddle points correspond to transition states the highest energy point on the reaction coordinate (which is the lower energy pathway connecting a chemical reactant to a chemical product).



5(a) Write short note on:

(i) Electrochemical Corrosion:

Corrosion of a metal by aqueous conducting medium with the formation of anodic and cathodic areas is known as wet or electrochemical corrosion.

The aqueous conducting medium like water, aqueous solution, sea-water, dew, fog, wet soil, high humidity. The corrosion involves anodic and cathodic area formation and corrosion occurs on anodic area only, while corrosion product either remain dissolved in medium or deposits on cathode.

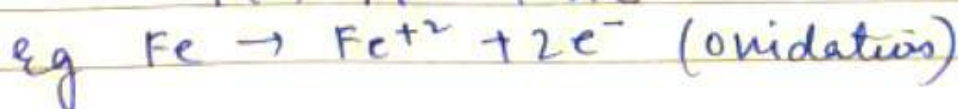
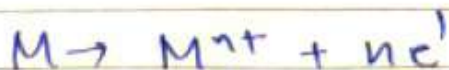
Mechanism of Electrochemical Corrosion:

The corrosion of anodic part takes place and corrosion product deposits on cathode area near the anode.

The rate of corrosion by cells formation is faster than the corrosion by dry O_2 gas.

Reaction at anode (oxidation):

At anode electron liberation takes place. metal atom on the surface of anode, pass into conducting medium by forming metal-ions leaving behind electrons.



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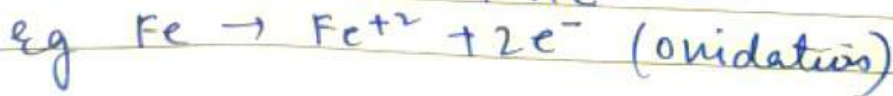
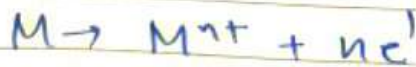
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(3)

Reaction on Cathode (Reduction)

The electrons left on anodic part, flow to cathodic part and depending upon the nature of conducting medium they bring about one the reactions:

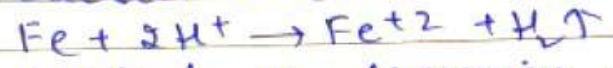
(1) H₂ liberation / evolution:

If the corroding medium is acidic then H⁺ from the medium capture electrons (reduction) from cathode and there is liberation of H₂ gas.

Cathode:



The overall reaction will be:

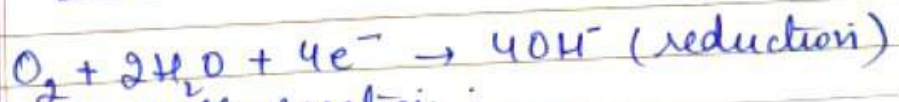


the product of corrosion is H₂ gas liberation at cathode and the corroding aqueous medium contains the dissolved compound of the anodic metal.

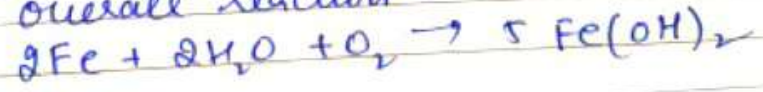
(2) O₂-absorption:

If the corroding medium is neutral or slightly alkaline some O₂ gas dissolved, the reaction of O₂ absorption takes place on cathode.

Cathode:

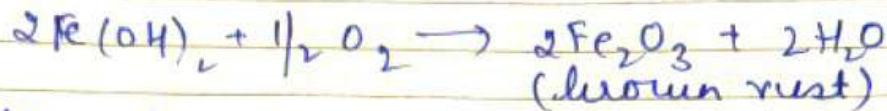


Overall reaction:



(32)

If enough oxygen is present in medium then the ferrous hydroxide gets oxidized further to rust.



thus the O_2 gas from the aqueous medium is utilized for reaction and there is formation of metal hydroxide as the corrosion product. The metal hydroxide if soluble in the aqueous medium it remains dissolved and if not soluble then it deposits on cathode area near the anode.

(ii) Hot lime soda method:

This method involves the treatment of water with lime $\text{Ca}(\text{OH})_2$ and soda (Na_2CO_3) which results in the formation of insoluble precipitates of Ca and Mg which can be removed by filtration.

Process:

(i) Reaction tank: The reactants i.e. hard water, steam and chemicals are mixed in ~~other~~ two outer chamber and moved on to the reaction tank.

(2) Conical sedimentation tank:

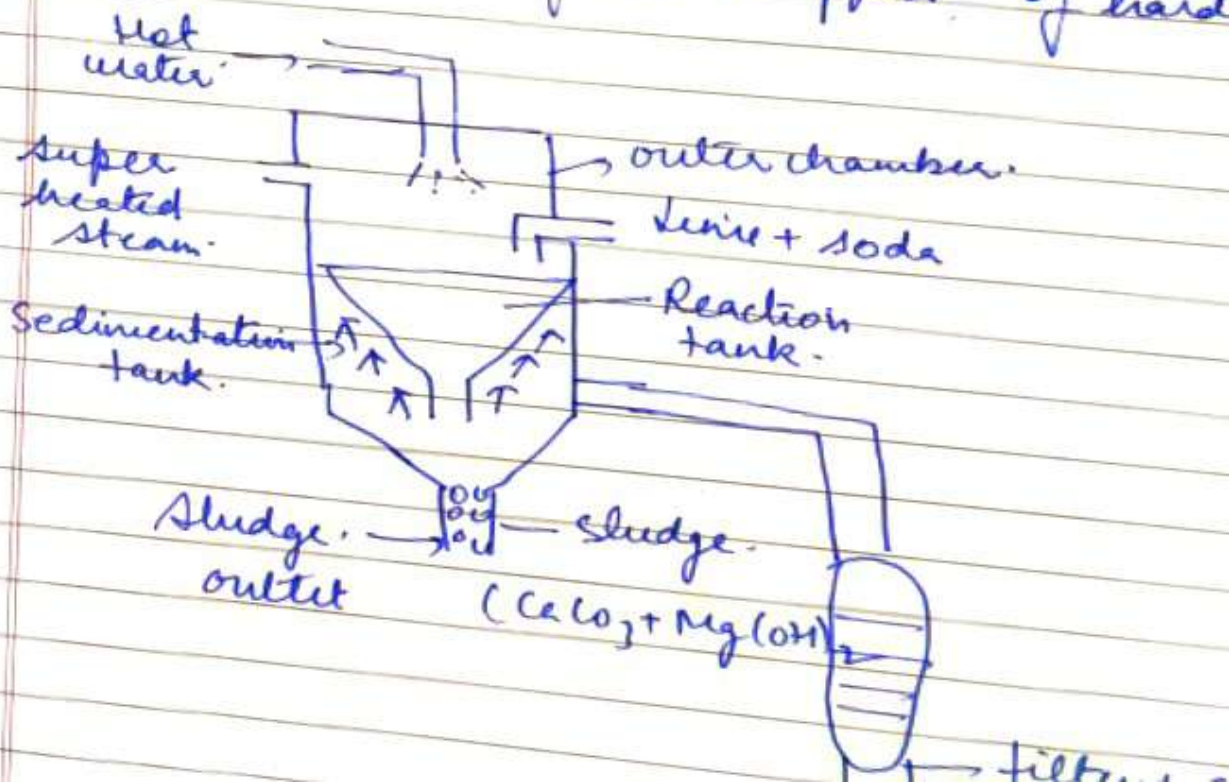
The chemical reaction is completed here. The precipitates get settled

(33)

down and form sludge.
(3) sand filter: water passes the sand filter and complete removal of sludge takes place.

In this process, the mixing of chemicals is done near boiling point of water rate of reaction becomes faster because of high temperature and complete precipitation takes place quickly and thus the settling rate is also high. Hence, no coagulant is required.

This is a better method than cold lime soda process because it gives water of 15-20 ppm hardness as compared to cold lime soda gives water of 50-60 ppm of hardness.



5 (iii) significance of Ellingham diagram

(i) Curves in the diagram for the formation of metallic oxides are straight lines with positive slope.

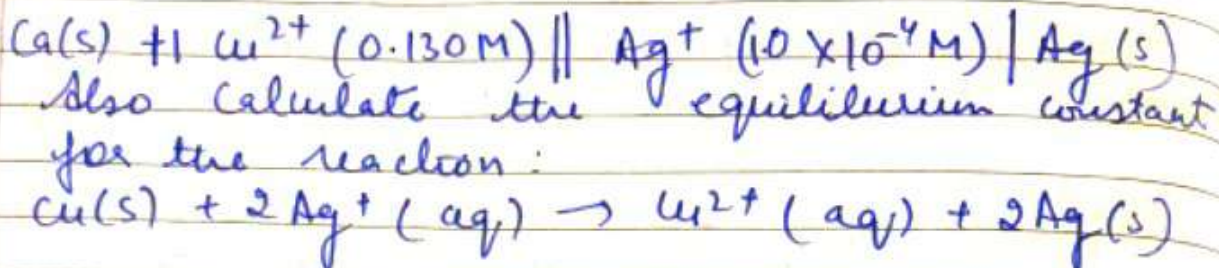
Lower the position of metal's line the greater is the stability of its oxide.

Stability of metallic oxides decrease with increase in temperature. Highly unstable oxides like Ag_2O and HgO easily undergo thermal decomposition.

The formation of free energy of CO is independent of temperature; CO has -ve slope and crosses the CO_2 line near 700°C . CO is the dominant oxide of carbon at higher temperature above 700°C . As higher the temperature the carbon becomes more effective reductant (reducing agent).

(35)

5 (b) Explain the Nernst equation & calculate the emf of the following cell at 298 K



Ans 5(b) Derivation of Nernst equation:

for a reversible cell, cell reaction is
 $aA + bB \rightarrow xX + yY$
 free energy change of this reaction is

$$\Delta G = \Delta G^\circ + RT \log \left(\frac{\text{Reactants}}{\text{product}} \right)$$

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

$T = 298 \text{ K}$, $R = 8.314 \text{ kJ/mol}$
 transference of 1 mol of e's = $1F$

$E =$ emf of cell. then electrical E produced in cell = nFE

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

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

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

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

Sub ΔG & ΔG° from (2) & (3) in (1)

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

calculate
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$$E = E^{\circ} + \frac{1}{-nF} RT \ln (P/R)$$

$$E = E^{\circ} - \frac{RT}{nF} \ln (P/R)$$

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

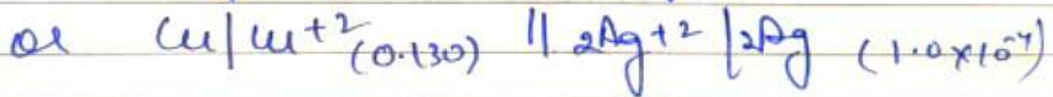
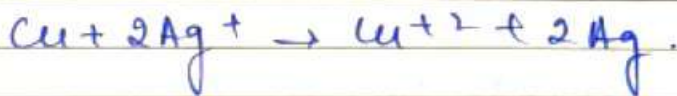
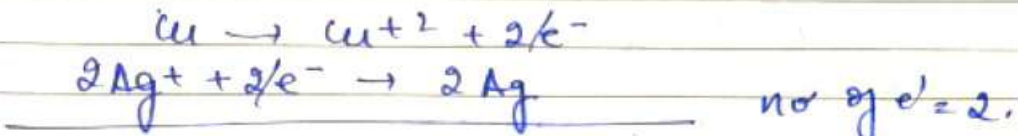
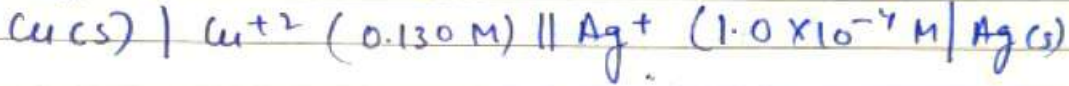
$$T = 25^{\circ}C \text{ or } 298 K \quad (25 + 273)$$
$$R = 8.314 \quad F = 96500$$

$$E = E^{\circ} - \frac{0.0591}{n} \log (P/R) \text{ or}$$

$$E = E^{\circ} + \frac{0.0591}{n} \log (P/R)$$

Activity (conⁿ) of pure liquid & pure solid = unity or 1.

Calculate the emf of the following cell at 298 K.



$$E = E^{\circ} - \frac{0.0591}{n} \log (P/R)$$

$$E^{\circ} = (R-L) = -(0.80) + 0.34 = 0.46$$

$$\therefore E = E^{\circ} - \frac{0.0591}{2} \log (P/R)$$

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$$E = 0.46 - \frac{0.0591}{2} \log 0.130 \times 10^4.$$

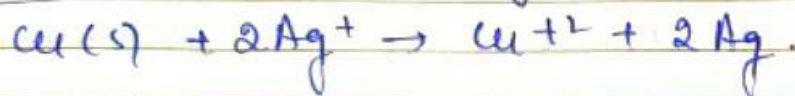
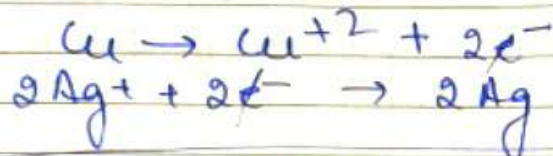
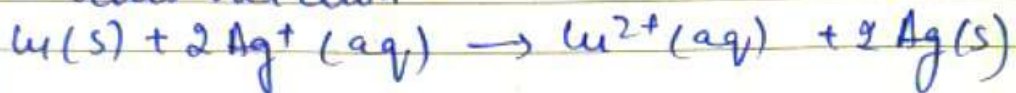
$$= 0.46 - 0.2955 \log 1300$$

$$E = 0.46 - 0.2955 \times 3.11$$

$$= 0.1645 \times 3.11$$

$$E = 5.11 \times 10^5 \text{ Ans}$$

Calculate equilibrium constant for this reaction.



$$E^\circ_{2\text{Ag}^+/\text{Ag}} = -0.80$$

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

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

$$\text{as } E_{\text{cell}} \text{ at eq}^n = 0$$

$$E^\circ = (R-L) = -0.80 + 0.34$$

$$= 0.46$$

$$0.46 = \frac{0.0591}{2} \log K.$$

$$0.46 = 0.295 \log K.$$

$$\therefore \log K = 0.46 - 0.295$$

$$\log K = 0.1645 \text{ Ans}$$

6(a) Suppose in an atom electrons are present in three different orbitals 3p, 5d and 5s. Arrange these orbitals in these orbitals in increasing order of effective nuclear charge.

Ans 6(a) order of shielding effect is

$$s > p > d > f$$

This is because s is near to nucleus so it will shield more the nuclear charge. as

$$Z_{\text{eff}} = Z - \text{shielding constant}$$

so answer is $5s > 3p > 5d$.

6(b) Give the significance of the following:
(i) Fajan's Rule.

Just as covalent bond develops ionic character due to difference of electronegativities of bonded atoms, the ionic bond also develop covalent character.

When two oppositely charged ions come close, the positive ion tends to distort the electron cloud of negative ion towards itself. so the electron cloud of negative ion gets polarised and electron density is pulled in between the nuclei of the two atoms. so the ionic bond does not remain 100% ionic but develops some covalent character then.

→ the power of cation to cause distortion in the electron cloud of -ve ion is

(29)

Called polarising power.

- * the ability of anion to undergo distortion is called its polarisability.
- * the extent of covalent character in compound depends on the polarising power of cation and polarisability of anion which are decided on the rules called Fajan's rules. as follows:
 - (1) smaller the size of cation, larger will be its polarising power. for eg Li^+ is smaller than K^+ ion. so LiI has more covalent character than KI .
 - (2) for the cation of same size the one with pseudo noble gas configuration $n^2 n p^6 n d^{10}$ has larger polarising power than the one with noble gas configuration $n^2 p^6$.
for eg: CuI is more covalent than NaI because polarising power of Cu^+ ion which has pseudo noble gas configuration is more than Na^+ ion.
 - (3) larger the size of anion, higher will be its polarisability. for eg LiI is more covalent than LiF . Similarly AlF_3 is ionic but AlCl_3 is covalent in nature.

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6(b) (ii) Hard and soft acid and bases:

It explains the thermodynamic stability of metal complexes which depends on the nature of ligand and metal ion forming the complex. and type of bonding between them.

It explains the stability of compounds, reaction mechanism.

Metal ligand interaction is an eg. of Lewis acid-base interactions.

According to HSAB- the Lewis base can be divided into 2 types:

- (1) Hard base contain small relatively non polarizable donor atom (N, O, F)
- (2) Soft base containing large, polarizable donor atom (P, S, I)
- (3) Harderline acid. are trimethyl borane, sulphur dioxide, Fe^{+2} , cobalt Co^{+2} , Cs^{+2}
- (4) Harderline bases are amine, N_2

Principle of HSAB:

Hard acids prefer to bind to hard base to give ionic complexes and soft acids prefer to bind to soft bases to give stable ionic complexes.

Eg: It explains the stability of complexes.

The stability of complexes of hard acid and hard base increases as the positive charge on metal ion increases and as its radius decreases. because interaction between

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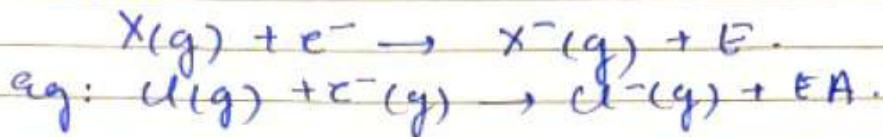
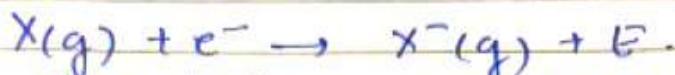
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acid and hard base is electrostatic in nature eg complex of Al^{+3} with four fluoride ligands (AlF_4^-) is about 10^8 times more stable than InF_4^- the corresponding fluoride complex of In^{+3} ($r = 80 \text{ pm}$)

(17)

6(b)(iii) Electron affinity:-

the amount of energy released when one electron is added to an isolated gaseous atom is called electron affinity as:



the magnitude of electron affinity measures the ability of an atom to hold on additional electron. if an atom has more tendency to accept an electron large energy will be released. so the electron affinity will be high. if atom has less tendency to hold the electron, small amount of energy will be released leading to a small value of electron affinity. it can be +ve or -ve. it is expressed in KJ/mol.

(i) Variation of electron affinity down a group:

On moving down a group, the atomic size and nuclear charge increase. but the effect of increase in atomic size is much more pronounced than that of nuclear charge and thus the additional electron feels less attraction by the large atom \therefore electron affinity decreases.

eg decrease in group from Cl_2 to I_2

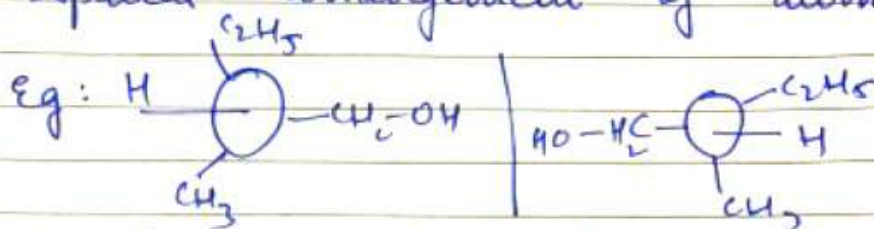
- (b) Variation along a period:
On moving across a period, the size of the atom decreases and nuclear charge increases. Both these factors result into greater attraction for incoming e's
 \therefore electron affinity in general increases in a period from left to right.
- (c) Electron affinity of F is unexpectedly less than that of chlorine: the electron affinity decreases from top to bottom in a group. F atom has unexpectedly less electron affinity than Cl. due to very small size of F atom. \therefore a small size, strong inter-electron repulsion in the compact 2p sub-shell of fluorine and thus the incoming does not feel much attraction. \therefore electron affinity value is small. The electron affinity of Cl atom is large than F atom where electron is added to large 3p orbital which can accommodate additional electron.

7(a) Explain the terms:

(a) Enantiomerism.

The isomers whose molecular structures are non-superimposable mirror image of each other and which rotate the plane-polarised light equally but in opposite direction are called enantiomers and this phenomenon is called enantiomerism.

Object and mirror image differ in spatial arrangement of atom.

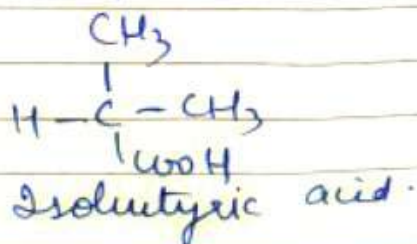
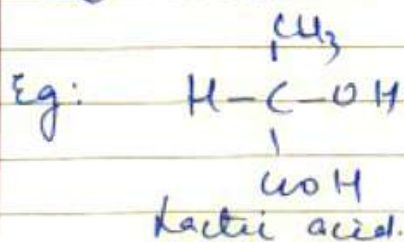


enantiomers form of 2-methylbutanol.

Essential condition for enantiomerism:

(1) Tetrahedral concept of carbon-atom: all the four substituents attached to central C-atom are different (Vant-Hoff)

(2) Enantiomers should be non-superimposable mirror images. This is due to chiral C-molecule. A molecule is termed as chiral if it has no plane of symmetry.



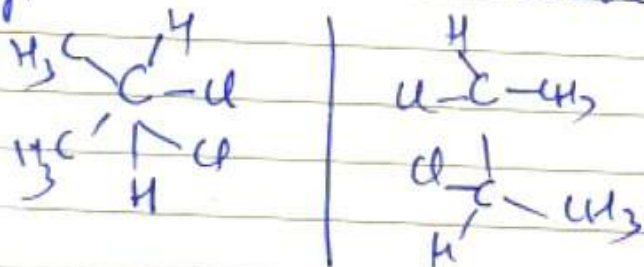
(ii) Mesocompounds:

meso compound is a stereoisomer with two or more chiral centers no. optical activity due to an internal plane of symmetry. They are compounds with zero net rotation of plane polarized light.

mesomers are organic molecule that have two chiral carbons that are identical resulting in zero net rotation

An achiral compound with chiral centers is known as meso compound. though it has two or more stereocenters a meso compound has an internal plane of symmetry that makes it superimposable on its mirror image and is optically inactive.

eg: 2,3 dichlorobutane.



identical (meso-compounds)

(iii) Optical activity:

When ordinary light is passed through a Nicol prism, the vibrations are adjusted in a

single plane only. The light whose vibrations occur only in one plane is called as plane polarised light. The device that brings polarisation in light is called a polarimeter.

Some substances have the ability to rotate the plane polarised light either to right (clock-wise) or to the left (anticlock-wise). These substances is called optically active substance and the property is called optical activity.

The measurement of optical activity is done in terms of specific rotation.

$$\text{specific rotation } [\alpha]^{t^{\circ}}_c = \frac{\alpha_{obs}}{l \times c}$$

α_{obs} = rotation observed.

l = length of solution (dm)

c = no of grams in 1 ml of solnⁿ.

8 (b) Write short note on the following organic reaction:

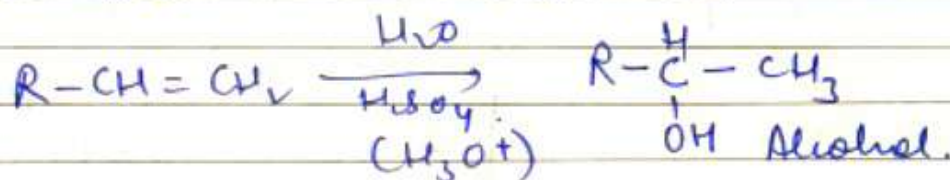
(1) Hydration of alkene: (direct addition of H_2O)

(a) When alkene are treated with aqueous acid (H_3O^+) they are converted to alcohols.

Formation of new C-OH bond tends to occur on the most substituted carbon of the alkene (Markovnikov's reaction)

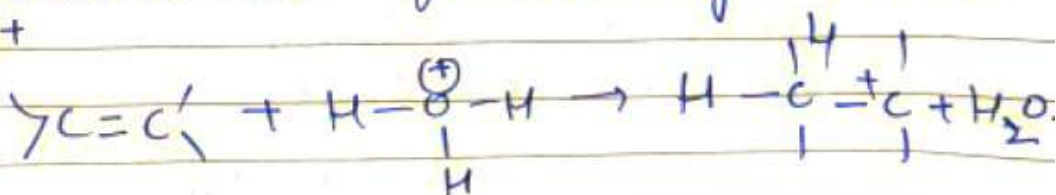
The reaction proceeds through a carbocation intermediate. Protonation of alkene occurs in such a manner that most stable carbocation is formed.

Here are the reaction as:

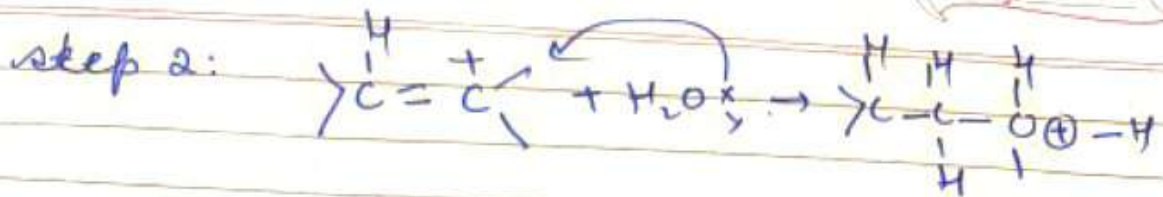


There are 3 steps in the mechanism:
(mechanism of acid catalysed hydration of an alkene to form corresponding alcohol.)

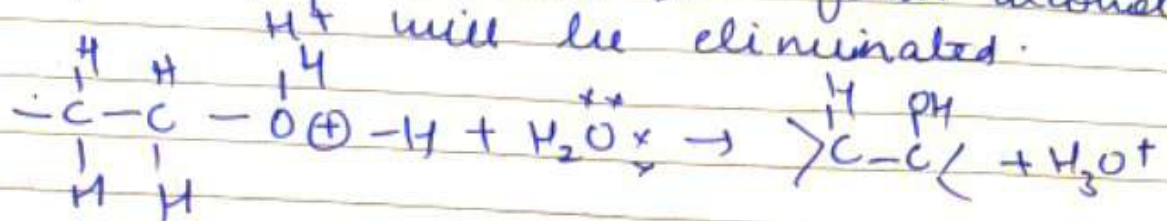
Step 1: Carbocation formation and.
Carbocation is formed by attack of H_3O^+



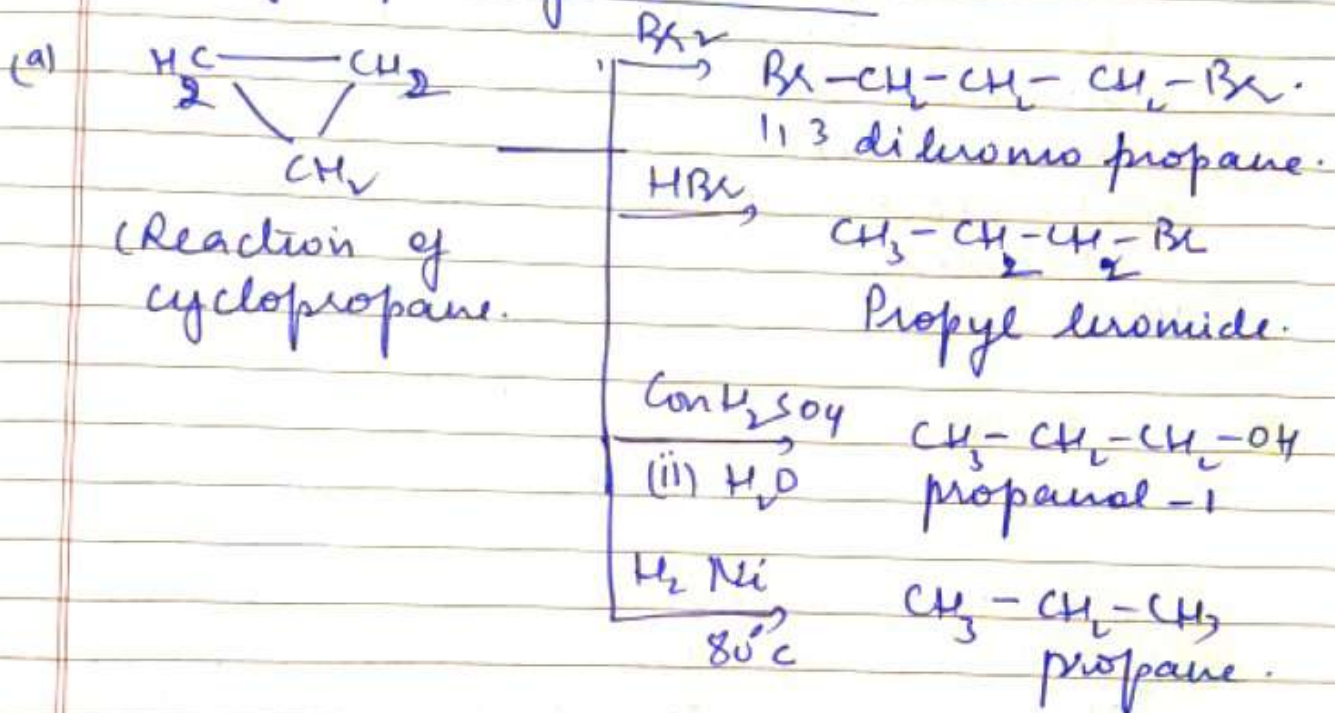
Step 2: Nucleophile H_2O attacks on carbocation.



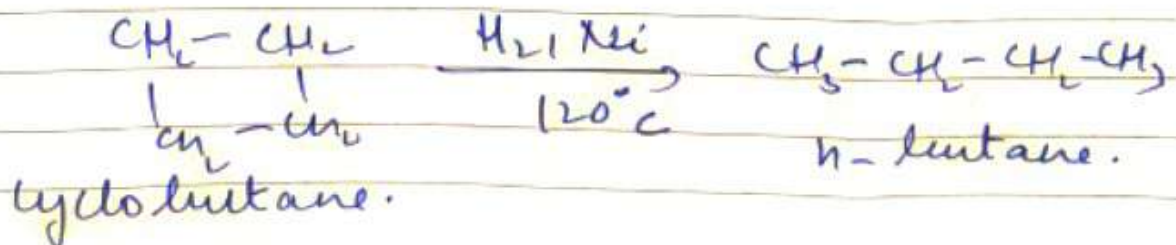
Step 3: Deprotonation to form alcohol.
 H^+ will be eliminated.



(iii) Ring-opening reaction:



(2) Cyclobutane (bond angle 90°) is generally less reactive because of less ring strain and do not undergo addition reaction under normal conditions.



(3) Dicarboxylic acid formed when cyclo-alkanes are oxidised by alkaline KMnO_4 .

