Lucky

Aakash Kumar

1ST SEM

CHEMISTRY

LUCKY
SPIRAL
NOTEBOOK
for bright future....

OBJECTIVE

① State de Broglie's principle

→ According to De-Broglie's e^- and proton particle can exhibit both wave-like and particle-like behavior.

$$\lambda = \frac{h}{p}$$

② what is an orbital?

→ An orbital is a three diamational space where the possibility of finding an e^{-1} is maximum.

③ Bond order ∝ Bond Angle

" ∝ Bond strength
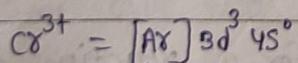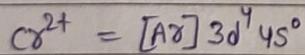
" ∝ ⅟.S character

" ∝ Bond stability

" ∝ $\dfrac{1}{\text{Bond length}}$

④ Out of Cr^{2+} and Cr^{3+}, which one is stable in aqueous solution.

→ Cr^{3+} is most stable in aqueous solution.

$Cr^{2+} = [Ar] 3d^4 4s^0$

$Cr^{3+} = [Ar] 3d^3 4s^0$

| 1 | 1 | 1 | | |

Electronic configuration of Cr^{+3}

| 1 | 1 | 1 | t_{2g}

(Half Field)

⑤ Cu^+ is colourless but Cu^{2+} is coloured. why?

→ Cu^+ ion has an electronic configuration $3d^{10}$ whereas Cu^{2+} ion has an electronic configuration $3d^9$ Hence an ~~upp~~ unpaired electron is Present in Cu^{2+}.

→ Due to lack of ~~up~~ unpaired electrons, Cu^+ is colorless.

⑥ what is selection Rule.?

→ A restriction in the transition between quantum state of atoms molecules or metal.

⑦ A gas expands against vacuum. what is the work done on it?

→ No work

In vacuum there is no resistance i.e

$P = 0$

$w = -P\Delta V$

$w = 0$
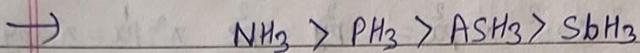
⑧ what is the condition for a reaction to be in equilibrium?.

→ Rate of Forward ~~direction~~ Reaction = Rate of Backward Reaction.

⑨ The Presence of CO_2 in boiler Feed water should be avoided. why?
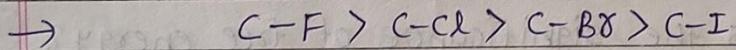
→ CO_2 can makes water acidic, which contributes to the Pitting of the metal.

(10) Out of NH_3, PH_3, ASH_3 and SbH_3 which possesses largest bond angle? Give reason.

→ $NH_3 > PH_3 > ASH_3 > SbH_3$
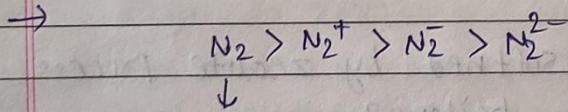
As we move top to bottom electronegativity decreases so bond angle decreases.

(11) Arrange the covalent bonds $C-F$, $C-Br$, $C-Cl$ and $C-I$ in increasing order of strength.

→ $C-F > C-Cl > C-Br > C-I$

(12) Arrange molecular species N_2, N_2^+, N_2^- and N_2^{2-} in increasing order of stability.

→ $N_2 > N_2^+ > N_2^- > N_2^{2-}$

$\downarrow$

B.O   3   2.5   2.5   2
                      $\downarrow$
   one antibonding e^- present

(13) Name any two coagulants.
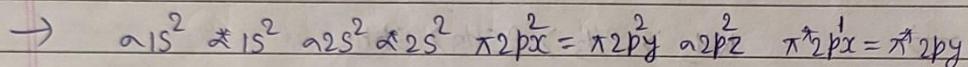
→ (i) $NaCl$

(ii) $Al_2(SO_4)_3$

(14) Under what condition, $\Delta H = \Delta U$?

→ ~~$\Delta U = 0$~~ when the number of moles of the gaseous reactants is equal to the number of moles of the gaseous products.

(15) write the ground state electronic configuration of N_2^-
(15e⁻)

→ $\sigma 1s^2 \; \ast 1s^2 \; \sigma 2s^2 \; \ast 2s^2 \; \pi 2p\overset{2}{x} = \pi 2p\overset{2}{y} \; \sigma 2p\overset{2}{z} \; \pi^* 2p\overset{1}{x} = \pi^* 2py$

(16) what is the basic criterion for a nucleus to show NMR spectrum?

→ (i) we should apply external magnetic Field.
(ii) Radio waves.
(iii) Nuclei should have spin quanton $l > 0$

(17) what is the significance of free energy?
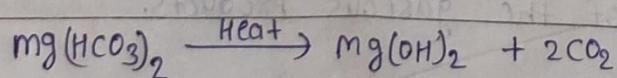
→ If the free energy of the system increases the reaction cannot Proceed and no work can be done,

(18) why is water softned by zeolite process unfit for use in boilers?
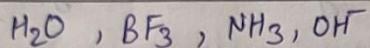
→ Because this water softening system contains $NaHCO_3$ in the water; when this water is heated, it Produces CO_2 which is corrosive for boilerplates.

(19) what happens when temporary hard water is boiled? (give equation)

→ when we boil water the soluble salts magnesium bicarbonate are converted to insoluble magnesium hydroxide.

$$mg(HCO_3)_2 \xrightarrow{Heat} mg(OH)_2 + 2CO_2$$

(20) which of the following is not a nucleophile?

H_2O , BF_3 , NH_3, OH^-

→ BF_3

Electron donars are nucleophiles. BF_3 is e^- deficient compound.

(21) why are Br^+ and CCl_2 electrophiles?

→ since Br^+ and CCl_2 wants to gain electron to attain stability.

(22) ^{13}C is NMR active, but ^{12}C is not why?

→ ^{13}C is NMR active because it has non-zero nuclear spin while ^{12}C has a nuclear spin equal to zero.

(23) what is the direction of a reaction when $\Delta G = 0$?

→ the system is at equilibrium and there is no net change either in Forward or backward direction.

(24) why is work not a state function.
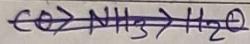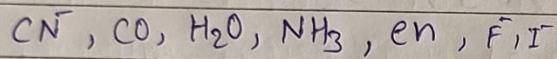
→ because it is proportional to the distance an object is moved.

$W = F \cdot \Delta S$

(25) what is critical temperature of a gas?

→ critical tempr of a gas is the temperature at or above which vapour of the gas cannot be liquefied.

26. Arrange the following ~~in order~~ ligands in order of increasing field strength

CN^-, CO, H_2O, NH_3, en, F^-I

~~$CO > NH_3 > H_2O$~~

$\longrightarrow$ $CO > CN^- > en > NH_3 > H_2O > F^- > I^-$

27. which quantum number specifies the shape of an orbital?

$\rightarrow$ angular quantum number (l)
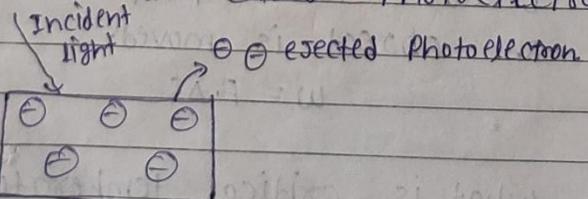
28. what is the designation of the orbital having $n=4$ and $l=3$?

$\rightarrow$ $4F$

SUBJECTIVE   Atomic and molecular structure.

① Discuss photoelectric effect and explain equation involved with this effect.

$\rightarrow$ It is phenomenon in which electrons are emitted from a ~~material~~ the surface of a metal when light is incident on it. These ejected electrons are called photoelectrons

Incident
light   ⊖⊖ ejected photoelectron

$E = \phi + K \cdot E = hf$

$\underset{\text{work function}}{\phi}$ $\underset{\text{frequency}}{f}$

② How many Photons of light having a wavelength of 4000 A are necessary to provide 1J of energy?

$$(h = 6.626 \times 10^{-34} \text{ J-S})$$

$\lambda = 4000 \text{ A}°$ $\boxed{1\text{A}° = 10^{-10}\text{m}}$
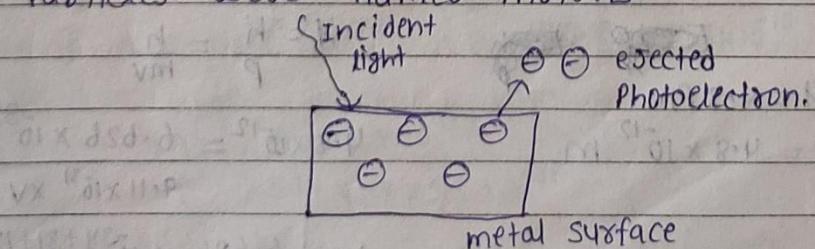
$\lambda = 4 \times 10^{-7} \text{m}$

$E = \dfrac{hc}{\lambda} = \dfrac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{4 \times 10^{7}} = 4.9695 \times 10^{-19}$

```
 3.313
× 1.5
16565
3313
49695
```

No. of Photons $= \dfrac{1}{4.9695 \times 10^{-19}}$

③ Discuss Photoelectric effect (with mathematical eqn) for explaning the particle nature of light.

→ The emisson of free electron from a metal surface when light is slone on it, is called Photoemission or Photoelectric effect. This effect led to the conclusion that light is made of Packets or quantum of energy. Einstein had already associated the light quantum with momentum. This strongly support the Partcle nature of light and these Particles were named Photons

Incident light → metal surface with electrons → ejected Photoelectron.

$$E = \phi + K.E = hf$$

The energy of a Photon is given $E = h\nu$

momentum $p = \dfrac{h\nu}{c}$

④ Wave particle duality.

→ Wave particle duality is the concept in quantum mechanics that every particle or quantum entity may be described as either a particle or a wave.

⑤ Heisenberg's uncertainty principle.

→ Heisenberg's uncertainty principle states that it is impossible to determine simultaneously both the position and the momentum of a particle with accuracy

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

The above expression is known as Heisenberg's uncertainty principle relation where Δx = change in position, Δp = change in momentum and h is Plank constant.

⑥ Calculate the kinetic energy of a moving electron which has a wavelength of 4.8 pm. (mass of $e^- = 9.11 \times 10^{-31} kg$)

→ $\lambda = 4.8$ pm

$\lambda = 4.8 \times 10^{-12} m$

$\lambda = \frac{h}{P} = \frac{h}{mv}$

$4.8 \times 10^{-12} = \frac{6.626 \times 10^{-34}}{9.11 \times 10^{-31} \times V}$

$V = \frac{6.626 \times 10^{-34+31+12}}{4.8 \times 9.11}$

$V = \frac{6.626}{43.728} \times 10^{9}$

9.11
-4.8
_____
7288
3644
_____
43728

$$V = 0.15 \times 10^9$$

$$V = 15 \times 10^7 \, m/s$$

$$K.E = \frac{1}{2} mv^2$$

$$= \frac{1}{2} \times 9.11 \times 10^{-31} \times (15 \times 10^7)^2$$

$$= \frac{1}{2} \times 9.11 \times 10^{-31} \times 225 \times 10^{14}$$

$$= \frac{2049.75 \times 10^{-17}}{2}$$

$$K.E = 1024.875 \times 10^{-17} \, J$$

```
    9.11
  × 225
  45 5 5
  18 2 2
  18 2 2
  2049.7 5
```

⑦ The uncertainties in the position and velocity of a particle are $9.5 \times 10^{-10} \, m$ and $5.5 \times 10^{-20} \, ms^{-1}$, respectively. calculate the mass of the particle. $(h = 6.626 \times 10^{-34} \, J\text{-}s)$

→ According to Heisenberg's uncertainty Principle.

$$\Delta x . \Delta P = \frac{h}{4\pi}$$

$$\Delta x . m \Delta V = \frac{h}{4\pi}$$

$$or \quad m = \frac{h}{4\pi \, \Delta x \, \Delta V} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 9.5 \times 10^{-10} \times 5.5 \times 10^{-20}}$$

$$m = \frac{6.626 \times 10^{-34}}{3.14 \times 38 \times 5.5 \times 10^{-30}}$$

$$m = \frac{6.626}{17.27 \times 38} \times 10^{-4} = \frac{6.626 \times 10^{-4}}{656.26}$$

$$m = \frac{6626}{6562} \times 10^{-6} = 1.0097 \times 10^{-6} = 10.09 \times 10^{-7}$$

```
  3.14
  ×5.5
  1570
  1570
  17.27

  17.27
  × 38
  1381
  5181
  656.26
```

(8) Electromagnetic radiation of wave length 242 nm is just sufficient to ionize ~~sodium~~ sodium ion. Calculate the ionization energy of sodium atom in KJ/mol $(c = 10^8 \, ms^{-1}, \, h = 6.626 \times 10^{-34} \, Js)$.

→ The ionization energy of sodium will be equal to the energy prossessed by the radiation of wavelength 242 nm. ~~$E = hc$~~

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{242 \times 10^{-9} \, m}$$

$$= 250.52 \times 10^{-17}$$

$$= 2.5 \times 10^{-19} \, J.$$

The ionization energy per mole is ~~2.5×10^{-19}~~

$$= 2.5 \times 10^{-19} \times 6.023 \times 10^{23}$$

$$= 15.05 \times 10^4 \, \text{RJ}$$

$$= 150500 \, \text{RJ}$$

$$= 150.5 \, KJ.$$

(9) If the electron in an unexcited hydrogen atom is excited by absorption of $1.76 \times 10^{-18} \, J$ per atom, what would be the wavelength of radiation emitted when the atom returns to its ground state?
$(c = 3 \times 10^8 \, ms^{-1}, \, h = 6.626 \times 10^{-34} \, J \text{-} S)$

$$\frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$E = 1.76 \times 10^{-18} \, J$

$E = \frac{hc}{\lambda}$

$n_1 = 1$ $R = 1.097 \times 10^7 \, m^{-1}$

$n_2 =$

when the atom returns to its ground state, it will radiate the same amount of energy it absorbed during the excitation

$E = hc \rightarrow \lambda = \dfrac{hc}{E} = \dfrac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{1.76 \times 10^{18}} = 1.13 \times 10^{-7} m\, atom^{-1}$

$\lambda = 113\, nm\, atom^{-1}$

(10) Explain dual nature of light and give one example (property/experiment) in favour of its particle nature and wave nature.

→ Light consists of dual nature which means sometimes it behaves like a particle (know as Photon), which explains how the light travels in straight lines. sometimes light behaves as the wave, which explain how light ~~behaves~~ bends around an object.

The Dual nature of light is exhibited by:
Photoelectric effect
Refraction and interference
Diffraction and reflection
Diffraction and Photoelectric effect.

The Photoelectric effect is an example of light behaving as a particle (Proton) whereas the diffraction and interference are example of light acting as a wave. so it is confirmed now that light is dual nature.

WATER CHEMISTRY
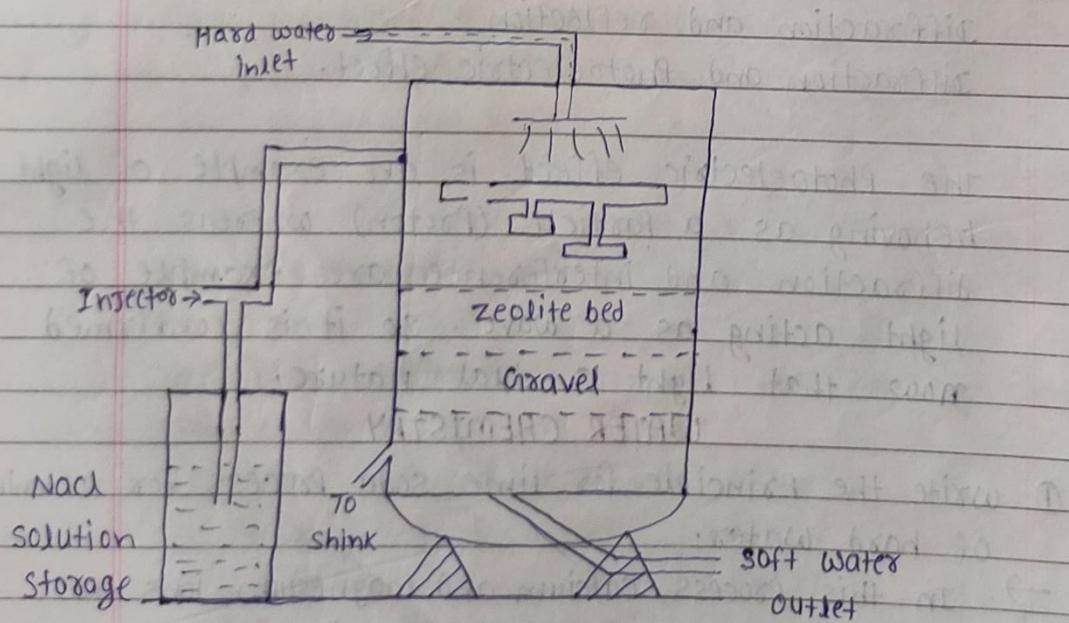
① write the Principle for lime soda process for softening of hard water.

→ In this process calcium and magnesium ions are precipitated by the addition of lime $Ca(OH)_2$ and soda ash (Na_2CO_3).

② Give the theory of zeolite method, its
limitations and advantages.
→ The zeolite method is a technique used to
soften hard water by removing calcium
and magnesium ions and replacing them
with sodium ions.

* The zeolite method works by Passing hard
water through a bed of zeolite resin, which
is made up of tiny beads that are coated
with sodium ions. As the hard water flows
through the resin bed, the ca and mg ions are
attracted to the resin beads and are
exchanged with the sodium ions, which are
released into the water. This process
effectively removes the calcium and magnesium
ions from the water,

Hard water →
Inlet

Injector →

Zeolite bed

Gravel

Nacl
solution
storage

To
shink

Soft water
outlet

Advantages of zeolite process.

① it removes the hardness almost completely and water of about 10 ppm hardness is produced.

② The equipment used is compact, occupying a small space.

③ No impurities are precipitated.

④ it requires less time for softening.

⑤ The process automatically adjusts itself for variation in hardness of incoming water.

Limitation of zeolite process.

① This method is not suitable for use in high levels of iron or ~~men~~ manganese in the water.

② The regeneration process can consume large amount of salt and water, which can be costly.

③ The process of removing calcium and magnesium ions also removes some of the beneficial minerals in water, which may be important for human health.

③ A water sample had the following constituents per litre: $CaCO_3 = 160$ mg, $MgHCO_3 = 150$ mg, $CaSO_4 = 136$ mg, $MgSO_4 = 120$ mg, $NaCl = 10$ mg. Calculate the quantity of temporary and permanent hardness in the water sample. calculate the quantity of lime (78% purity) and soda (92% purity) required for softening of 25 million litre of above water sample.

Note:- $CaCO_3$ and $MgCO_3$ impurities are considered as bicarbonate of calcium and magnesium respectively.

Temporary hardness $= MgHCO_3 + CaCO_3$

$\quad\quad\quad\quad\quad\quad = 150 mg + 160 mg$

$\quad\quad\quad\quad\quad\quad = 310 mg$

Permanent hardness $= CaSO_4 + MgSO_4$

$\quad\quad\quad\quad\quad\quad = 136 mg + 120 mg$

$\quad\quad\quad\quad\quad\quad = 256 mg$

lime requirement.

$CaCO_3$
$\downarrow$
$40+12+48$

$$= \frac{74}{100}\left[CaCO_3 + 2 MgHCO_3 + MgSO_4 \right] \times vol.\ of\ water$$
$$all\ in\ terms\ of\ CaCO_3\ eqv.$$

$MgHCO_3$
$\downarrow$
$24+1+12+48$

$$= \frac{74}{100}\left[\frac{160\times100}{100} + 2\times\frac{\overset{30}{150}\times100}{\underset{17}{85}} + \frac{120\times100}{120} \right] \times 25\times10^6 \times \frac{1}{10^6} \times \frac{100}{78}\ kg$$

$MgSO_4$
$\downarrow$
$24+32+64$

$$= \frac{74}{78}\left[160 + \frac{6000}{17} + 100 \right] \times 25\ kg$$

$CaSO_4$
$40+32+64$

$$= \frac{74}{78}\left[260 + 352.94 \right] \times 25\ kg$$

$$= \frac{74}{78} \times 612.94 \times 25\ kg$$

$$= 14537.67\ kg$$

soda requirement

$$= \frac{106}{100}\left[CaSO_4 + MgSO_4 \right] \times vol.\ of\ water$$
$$all\ in\ terms\ of\ CaCO_3\ eqv.$$

$$= \frac{106}{100}\left[\frac{136\times100}{136} + \frac{120\times100}{120} \right] \times 25\times10^6 \times \frac{1}{10^6} \times \frac{100}{92}\ kg$$

$$= \frac{\overset{53}{106}\times25}{\underset{46\ 23}{92}} \left(\overset{100}{200} \right) kg \implies \frac{53\times25\times100}{23} = 5760.86\ kg$$

④ In an experiment to determine the hardness of a sample of water, 50 ml of $\frac{N}{50}$ Na_2CO_3 solution was added to 200 ml of water sample. After complete precipitation of insoluble carbonate, the unreacted Na_2CO_3 was titrated against $N/50$ H_2SO_4 solution, when 20 ml of acid was required. Calculate the hardness and comment on the nature of hardness so determined.

→ milli equivalent of $Na_2CO_3 = 50 \times \frac{1}{50} = 1$

milli equivalent of $H_2SO_4 = 20 \times \frac{1}{50} = \frac{2}{5}$

milli equivalent of Na_2CO_3 absorbed by $H_2O = 1 - \frac{2}{5} = \frac{3}{5}$

meq $CaCO_3$ = meq Na_2CO_3 absorbed

$W = 53 \times \frac{3}{5} \times 10^{-3}$

$W = 10.6 \times 3 \times 10^{-3} = 31.8 \times 10^{-3}$

$W = 0.0318\ g$

$W = \frac{0.0318}{200} = \frac{0.0159}{100} = 0.000159\ g$

$W = 0.159\ kg$

Hardness $= \frac{0.159}{200} \times 1000 = 0.795\ ppm.$

③ 20 ml of standard hard water (containing 15g $CaCO_3$ per litre) required 25 ml of EDTA solution for end point. 100 ml of water sample required 18 ml of EDTA solution, while same water after boiling required 12 ml EDTA solution. Calculate carbonate and non-carbonate hardness of the water sample.

→ 1000 ml of H_2O contains 15g of $CaCO_3$

| 1 | " | " | " | " | $\frac{15}{1000}$ | " | " |

100 ml " " " $\frac{15}{1000} \times 100$ " "

100 ml of H_2O contains 1.5g of $CaCO_3$

1 ml of SHW = 1.5mg of $CaCO_3$

25 ml EDTA required 20 ml of SHW

= 20 × 1.5 mg of $CaCO_3$

1 ml EDTA required = $\frac{20 \times 1.5}{25} = \frac{30}{25}$ mg of $CaCO_3$

100 ml of hard water sample required = 18 ml EDTA soln

1 ml " " " " " = $\frac{18}{100} \times \frac{30}{25}$ mg of $CaCO_3$

1000 ml " " " " " = $\frac{18}{100} \times \frac{\overset{6}{30}}{\underset{5}{25}} \times 1000$ mg/L

= 18 × 12 mg/L

= 216 mg/L

Determination of permanent (non-carbonate) hardness.

100 ml of solid water sample required 12 ml of EDTA

1 ml " " " " " $\frac{12}{100} \times \frac{30}{25}$

1000 ml " " " " " $\frac{12}{100} \times \frac{\overset{6}{30}}{\underset{5}{25}} \times 1000 = 144$ mg/L

$\frac{\times 12}{36}$
$\frac{18}{216}$

Total hardness = 216 PPM

Non - carbonate = 144 PPM
hardness

carbonate hardness = Total hardness - Non-carbonate hardness
= 216 - 144
= 72 PPM
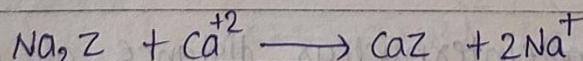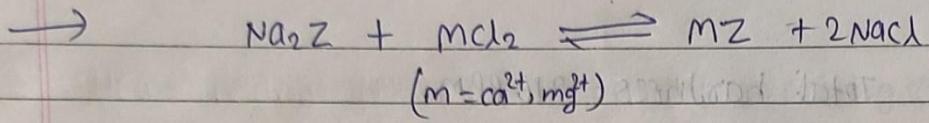
⑥ Describe the removal of hardness of water by ion-exchange method.

→ ~~Removal of hardness of water of ion by~~ ion - exchange method is used to remove the hardness of water, different ions which is responsible for causing the hardness of water. ion- exchange is of two types namely inorganic ion exchange or organic ion exchange.
For example, in order to remove the hardness of ion by inorganic ion exchange hard water is poured ~~into~~ into the tank which has hydrated sodium, aluminium, silicate as an exchanger which reacts with the calcium ion of hard water to form calcium zeolite.

$$Na_2 Z + Ca^{+2} \longrightarrow CaZ + 2Na^+$$

⑦ The hardness of 50000 litres of water sample was removed by passing it through a zeolite softener. The softener then required 200 L of Nacl solution containing 125 g/L of Nacl for regeneration. calculate the hardness of the sample of water.

→ $Na_2Z + MCl_2 \rightleftharpoons MZ + 2NaCl$

$(m = Ca^{2+}, Mg^{2+})$

Mole of $NaCl = \dfrac{w}{m} = \dfrac{125}{58.5}$

Mole of $NaCl$ = mole of eq. of Permanent hardness

$M_1V_1 = M_2V_2$

$\dfrac{125}{58.5} \times 200 = M_2 \times 50,000$

$M_2 = \dfrac{1}{58.5 \times 2} = \dfrac{1}{117.0}$

$M_2 = \dfrac{1}{117}$ eq. l^{-1}

$= 50 \times \dfrac{1}{117}$ g $CaCO_3$ l^{-1}

$= 0.42$ PPm

hardness $= 0.42$ PPm

spectroscopic

① The ~~intermole~~ internuclear distance of $NaCl$ is
2.36×10^{-10} m. calculate the reduced mass and
moment of inertia of $NaCl$. (Atomic mass of
$Cl = 35 \times 10^{3}$ kg mol^{-1} and $Na = 23 \times 10^{3}$ kg mol^{-1})

→ $Na - Cl$

$\gamma = 2.36 \times 10^{-10}$ m

$\mu = \dfrac{m_1 m_2}{m_1 + m_2} = \dfrac{35 \times 10^{-3} \times 23 \times 10^{-3}}{(35 + 23) 10^{-3}} = \dfrac{805 \times 10^{-3}}{58} = 13.87 \times 10^{-3}$ Na

35
×23
105
70
58)805 (19.8
...

(8)

$$\mu = \frac{13.87 \times 10^{-3} \times 1}{6.023 \times 10^{23}}$$

$$\mu = 2.3 \times 10^{-26}$$

$$I = \mu r^2$$

$$I = 2.3 \times 10^{-26} \times 2.36 \times 10^{-10} \times 2.36 \times 10^{-10}$$

$$I = 12.8 \times 10^{-46}$$

$$I = 1.28 \times 10^{-45}$$

② Calculate the force constant for CO, if it absorbs at $2.143 \times 10^5 \, m^{-1}$. (Atomic mass of $C = 12 \times 10^{-3} \, kg \, mol^{-1}$ and $O = 16 \times 10^{-3} \, kg \, mol^{-1}$).

→ wave no.

$$\frac{1}{\lambda} = 2.143 \times 10^5 \, m^{-1}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

$$\frac{1}{\lambda} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

$$\mu = \frac{\overset{6}{12 \times 10^{-3}} \times \overset{8}{16 \times 10^{-3}}}{\underset{14}{28 \times 10^{-3}}} \times \frac{1}{6.023 \times 10^{23}}$$

$$\mu = \frac{48}{7} \times 10^{-3} \times 1 = \frac{6.85 \times 10^{-3}}{6.023 \times 10^{23}} \quad 6.023 \times 10^{23}$$

$$\mu = 1.14 \times 10^{-26} \, kg$$

$$2.143 \times 10^5 = \frac{1}{2 \times 3.14 \times 3 \times 10^8}\sqrt{\frac{K}{6.85 \times 10^{-3}}}$$

$$(2.143 \times 10^5)^2 = \left(\frac{1}{2 \times 3.14 \times 3 \times 10^8}\right)^2 \frac{K}{6.85 \times 10^{-3}}$$
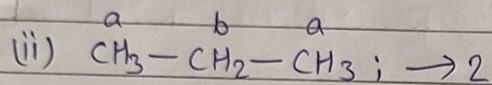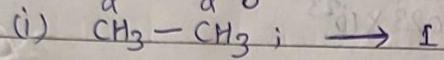
$$K = (2.143)^2 \times 10^{10} \times 4 \times (3.14)^2 \times 9 \times 10^{16} \times 6.85 \times 10^{-3}$$

$$K = 1132.49792 \times (3.14)^2 \times 10^{23}$$
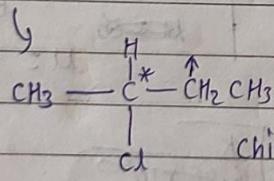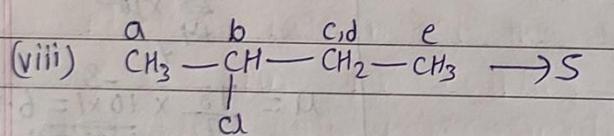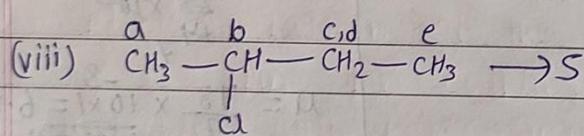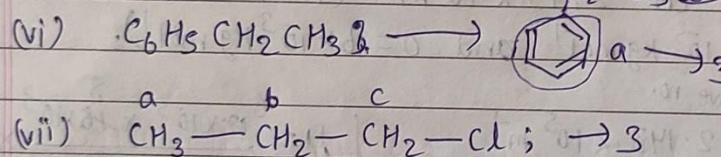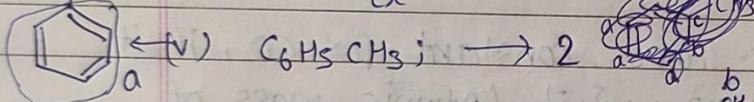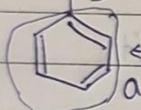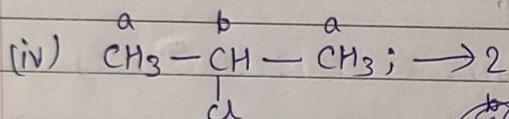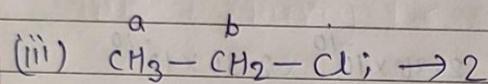
$$K = 11,165.9765 \times 10^{23}$$

$$K = 1.1 \times 10^{19}$$

③ How many ^1H NMR signals are there in -

(i) $\overset{a}{C}H_3 - \overset{a}{C}H_3 ; \longrightarrow 1$

(ii) $\overset{a}{C}H_3 - \overset{b}{C}H_2 - \overset{a}{C}H_3 ; \longrightarrow 2$

Special case $^1Hydrocarbon$

(iii) $\overset{a}{C}H_3 - \overset{b}{C}H_2 - Cl ; \longrightarrow 2$

(iv) $\overset{a}{C}H_3 - \overset{b}{C}H - \overset{a}{C}H_3 ; \longrightarrow 2$
          |
          Cl

$b \uparrow$
CH_3

(v) $C_6H_5 CH_3 ; \longrightarrow 2$


(vi) $C_6H_5 CH_2 CH_3$? $\longrightarrow$ $a \longrightarrow 3$

(vii) $\overset{a}{C}H_3 - \overset{b}{C}H_2 - \overset{c}{C}H_2 - Cl ; \longrightarrow 3$

(viii) $\overset{a}{C}H_3 - \overset{b}{C}H - \overset{c,d}{C}H_2 - \overset{e}{C}H_3 \longrightarrow 5$
          |
          Cl

$\downarrow$

$CH_3 - \overset{H}{\underset{Cl}{\overset{|}{C}}}{}^{*} - \overset{\uparrow}{C}H_2 CH_3$
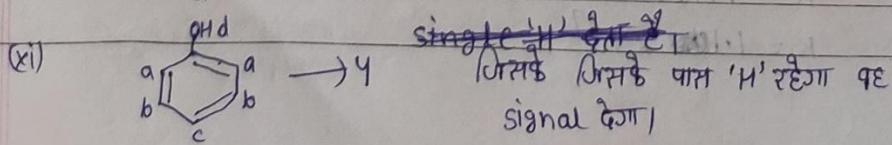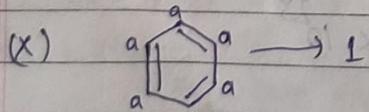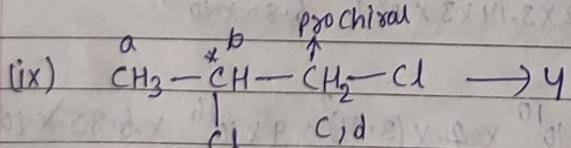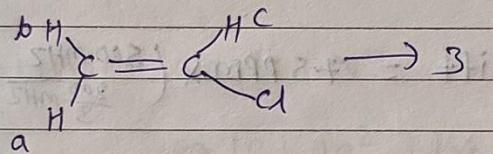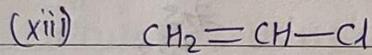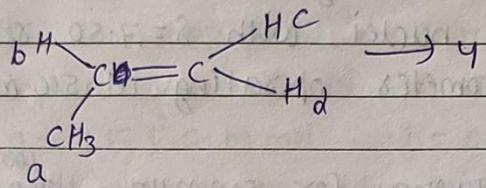
chiral carbon then
adjecent carbon prochiral carbon
(Both hydrogen not
equivalent.

(ix) $\overset{a}{C}H_3 - \overset{*b}{C}H - \overset{prochiral \uparrow}{C}H_2 - Cl \longrightarrow 4$
          |
          Cl c,d

(x) $\longrightarrow 1$

(xi) $\longrightarrow 4$

single ^1H होगा
जिसके जिसके पास 'H' रहेगा वह
signal देगा।

(xii) $CH_3 - CH = CH_2$

$$\underset{a}{\overset{b\;H}{\underset{CH_3}{C}}}\!\!=\!\!C\!\!\overset{H^c}{\underset{H_d}{<}} \longrightarrow 4$$

(xii) $CH_2 = CH - Cl$

$$\underset{a}{\overset{b\;H}{\underset{H}{>}}}C = C\overset{H^c}{\underset{Cl}{<}} \longrightarrow 3$$

④ microwave spectrum of gaseous HCl molecule exhibits a series of equally spaced lines with interspacing of $20.7\ cm^{-1}$. calculate the internuclear distance of HCl molecule.

$\longrightarrow 2B = 20.7\ cm^{-1}$

$B = 10.35\ cm^{-1}$

$$\mu = \frac{35.5 \times 1}{36.5} \times \frac{1}{6.022 \times 10^{23}} \times 10^{3}\ \frac{kg}{}$$

$$\mu = 1.62 \times 10^{-27}\ kg$$

$$B = \frac{h}{8\pi^2 IC}$$

$$10.35 = \frac{6.626 \times 10^{-34}}{8 \times 3.14 \times 3.14 \times I \times 3 \times 10^{10}}$$

$$I = \frac{6.626 \times 10^{-34} \times 10^{-10}}{24 \times 3.14 \times 3.14 \times 10.35}$$

$$I = \frac{6.626}{2449.12} \times 10^{-44} = 0.0027 \times 10^{-44}$$

$$I = 2.7 \times 10^{-47}$$

$$I = \mu r_0^2$$

$$2.7 \times 10^{-47} = 1.62 \times 10^{-27}\ r_0^2$$

$$1.67 \times 10^{-20} = r_0^2 \qquad \Rightarrow r_0 = \sqrt{1.67 \times 10^{-20}}$$

$$r_0 = 1.29 \times 10^{-10}$$

③ At what Frequency shift From TMS, would a group of nuclei with $\delta = 7.50$ resonate in an NMR spectrometer operating at 500 mHz?

→
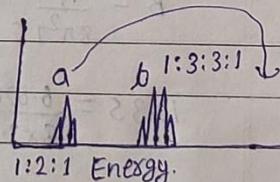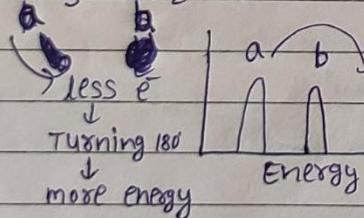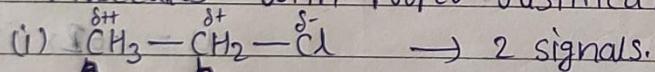
$$\text{TMS Frequency for 500 MHz} = \frac{500 \, MHz \times 10}{7.5} = \frac{200}{3} \, MHz$$

$$\text{Frequency shift} = 7.5 \, ppm \times \left(\frac{500 \, MHz}{\frac{200}{3} \, MHz} \right)$$

$$= \frac{7.5 \times 500}{200} \times 3$$

$$= \frac{37.5 \times 3}{2} \Rightarrow \frac{112.5}{2} \Rightarrow 56.25 \, ppm$$

$$Hz$$
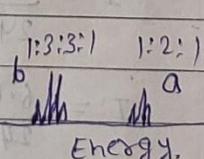
⑥ write the number of ^1H-NMR signals and splitting pattern of the signals (single, double etc) due to spin-spin coupling for the following molecules with proper Justification,

(i) $\overset{\delta++}{C}H_3 - \overset{\delta+}{C}H_2 - \overset{\delta-}{C}l \longrightarrow$ 2 signals.

less $\bar{e}$
↓
Turning 180°
↓
more energy

a   b
Energy

a   b   1:3:3:1
1:2:1 Energy.

Splitting → N+1

• For a → N is the no. of 'H' on b.

• For b → N is the no. of 'H' on a.

1:3:3:1   1:2:)
b   a
Energy.

Intensity Ratio:

```
        1
     1     1
   1     2     1
 1     3     3     1
1     4     6     4     1
```

⑦ Use the equation of state of vander waals to calculate the pressure of 5 moles of $NH_3 (g)$ occoupying a volume of 7L at 373 K.

[Given $a = 4.17 \, L^2 \, atm \, mol^{-2}$, $b = 0.0371 \, L \, mol^{-1}$].

compare the above result with the pressure calculated using ideal gas equation.

→ vander waals eqn

$$\left[P + \frac{an^2}{v^2}\right]\left[V - nb\right] = nRT$$

$$P = \frac{nRT}{V-nb} - \frac{an^2}{v^2}$$

$$= \frac{5 \times 0.0821 \times 373}{7 - 5 \times 0.0371} - \frac{4.17 (5)^2}{(7)^2}$$

$$= \frac{153.1165}{6.8145} - \frac{104.25}{49}$$

$$= 22.46 - 2.12$$

$$= 20.34 \, atm$$

Ideal gas equation

$V = 7L$

$n = 5 \, mol$

$T = 373 \, K$

$PV = nRT$

$$P = \frac{nRT}{V} = \frac{5 \times 0.082 \times 373}{7} = \frac{152.93}{7} = 21.84 \, atm.$$

actual pressure = 20.34 atm.

% deviation $= \frac{|20.34 - 21.84|}{20.34} \times 100$

$$\Rightarrow \frac{1.5}{20.34} \times 100 \Rightarrow 7.3\%.$$

⑧ The spacing between lines in rotational spectra of HBr is 16.94 cm⁻¹. Calculate the bond length of the molecule (H=1, Br = 80).

$2B = 16.94 \, cm^{-1}$

$B = 8.47 \, cm^{-1}$

$\mu = \dfrac{m_1 m_2}{m_1 + m_2}$

$B = \dfrac{h}{8\pi^2 I C}$

$\mu = \dfrac{1 \times 80}{81} \times \dfrac{1}{6.023 \times 10^{23}} \times \dfrac{1}{10^3} \, kg$

$8.47 = \dfrac{6.626 \times 10^{-34}}{8 \times 3.14 \times 3.14 \times I \times 3 \times 10^{10}}$

$\mu = \dfrac{80}{81} \times \dfrac{1}{6.023} \times 10^{-26} \, kg$

$I = \dfrac{6.626 \times 10^{-34}}{24 \times 3.14 \times 3.14 \times 8.47 \times 10^{10}}$

$\mu = \dfrac{80}{487.863} \times 10^{-26} \, kg$

$\mu = 0.163 \times 10^{-26} \, kg$

$I = \dfrac{6.626 \times 10^{-34}}{2002 \times 10^{10} \times 10^3}$

$\mu = 1.65 \times 10^{-27} \, kg$

$I = 3.309 \times 10^{-47}$

$I = \mu r_0^2$

$3.309 \times 10^{-47} = 0.163 \times 10^{-26} \, r_0^2$

$r_0^2 = \dfrac{3.309}{0.163} \times 10^{-47+26}$

$r_0^2 = \dfrac{3309}{163} \times 10^{-21}$

$r_0^2 = 20.3 \times 10^{-21}$

$r_0^2 = 203 \times 10^{-22}$

$r_0 = 14.24 \times 10^{-11} \, m$

3.14
× 3.14
1256
314
942
9.8596

9.85
8.47
×.95
68 0
3940
7880
83.4295

83.42
× 24
33368
16684
2002.08

2002) 6626 (3.309
6006
x 6200
6006
X 19400
18018
x1382

⑨ The speed of an electron moving at $600 \, ms^{-1}$ is measured to an accuracy of 0·005·% . what would be the minimum error in determining its Position?. (mass of electron $9·1 \times 10^{-31} kg$ and Planck constant, $h = 6·6 \times 10^{-34} kg \, m^2 s^{-1}$.)

→ Heisenberg's uncertainty Principle.

$$\Delta x \cdot \Delta P \geqslant \frac{h}{4\pi}$$

$$\Delta x \cdot m \Delta v \geqslant \frac{h}{4\pi}$$

$$\Delta x \geqslant \frac{h}{4\pi \, m \, \Delta v} \quad ——— ①$$

here

$$\Delta v = 0·005·\% \text{ of } 600 \, ms^{-1} = 600 \times \frac{0·005}{100} = 0·03 \, m/s$$

$$\Delta x \geqslant \frac{6·6 \times 10^{-34}}{4 \times 3·14 \times 9·1 \times 10^{-31} \times 0·03}$$

$$\Delta x \geqslant 1·9248 \times 10^{-3} \, m$$

⑩ Discus the failures of classical mechanics to Explain Properties of Particles at atomic and Sub-atomic level.

→ classical or Newtonian mechanics cannot explain such Phenomena as ~~black explain~~ ~~such Phenomena as~~ black body radiation, the photoelectric effect, or the ~~s~~ dependence of the heat capacity of a substance on temperature, quantum mechanical tunneling and the Raman effect. Cannot be explained by classical mechanics.

⑪ What is an absorption spectrum? Discuss about $\pi-\pi^*$ and $n-\pi^*$ transitions giving Examples.

→ An absorption spectrum occurs when light passes through a cold, dilute gas and atoms in the gas absorb at characteristic Frequencies.

• $\pi-\pi^*$ transitions occur when an electron in a π molecular orbital is excited to a higher energy π^* orbital.

$n-\pi^*$ transitions occur when an electron in a non-bonding orbit is excited to a higher energy • π^* orbital.

⑫ With reference to NMR spectroscopy, discuss chemical shift, shielding and deshielding of Protons and spin-spin interaction.
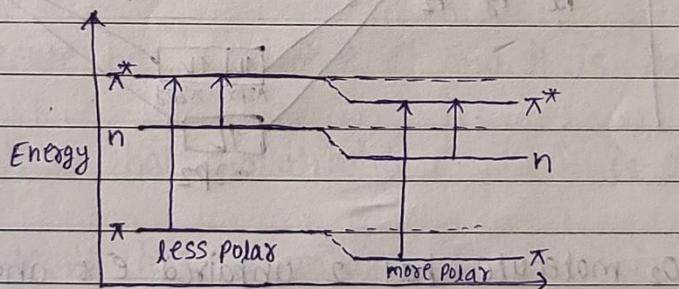
→ Chemical shift :- The separation of ~~signals~~ Position of signal of nucles of particular type of Hydrogen from refrance standard (T.M.S) is called chemical shift.

Shielding :- In NMR, when the electron density is high around the nucleus, the opposing magnetic Field to electron is also. ~~bigger~~ higher which in turn gives huge shielding.

Deshielding:- Deshielding is when electron density falls around the nucleus, the magnetic field opposing it reduces. then the nucleus feeds more of the external magnetic field.
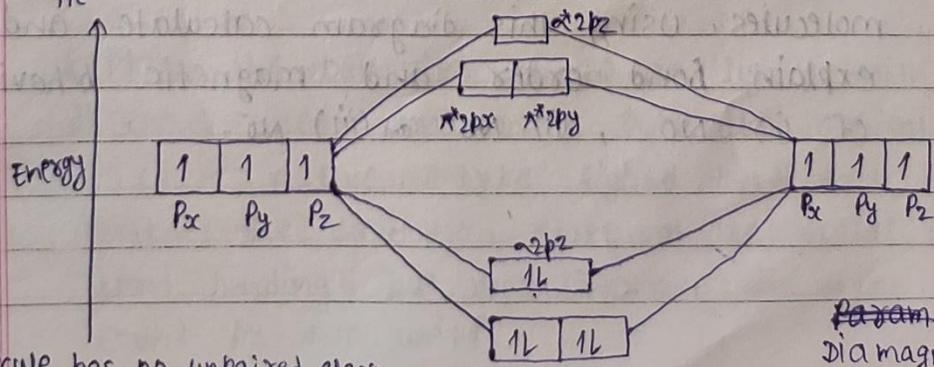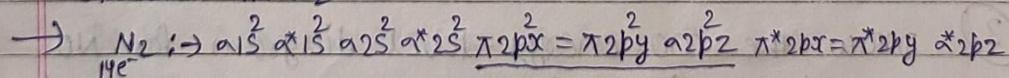
(B) Explain the effect of solvent on $n-\pi^*$ and $\pi-\pi^*$ electronic transition.

→ As the polarity of solvent increases the $\pi-\pi^*$ transition to a lower energy whereas the polarity of solvent increases the $n-\pi^*$ transition goes to a higher energy.


less polar   more polar

M.O.T
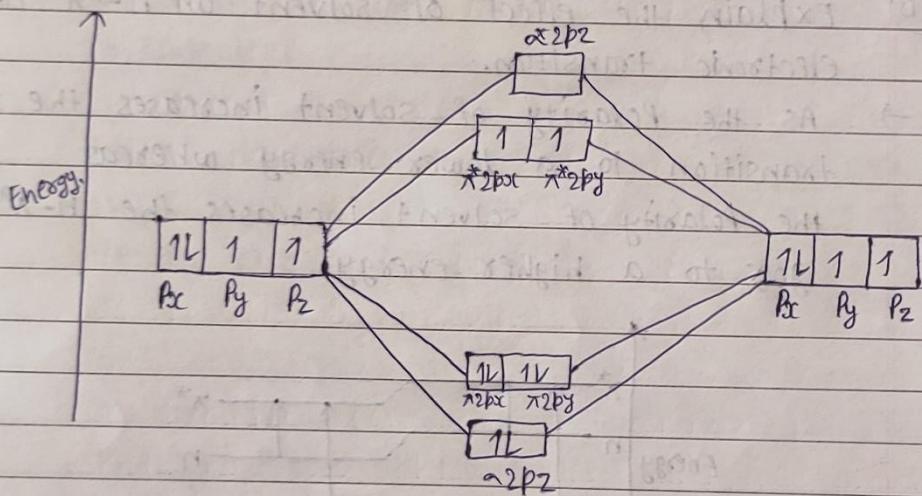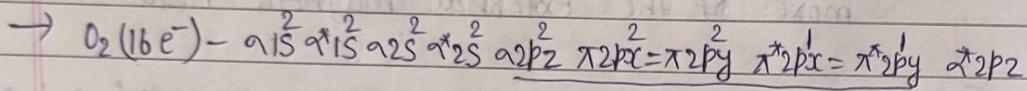
① Draw the mo energy-level diagram for N_2 and based on the diagram, explain the magnetic property observed in N_2.

→ $N_2 :\to \sigma 1s^2 \, \sigma^* 1s^2 \, \sigma 2s^2 \, \sigma^* 2s^2 \, \pi 2p_x^2 = \pi 2p_y^2 \, \sigma 2p_z^2 \, \pi^* 2p_x = \pi^* 2p_y \, \sigma^* 2p_z$
14e⁻

Energy

$\sigma^* 2p_z$

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

| 1 | 1 | 1 |
Px Py Pz

| 1 | 1 | 1 |
Px Py Pz

$\sigma 2p_z$
| 1↓ |

| 1↓ | 1↓ |
$\pi 2p_x$ $\pi 2p_y$

Param
Diamagnetic
↳ No Unpaired e⁻!

→ N_2 molecule has no unpaired electrons and is diamagnetic.

(2) Draw the mo ~~Diagram~~ energy-level diagram for O_2 and based on the diagram, and explain the magnetic property observed in O_2, O_2^+ and O_2^-

→ $O_2 (16 e^-) - \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^1 = \pi^* 2p_y^1 \sigma 2p_z$
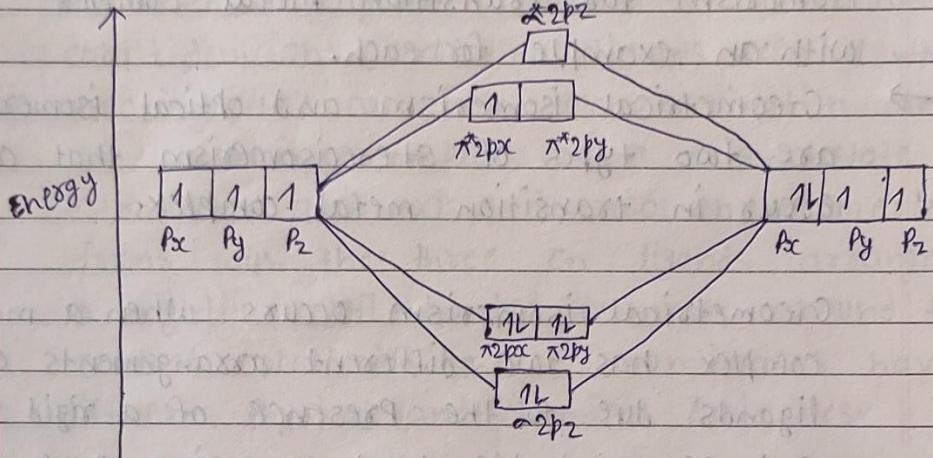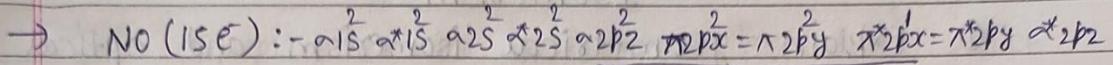

O_2 molecule has 2 unpaired $e's$ and it is Paramagnetic

O_2^+ molecule has 1 unpaired $e's$ and it is paramagnetic.

O_2^- molecule has 1 unpaired e^- and it is paramagnetic.

(3) Draw the mo energy-level diagram for NO molecules. Using this diagram calculate and explain bond order and magnetic behavier of (i) NO , (ii) NO^+ and (iii) NO^-.

→ NO $(15\bar{e})$:- $\sigma 1s^2$ σ^*1s^2 $\sigma 2s^2$ σ^*2s^2 $\sigma 2p_z^2$ $\pi 2p_x^2 = \pi 2p_y^2$ $\pi^*2p_x^1 = \pi^*2p_y$ σ^*2p_z

NO molecule has 1 unpaired e^1 and it is paramagnetic.

NO^+ molecule has no unpaired $\bar{e}$ and it is Diamagnetic.

$N\bar{O}$ molecule has 2 unpaired $\bar{e}$ and it is Paramagnetic.

Bond order of $NO = \dfrac{10-5}{2} = \dfrac{5}{2} = 2.5$

Bond order of $NO^+ = \dfrac{10-4}{2} = 3$

Bond order of $N\bar{O} = \dfrac{10-6}{2} = 2$

④ Explain the behavier of CO as ligand with different metal ions using molecular orbital theory.
→ CO is a dative, L-type ligand that does not effect the oxidation state of the metal centre upon binding, but does increase the total electron count by two units.

Isomerism

① Explain geometrical isomerism and optical isomerism for transition metal complex with an example for each.

→ Geometrical isomerism and optical isomerism are two types of stereoisomerism that can occur in transition metal complex.

Geometrical isomerism occurs when a metal complex has two different arrangements of ligands due to the presence of a rigid structure, such as a double bond or a ring. there are two possible arrangements exist: cis and trans.

For Example, consider the complex $[Co(NH_3)_4Cl_2]^+$ which has two chloride ions and four ammonia ligands around a central cobalt ion. The cis-isomer has the two chloride ions on adjacent corners of the square plane and the four ammonia ligands on the other two corners, while the trans-isomer has the two chloride ions on opposite corners. and the four ammonia ligands on the other two corners. These isomers have different physical and chemical properties.

Optical isomerism occurs when a metal complex has a non-superimposable mirror image, called an enantiomer. in transition metal complexes, optical isomerism is often seen in octahedral complexes.

For example, consider the complex $[Co(en)_3]^{3+}$ which has three en ligands attached to a central cobalt ion. The three en ligands are bidentate, meaning they can form two coordination bonds each. The resulting complex has a tris-chelate structure and exists in two enantiomeric forms, with the three en ligands arranged in a right-or left-handed manner around the central cobalt ion. These enantiomers have different physical and chemical properties.

② Explain ionization isomerism and linkage isomerism for transition metal complex with an example for each.

➤ **Heisenberg's uncertainty Principle**

The dual nature of the electron implies that any precise measurment of its position would create uncertainty in measurement and position. The Heisenberg uncertainty principle states that
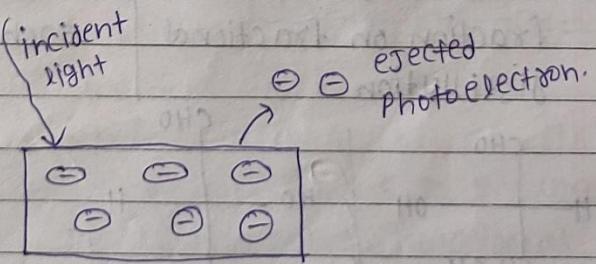
It is impossible to determine simultaneously both the position and the momentum of a particle with accuracy.

$$\Delta x \cdot \Delta P \geqslant \frac{h}{4\pi}$$

The above expression is known as uncertainity relation where $\Delta x =$ change in position, $\Delta P =$ change in momentum and $h = $ planck's constant.

➤ **Photoelectric effect.**

It is a phenomenon in which electrons are ejected from the surface of a metal when light is incident on it. These ejected electrons are called photo electrons.
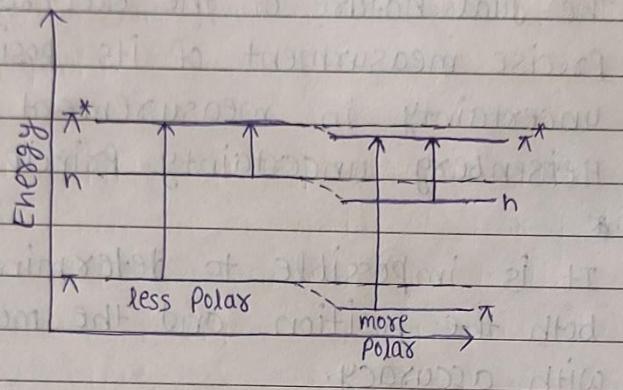
$$E = \phi + K \cdot E$$

➤ **Explain the effect of solvent on $n \rightarrow \pi^*$ and $\pi - \pi^*$ electronic transition.**

Solⁿ: As the polarity of solvent increases, the $\pi - \pi^*$ transition to a lower energy whereas

the n→π* transition goes to a higher energy.

less Polar

more Polar
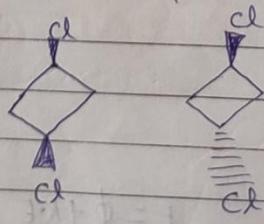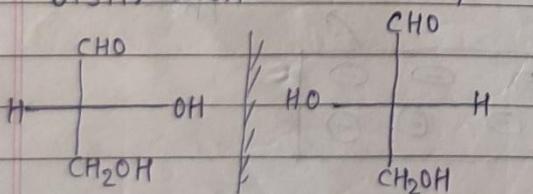
> Difference between enantiomers and diastereomers.

Enantiomers	diastereomers
• They are mirror image of each other	• They are not mirror images of each other.
• have identical physical Properties	• have distinct physical properties.
• Present in pair	• can be several molecules.
• Similar molecular shape	• Different molecular shape.
• always give one fraction on fractional distillution	• give separate fraction for each molecule.

➤ Difference between SN_1 and SN_2
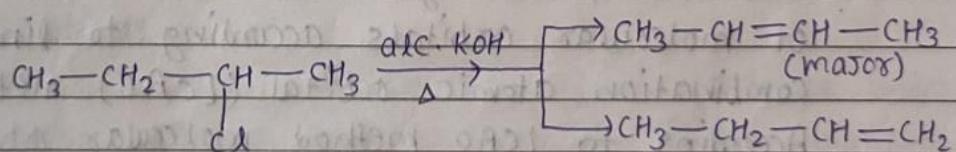
SN_1	SN_2
• This is a two step reaction	• This is a one step reaction
• formation of carbocation	• No formation of carbocation
• Rate of reaction depends only on the concentration of organic reactant	• Rate of reaction depends on both the concentration of the reactant and reagent.
• No inversion in the final product	• There is optical inversion in product.

➤ Explain the following terms.

(i) Saytzeff Rule with example.

It states that in dehydrohalogenation reactions, the preferred product is that alkene which has a greater number of alkyl groups attached to the doubly bonded carbon atoms.

example

$$CH_3-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_3 \xrightarrow[\Delta]{alc. KOH} \begin{cases} CH_3-CH=CH-CH_3 \quad (major) \\ CH_3-CH_2-CH=CH_2 \end{cases}$$

(ii) functional group region

The functional group region is 2.5 to 7.4 μm (4000 − 1430 cm^{-1}). In this region, functional groups of organic compound is detected.
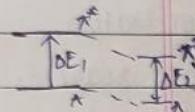
(iii) Fingerprint region

The fingerprint region is 7−11 μm (1430 − 910 cm^{-1}) gives a good deal of information about the molecule
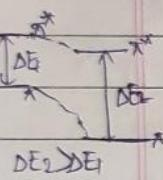
besides the functional groups of the compound.
The fingerprint can lead us to identify an
organic compound.

(iv) Bathochromic shift and Hypsochromic shift
 • Bathochromic shift is a shift of peak position
   (λ_{max}) to a higher wavelength due to the effect
   of a substituent group or solvent. It is also
   called 'red shift'.
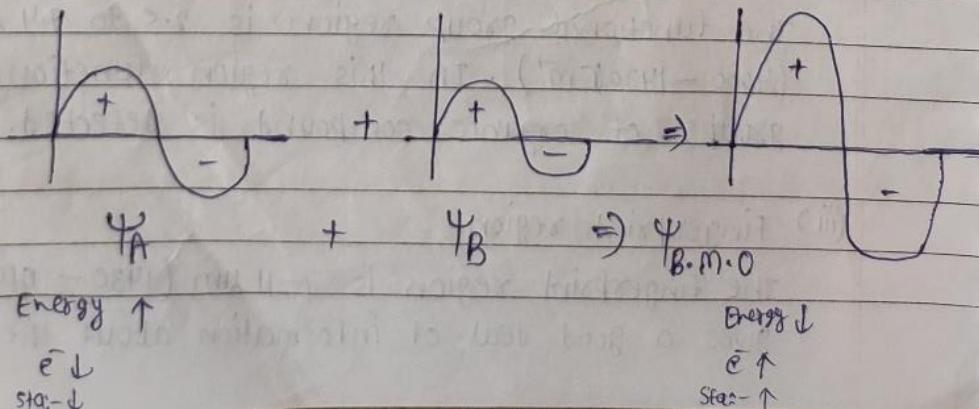
 • Hypsochromic shift: It is a shift of λ_{max} to a
   lower wavelength. It is also called 'Blue shift'.
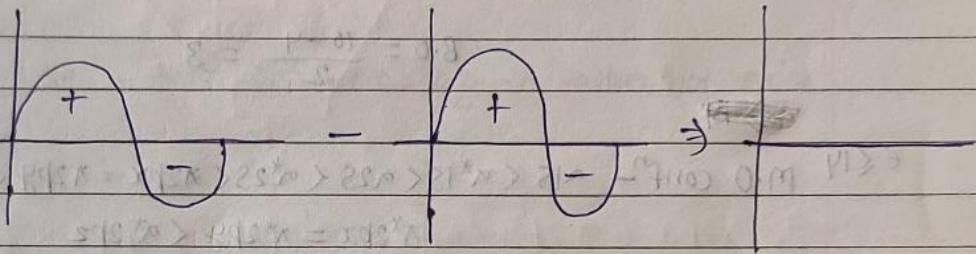
➤ molecular orbital theory (MOT):— This theory is
   given as idea about distribution of electron
   around a group of Nuclei depending upon the
   number of atoms. Presenting the molecules.
   This theory also gives an idea about formation
   of molecular orbitals according to linear
   combination atomic orbital (LCAO) method.
   According to LCAO method molecular orbitals.
   are from in the two different ways.
(i) by the addition of atomic orbitals.

Ψ_A + Ψ_B ⇒ $\Psi_{B.M.O}$

Energy ↑   Energy ↓
ē ↓   ē ↑
Sta:- ↓   Sta:- ↑

Thus m.o from by the addition of atomic
orbitals is called bonding molecular orbital
which has more charge density, less energy,
and so as more stability than constituent
atomic orbitals.
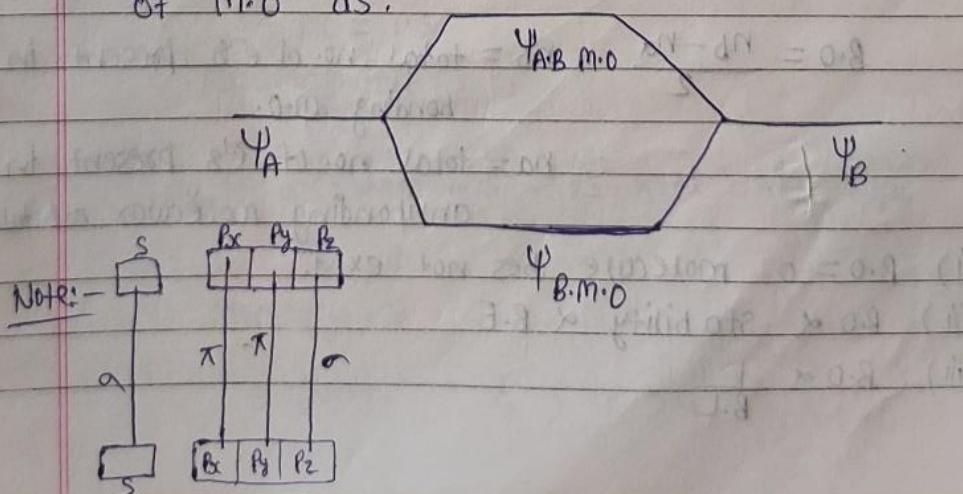
(ii) by the substration of atomic orbitals.
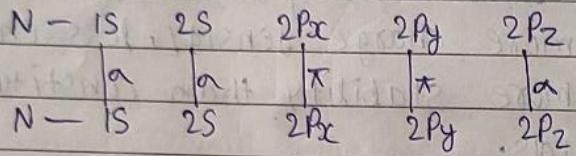
$$\Psi_A - \Psi_B \Rightarrow \Psi_{Anti\ bonding\ molecular\ orbital}.$$

Thus m.o forms by the substraction of atomic
orbital is called anti bonding molecular orbital
which has less charge density, more energy
and so as less stability than consitutent atomic
orbitals.
that is the number of atomic orbitals under
goes LCAO method to give the same number
of m.o as.

$\Psi_{A\cdot B\ m.o}$

Ψ_A Ψ_B

$\Psi_{B\cdot m\cdot o}$

Note:-

s	Px	Py	Pz
σ	π	π	σ

| Px | Py | Pz |

M.O configuration upto N_2 ($14\bar{e}$)

N – 1S	2S	2Px	2Py	2Pz
α	α	↑	↑	α

N – 1S	2S	2Px	2Py	2Pz

$$14\bar{e} \rightarrow \sigma 1S^2 \; \sigma^*1S^2 \; \sigma 2S^2 \; \sigma^*2S^2 \; \pi 2px^2 = \pi 2py^2 \; \sigma 2Pz^2$$

$$B.O = \frac{10-4}{2} = 3$$

$\bar{e} < 14$ M.O conf^n $\sigma 1S < \sigma^*1S < \sigma 2S < \sigma^*2S < \pi 2px = \pi 2py < \sigma 2pz <$
$$\pi^* 2px = \pi^* 2py < \sigma^* 2pz$$

M.O configuration onward N_2 ($> 14\bar{e}$)

M.O conf^n = $\sigma 1S < \sigma^*1S < \sigma 2S < \sigma^*2S < \sigma 2pz < \pi 2px = \pi 2py < \pi^* 2px = \pi^* 2py$
$$< \sigma^* 2pz$$

Bond order :- It is half of the difference between electrons presenting Bonding molecular orbital and Anti Bonding molecular orbital.

$$B.O = \frac{n_b - n_a}{2}$$

n_b = total no. of $\bar{e}$'s present in bonding m.o.

n_a = total no. of $\bar{e}$'s present in antibonding molecular orbitals.
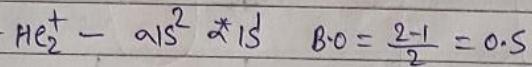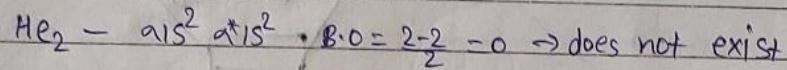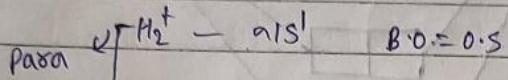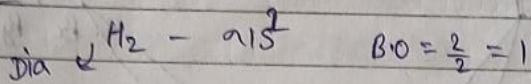
(i) $B.O = 0$ molecule does not exist.

(ii) $B.O \propto$ stability $\propto B.E$
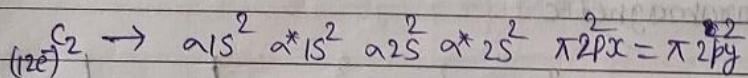
(iii) $B.O \propto \dfrac{1}{B.L}$

(iv) B.O's are same then ~~greater~~ less the no. of Antibonding
e's . more stable will be ~~at~~ the molecule.

Ex:-

Dia $\swarrow$ H_2 — $\sigma 1s^2$ $B.O = \frac{2}{2} = 1$

Para $\swarrow$ ⌈H_2^+ — $\sigma 1s^1$ $B.O = 0.5$

├ He_2 — $\sigma 1s^2 \, \sigma^* 1s^2$. $B.O = \frac{2-2}{2} = 0 \rightarrow$ does not exist

└ He_2^+ — $\sigma 1s^2 \, \sigma^* 1s^1$ $B.O = \frac{2-1}{2} = 0.5$

Stability :— $H_2^+ > He_2^+$
                        stable

$\underset{(12e^-)}{C_2} \rightarrow \sigma 1s^2 \, \sigma^* 1s^2 \, \sigma 2s^2 \, \sigma^* 2s^2 \, \pi 2p_x^2 = \pi 2p_y^2$

$B.O = 2$

Diamagnetic

$C_2^+ \rightarrow \sigma 1s^2 \, \sigma^* 1s^2 \, \sigma 2s^2 \, \sigma^* 2s^2 \, \pi 2p_x^2 = \pi 2p_y^1$

$B.O = 1.5$

Paramagnetic

$C_2^- \rightarrow \sigma 1s^2 \, \sigma^* 1s^2 \, \sigma 2s^2 \, \sigma^* 2s^2 \, \pi 2p_x^2 = \pi 2p_y^2 \, \sigma 2p_z^1$
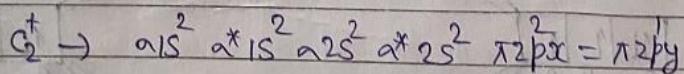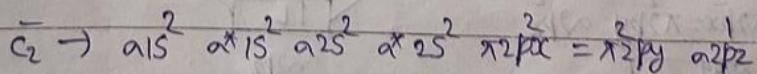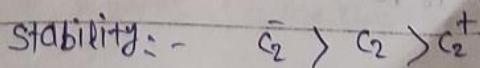
$B.O = 2.5$

Paramagnetic

Stability :— $C_2^- > C_2 > C_2^+$

CFT
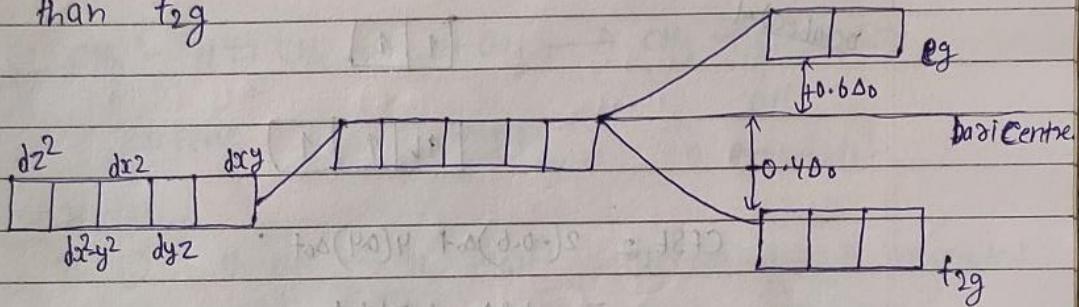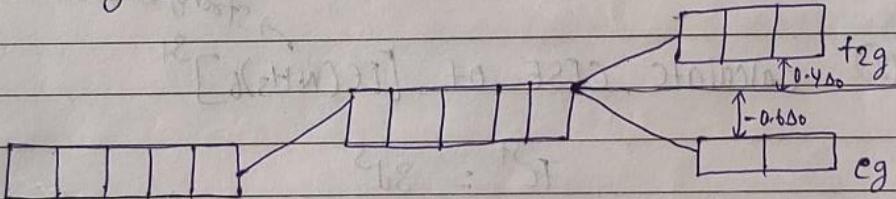
① spliting of d-orbital in ~~oo~~ octaheadral field.
→ due to octaheadral approch of ligends eg lobs
face direct repulsion of o' while lobes of t_{2g}
face less repulsion (at 45) so eg energy more
than t_{2g}

$$dz^2 \quad dr2 \quad dxy$$

$$d x^2 y^2 \quad dyz$$

eg

$\uparrow 0.6\Delta_0$

bari Centre

$\uparrow 0.4\Delta_0$

t_{2g}

② spliting of d-orbital in tetraheadral field.

t_{2g}

$\uparrow 0.4\Delta_0$

$\downarrow 0.6\Delta_0$

eg

replusing face by t_{2g} orbitaus is greater at
35° 16' then that in easy orbital at 54° 44'
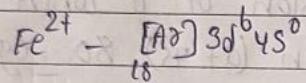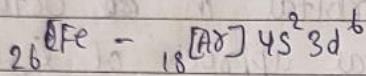
① $\Delta_0 > P.E \Rightarrow$ low spin complex

② $\Delta_0 < P.E \Rightarrow$ high spin complex

The amount of enery required to pair an intercoming
electron is called paring energy.

$$CFSE = n_{t2g}(-0.4\Delta_0) + n_{eg}(0.6\Delta_0)$$

→ no. of pair e'g.

$$= (-0.4 n t_{2g} + 0.6 n_{eg})\Delta_0 + n P.E \text{ (P.E is used in}$$
case of low spin
complex).

① calculate CFSE of $[Fe(H_2O)_6]^{2+}$ ↙ weak legands

$_{26}Fe - _{18}[Ar] 4s^2 3d^6$

$Fe^{2+} - _{18}[Ar] 3d^6 4s^0$

octahedral

1	1

1L	1	1

$CFSE = 2(-0.6)\Delta_0 + 4(0.4)\Delta_0$

$= -1.2\Delta_0 + 1.6\Delta_0$

$= -0.4\Delta_0$
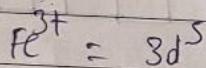
② calculate CFSE of $[Fe(NH_3)_6]^{3+}$ ↙ strong reagands

$Fe^{3+} = 3d^5$

| 1L	1L	1

$CFSE = (-0.4)5\Delta_0 + 2PE$

$= -2\Delta_0 + 2PE$
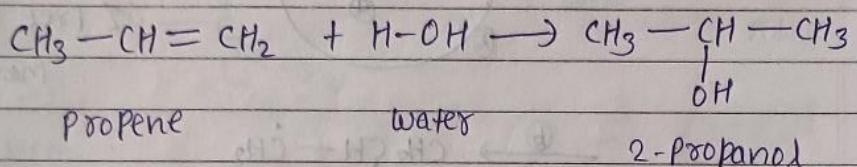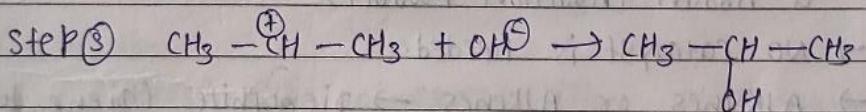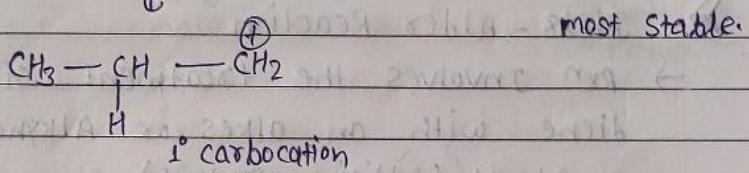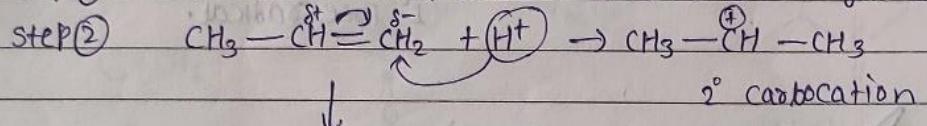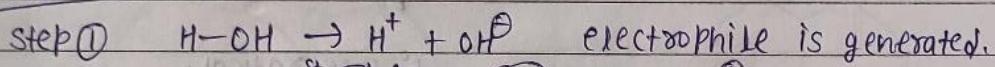
➤ **Markonikoff's Rule-**

According to this rule in addition reaction of alkene, +ve part of reactant attack on carbon having more no. of hydrogen and -ve part attack on carbon having less hydrogen.

$$CH_3-CH=CH_2 \ + \ H-OH \longrightarrow CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

Propene   water   2-Propanol

mechanism

Step① $\quad H-OH \rightarrow H^+ + OH^{\ominus} \quad$ electrophile is generated.

Step② $\quad CH_3-\overset{\delta +}{CH}=\overset{\delta -}{CH_2} \ + \ (H^+) \rightarrow CH_3-\overset{\oplus}{CH}-CH_3$

$$2° \ carbocation$$
$$most \ stable.$$

$$CH_3-\underset{\underset{H}{|}}{CH}-\overset{\oplus}{CH_2}$$

$$1° \ carbocation$$

Step③ $\quad CH_3-\overset{\oplus}{CH}-CH_3 + OH^{\ominus} \rightarrow CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$
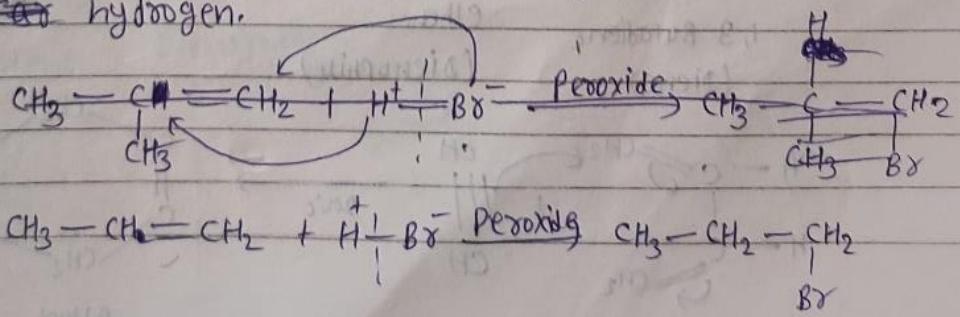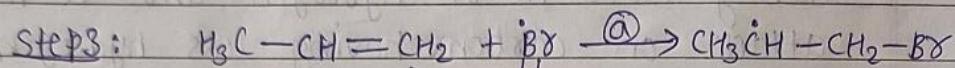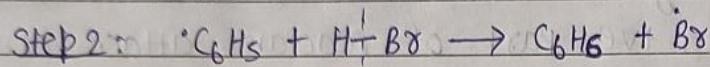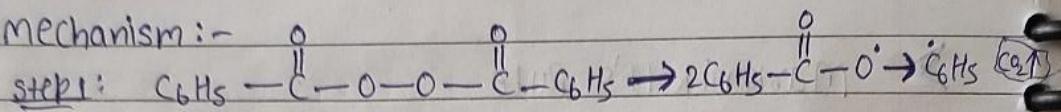
➤ **Antimarkonikoff's Rule-**
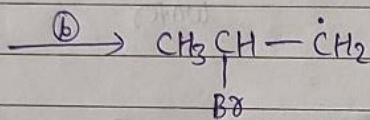
→ In the Presence of Peroxide in addition rex^n of unsymmetrical alkene, +ve part attack on that carbon having less no. of hydrogen and -ve part attack on that carbon having more no. of hydrogen.

$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + H^+ \overline{} Br^- \xrightarrow{Peroxide} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{Br}{|}}{CH_2}$$

$$CH_3-CH=CH_2 + H^+ \overline{} Br \xrightarrow{Peroxide} CH_3-CH_2-\underset{\underset{Br}{|}}{CH_2}$$

mechanism :-

step 1 : $C_6H_5 - \overset{O}{\overset{||}{C}} - O - O - \overset{O}{\overset{||}{C}} - C_6H_5 \longrightarrow 2C_6H_5 - \overset{O}{\overset{||}{C}} - O^{\cdot} \rightarrow \overset{\cdot}{C}_6H_5 \ (CO_2)$

step 2 : $\overset{\cdot}{C}_6H_5 + H \overset{|}{-} Br \longrightarrow C_6H_6 + \overset{\cdot}{Br}$

step 3 : $H_3C - CH = CH_2 + \overset{\cdot}{Br} \xrightarrow{\ \ @ \ \ } CH_3\overset{\cdot}{C}H - CH_2 - Br$

2° free radical
more stable.

$\xrightarrow{\ \ \textcircled{b} \ \ } CH_3 CH - \overset{\cdot}{C}H_2$

$\overset{|}{Br}$

1° Free radical.
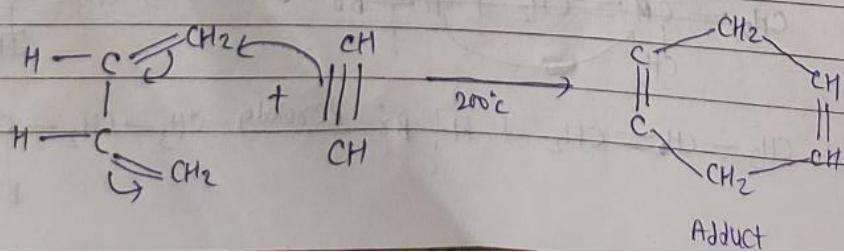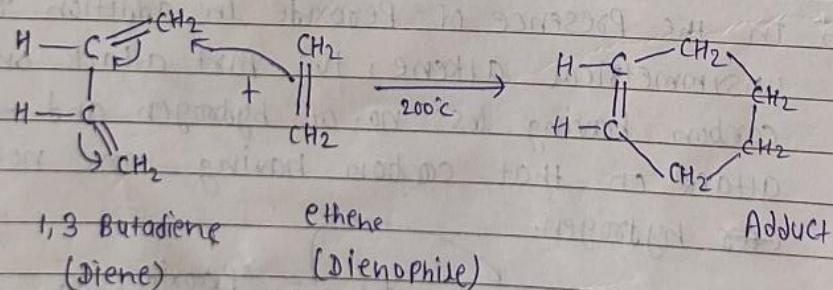
> ## Diels - Alder Reaction

→ Rxⁿ Involves the treatment of conjugated diene with an alkes or Alkynes. to give a Addult (Addition Product)

→ No catalyst is needed.
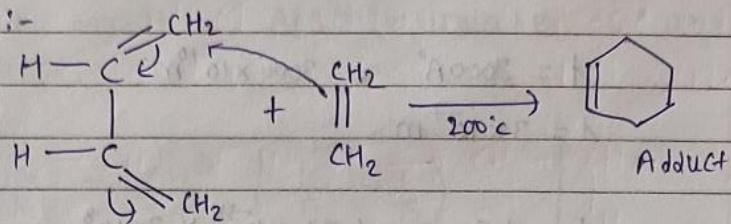
→ Alkynes or Alkenes → Dienophile (Diene loving)

→ The product of Diels-Alder is Adduct.

1,3 Butadiene   ethene
(Diene)   (Dienophile)   Adduct

Adduct
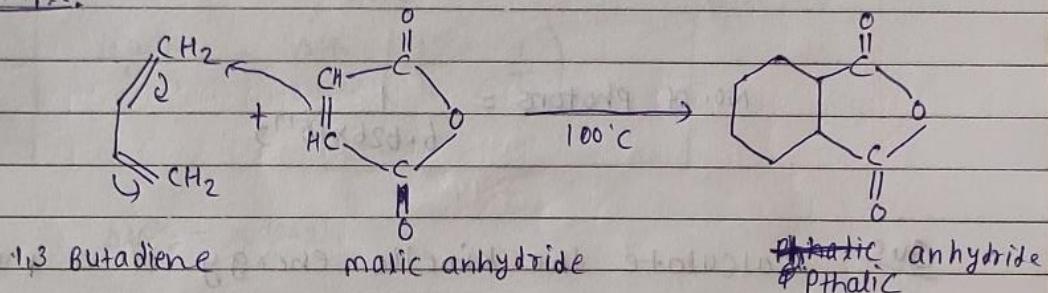
The net result is formation of two new σ bonds and one π bond. & breaking of 3 π bonds (original)

mechanism:-

Adduct

Example:-

1,3 Butadiene   malic anhydride   Phtalic anhydride
   & Pthalic
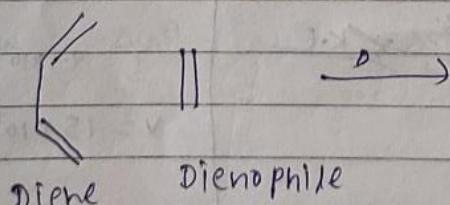
→ M.R.I (magnetic Resonance imaging)

Diels-Alder reaction
→ It is (4+2) type of cycloaddition reaxⁿ taking place in presence of Heat simplest example in the cycloaddition of 1,3 Butadiene & ethene.

Diene   Dienophile

Que The equilibrium constants for the reaction

$H_2(g) + S_{(s)} \rightleftharpoons H_2S_{(g)}$ are 18.5 at 925K and

9.25 at 1000K. Calculate standard enthalpy

of the reaction. Also calculate $\Delta G°$ and $\Delta S°$

at 925K.

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\ominus}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$\Delta H^\ominus = x$ (say)

$$\boxed{\Delta G^\ominus = \Delta H^\ominus - T \Delta S^\ominus}$$

?

$$\boxed{\Delta G^\ominus = -2.303 R T \log K_{eq}}$$

$\overset{925}{}$ $\overset{18.5}{}$

$\underset{8.314}{}$

$\Delta G^\ominus = y$ (say)

$$\Delta G^\ominus = \Delta H^\ominus - T \Delta S^\ominus$$
$$\underset{y}{\downarrow} \quad \underset{x}{\downarrow} \quad \underset{925}{\downarrow} \underset{?}{\downarrow}$$

WATER

$OX \cdot DP \geqslant \frac{h}{4\pi}$

(1) $Ca(HCO_3)_2$ ⎤ Temporary hardness

(2) $Mg(HCO_3)_2$ ⎦

(3) $CaSO_4$ ⎤

(4) $MgSO_4$ ⎬ permanent hardness

(5) $CaCl_2$ ⎪

(6) $MgCl_2$ ⎦

Lime requirement for softening (in mg/L)

$$= \frac{74}{100}\left[\begin{array}{l} Temp. \, Ca^{2+} + 2\times Temp \, Mg^{2+} + Perm(Mg^{2+} + Fe^{2+} + Al^{+3}) \\ + CO_2 + H^+(HCl \, or \, H_2SO_4) + HCO_3^- - Na \, AlO_2 \end{array}\right]$$

all in terms of $CaCO_3$ equivalents

Soda requirement for softening (in mg/L)

$$= \frac{106}{100}\left[\begin{array}{l} Perm.(Ca^{2+} + Mg^{2+} + Al^{+3} + Fe^{2+}) + H^+(HCl \, or \, H_2SO_4) \\ - HCO_3^- \qquad all \, in \, terms \, of \, CaCO_3 \, equivalents \end{array}\right]$$

2018

⑦(a) Calculate the quantity of lime and soda required for softening 50000 lit. of water containing the following.
$Ca(HCO_3)_2 = 8.1 \, ppm$, $Mg(HCO_3)_2 = 7.5 \, ppm$, $CaSO_4 = 13.6 \, ppm$,
$MgSO_4 = 12 \, ppm$, $MgCl_2 = 2 \, ppm$, $NaCl = 4.7 \, ppm$.

Sol^n

Constituent	multiplication factor	$CaCO_3$ equivalent.
$Ca(HCO_3)_2 = 8.1 \, ppm$	$\frac{100}{162}$	$\frac{8.1\times100}{162} = 5$
$Mg(HCO_3)_2 = 7.5 \, ppm$	$100/146$	$\frac{7.5\times100}{146} = 5.1$
$CaSO_4 = 13.6 \, ppm$	$100/136$	$\frac{13.6\times100}{136} = 10$
$MgSO_4 = 12 \, ppm$	$100/120$	$\frac{12\times100}{120} = 10$
$MgCl_2 = 2 \, ppm$	$100/95$	$2\times100/95 = 2.1$

$40+122 = 162$

$24 + 122 = 146$

$40 + 32 + 64 = 136$

$24 + 32 + 64 = 120$

$24 + 71 = 95$

$^1H.N.M.R$ Spectroscopy
(Nuclear magnetic Resonance.)

N.M.R active & inactive nuclei

Proton	Neutron	Spin quantum no.
even	even	$I = 0$ N.M.R inactive
odd	odd	I = integer
odd	even	$\left.\begin{array}{l} \\ \\ \end{array}\right\} I$ = fraction.
even	odd	
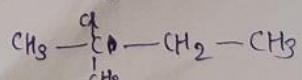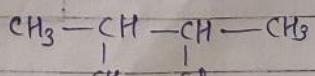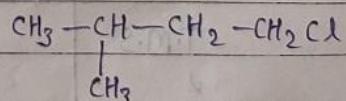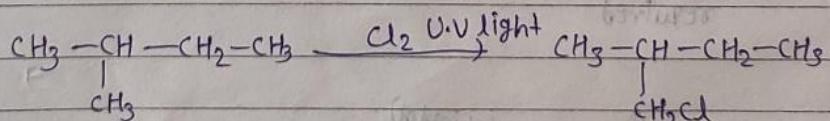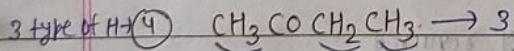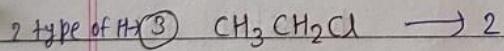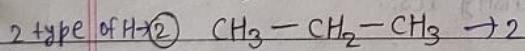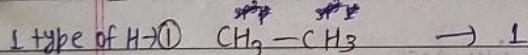
$$I = \frac{1}{2} \quad \text{For } 1H$$

No. of oritation $= 2I + 1$
$$= 2 \times \frac{1}{2} + 1$$
$$= 2$$
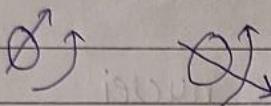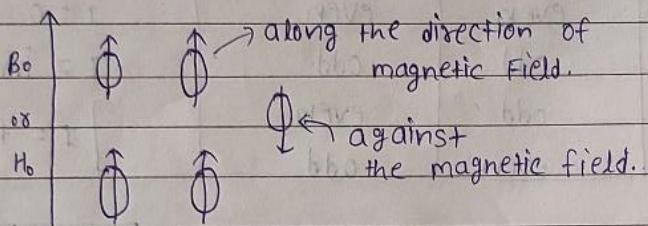
Que Prediction of No. of signal in 1H N.M.R.

1 type of H→① $CH_3 - CH_3 \longrightarrow 1$

2 type of H→② $CH_3 - CH_2 - CH_3 \rightarrow 2$

2 type of H→③ $CH_3 CH_2 Cl \longrightarrow 2$

3 type of H→④ $CH_3 CO CH_2 CH_3 \longrightarrow 3$

$$CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_3 \xrightarrow{Cl_2 \ U.V \ light} CH_3 - \underset{\underset{CH_2Cl}{|}}{CH} - CH_2 - CH_3$$

$$CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_2 Cl$$

$$CH_3 - \underset{\underset{CH_3}{|}}{CH} - \underset{\underset{Cl}{|}}{CH} - CH_3$$

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}} - CH_2 - CH_3$$

In the absence of magnetic Field.
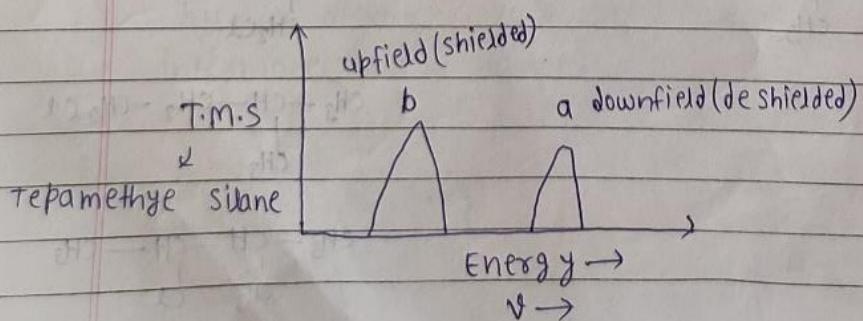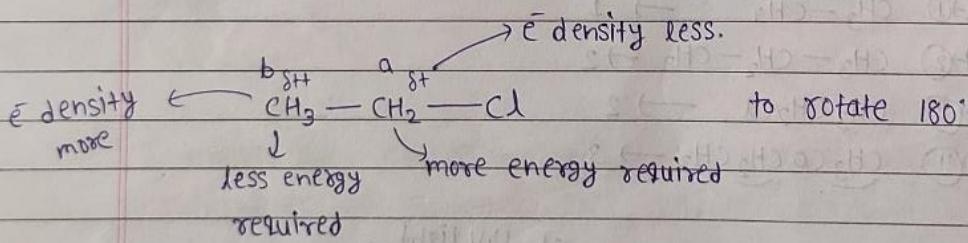
When external magnetic Field is applied.

B_o
or
H_o

→ along the direction of magnetic Field.

← against the magnetic field.
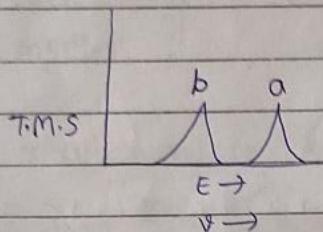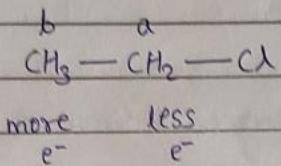
α spin — when external B is applied then spin
(State lower energy state) state change along the B field.

→ If the e^- sourding the H, then less energy is
required to rotate 180°.

→ e^- density less.

e^- density more ← $\overset{b\ \delta^{++}}{C}H_3 \longrightarrow \overset{a\ \delta^+}{C}H_2 \longrightarrow Cl$ to rotate 180°

↓
less energy required   ↘ more energy required

upfield (shielded)

T.M.S
↓
Tepamethye silane

b

a downfield (deshielded)

Energy →
ν →

chemical shift (δ)

$$\overset{b}{CH_3} - \overset{a}{CH_2} - Cl$$

more e^- less e^-

T.M.S

$E \rightarrow$
$\vartheta \rightarrow$
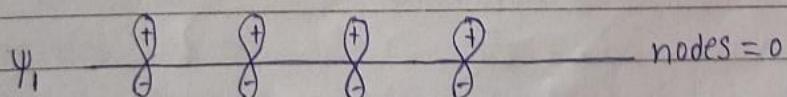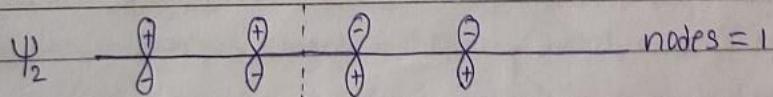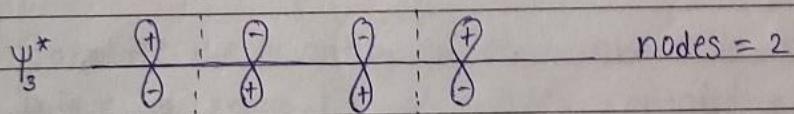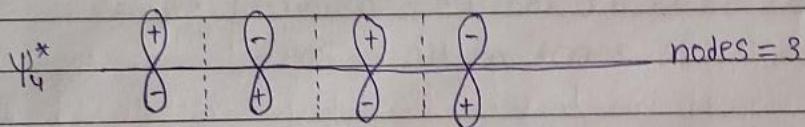
δ = observed chemical shift of hydrogen From T.M.S in Hz.
operating frequency of the instant in Hz.

▷ Diel's Alder reaction.

Ψ_4^* nodes = 3

Ψ_3^* nodes = 2

Ψ_2 nodes = 1

Ψ_1 nodes = 0

Spectroscopy → The branch of science concerned with the investigation and measurement of spectra produced when electromagnetic ~~radic~~ radication interacts with matter.

Types of spectroscopy

$$V = \frac{C}{\lambda}$$

① Radiowaves : $3 \times 10^6 - 3 \times 10^{10}$ HZ
   NMR (~~Ae~~ Nuclear magnetic Resonance spectroscopy).
   ESR (Electron spin resonance spectroscopy.)

② microwave : $3 \times 10^{10} - 3 \times 10^{12}$ HZ , To study rotational spectroscopy
③ Infrared : $3 \times 10^{12} - 3 \times 10^{14}$ HZ , To study vibrational spectroscopy
④ U.V-visible : $3 \times 10^{14} - 3 \times 10^{16}$ HZ , To study U-V visible spectroscopy
                                                    (electonic spectroscopy.)
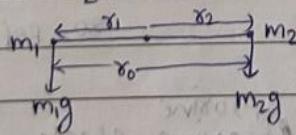
→ Conditions for molucule to be rotationaly active :—

① dipole moment $\neq 0$
② $\Delta J = \pm 1$, J = rotational quantum no.

Diatomic molecule (HCl)
   $m_1 = H$ & $m_2 = cl$

Anticlock wise → +ve
clock wise → −ve

$$\tau_1 = m_1 g \times r_1$$
$$\tau_2 = -m_2 g \times r_2$$

To In Equilibrium. $\tau_1 + \tau_2 = 0$

$$m_1 g r_1 - m_2 g r_2 = 0$$

$$\boxed{m_1 r_1 = m_2 r_2} \quad —①$$

Torque = Force $\times$ Perpendicular distance
$$\tau = F \times 1 r$$

$$r_0 = r_1 + r_2$$

From ① $m_1 r_1 = m_2 (r_0 - r_1)$

$$r_1 (m_1 + m_2) = m_2 r_0$$

$$r_1 = \left(\frac{m_2}{m_1 + m_2}\right) r_0$$

similarly,

$$m_1 (r_0 - r_2) = m_2 r_2$$

$$m_1 r_0 = r_2 (m_1 + m_2)$$

$$r_2 = \left(\frac{m_1}{m_1 + m_2}\right) r_0$$

Total moment of Inertia

$$I = m_1 r_1^2 + m_2 r_2^2$$

$$\boxed{I = \frac{m_1 m_2 \cdot r_0^2}{(m_1 + m_2)}} \quad I = \mu r_0^2 \quad I = \mu r_0^2$$

where μ = redused mass $= \frac{m_1 m_2}{m_1 + m_2}$

Que   Derivation of $I = \frac{m_1 m_2}{(m_1 + m_2)} r_0^2$

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \text{(Formula)}$$

$$r_1 = \left(\frac{m_2}{m_1 + m_2}\right) r_0 \quad \bigg| \quad r_2 = \left(\frac{m_1}{m_1 + m_2}\right) r_0$$

$$I = \frac{m_1 m_2^2 r_0^2}{(m_1 + m_2)^2} + \frac{m_2 m_1^2 r_0^2}{(m_1 + m_2)^2}$$

$$I = \frac{m_1 m_2 r_0^2 (m_2 + m_1)}{(m_1 + m_2)^2}$$

$$I = \frac{m_1 m_2 r_0^2}{(m_1 + m_2)}$$

Proved.

Angular momentum $(L) = I\omega$

$$L = \sqrt{J(J+1)} \frac{h}{2\pi} \qquad J = \text{Rotational quantum no.}$$

$$E_{rot} = \frac{1}{2} I\omega^2 = \frac{1}{2}\frac{I\omega^2 I}{I} = \frac{1}{2I}(I\omega)^2 = \frac{1}{2}\frac{L^2}{I}$$

$$E_{rot} = \frac{1}{2I} J(J+1) \frac{h^2}{4\pi^2}$$

$$\boxed{E_{rot} = \frac{h^2}{8\pi^2 I} J(J+1)}$$

Que calculate the reduced mass of CN molecule given atomic weight $C = 12.011$ and $N = 14.0067$

Reduced mass $(\mu) = \frac{m_1 m_2}{m_1 + m_2} \times \frac{1}{N_A}$

$$= \frac{12.011 \times 14.0067}{12.011 + 14.0067} \times \frac{1}{6.022\times10^{23}}$$

$$= \frac{43560837}{16.9621137}$$

$$= \frac{168.234474}{26.0177} \times \frac{1}{6.022\times10^{23}}$$

$$= 1.07375535 \times 10^{-23}$$

$$= 1.07 \times 10^{-26}$$

$$14.0067$$
$$\times 12.011$$
$$14.00.67$$
$$140.067$$
$$14.0067$$
$$280.134$$
$$14.0067$$
$$168.9621137$$

$$E = \frac{h^2}{8\pi^2 I} J(J+1)$$

$$\frac{E}{hc} = \frac{h^2}{8\pi^2 I} J(J+1) \, cm^{-1}$$
$$\quad \frac{}{hc}$$

$$\bar{v} = \mathcal{E}_J = \frac{h}{8\pi^2 Ic} J(J+1) \, cm^{-1}$$

$$E = h\nu = \frac{h \cdot c}{\lambda}$$

$$\frac{E}{hc} = \frac{hc}{hc} = \frac{1}{\lambda} = \bar{v}$$
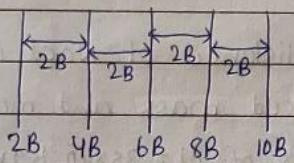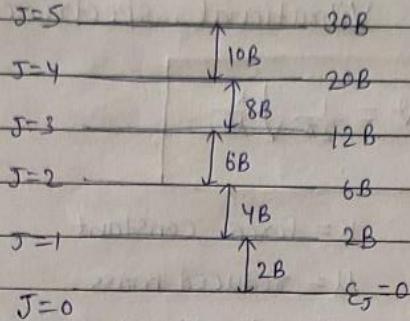
wave no. $\quad \mathcal{E}_J = BJ(J+1)\, cm^{-1}, \quad B = \frac{h}{8\pi^2 Ic} = \text{Rotational constant}$
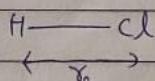
$$E_J = B J(J+1)$$

J=5 ————————————— 30B

        10B ↓

J=4 ————————————— 20B

        8B ↓

J=3 ————————————— 12B

        6B ↓

J=2 ————————————— 6B

        4B ↓

J=1 ————————————— 2B

        2B ↓

J=0 ————————————— $E_J = 0$

2B   2B   2B 2B

2B 4B 6B 8B 10B

Que microwave spectrum of gaseous HCl molecule exhibits a series of equally spaced lines with interspacing of 20.7 cm⁻¹ calculate the intermoleare distance of HCl molecule.

$$2B = 20.7 \, cm^{-1}$$

$$B = 10.35 \, cm^{-1}$$

$$r_0 = ?$$

H———Cl

$\xleftarrow{\hspace{1cm}}$ r_0 $\xrightarrow{}$

$$cm^{-1} \leftarrow B = \frac{h}{8\pi^2 I c} \quad \boxed{cm^{-1} s^{-1}}$$

$$\downarrow \downarrow \downarrow$$
$$Find$$

$$10.35 = \frac{1}{8\pi^2 I \times 3 \times 10^8} \quad \Rightarrow I = \frac{1}{24 \times 10.35 \times 10^6}$$

$$I = \mu \cdot r_0^2$$
$$\downarrow \quad \downarrow \downarrow$$
$$Find$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \, g = \frac{1 \times 35.5}{1 + 35.5} = \frac{35.5}{36.5} \times \frac{1}{N_A} \, gm$$

$$\frac{1}{24 \times 10.35 \times 10^6} = \frac{35.5}{36.5 \, N_A} \, r_0^2$$

$$r_0^2 = \frac{36.5 \, N_A}{35.5 \times 24 \times 10.35 \times 10^6}$$

Vibrational spectroscopy

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

K = force constant

μ = reduced mass

ν = vibrational frequency.

(4)(a) Que The intermolecular distance of NaCl is 2.36×10^{-10} m. calculate the reduced mass and moment of inertia of NaCl (atomic mass of $Cl = 35 \times 10^{-3}$ kg mol^{-1} and $Na = 23 \times 10^{-3}$ kg mol^{-1})

$r_0 = 2.36 \times 10^{-10}$ m

$\mu = ?$

$I = ?$

$$\text{Reduced mass}(\mu) = \frac{m_1 m_2}{m_1 + m_2} \times \frac{1}{N_A}$$

$$= \frac{35 \times 10^{-3} \times 23 \times 10^{-3}}{58 \times 10^{-3}} \times \frac{1}{6.022 \times 10^{23}}$$

$$= \frac{805}{58 \times 6.022} \times 10^{-26}$$

$$= \frac{805}{349.276} \times 10^{-26}$$

$$= 2.3 \times 10^{-26} \text{ kg}$$

$I = \mu r_0^2$

$I = 2.3 \times 10^{-26} \times (2.36)^2 \times 10^{-10} \times 10^{-10}$
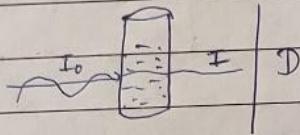
$I = 12.81 \times 10^{-46}$

$I = 1.28 \times 10^{-45}$

U.V - visible spectroscopy

$$200 - 400 - 800 \, nm$$

U.V   visible

Beer & Lamberf's Cave

Absorbance α C

$A \alpha l$

$A \alpha Cl$

$$\boxed{A = \varepsilon Cl}$$
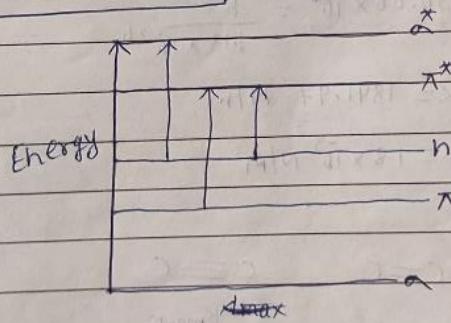
$$\boxed{A = \log \frac{I_0}{I}}$$ ε — molar absorptivity

                      molar extinition coefficient.

$$\boxed{A = \log \frac{1}{T}}$$

$$\boxed{n-\overset{*}{\pi} < \pi - \overset{*}{\pi} < n - \overset{*}{\sigma} < \sigma - \sigma^*}$$

Energy

λ_{max}

→ wave length increase (↑) : Bathochromic shift (Red)

~~Hypsochromic shift (↓~~

→ wave length (↓) : Hypsochromic shift (Blue)

$$A \alpha \, conjugation \, \alpha \frac{1}{E}$$

Frequency $\boxed{V = \frac{1}{2\pi}\sqrt{\frac{K}{u}}}$ $K =$ Force constant
$u =$ Reduced mass

$\mu = \dfrac{m_1 m_2}{m_1 + m_2}$

$m_1 =$ mass of 1st atom.
$m_2 =$ mass of 2nd atom.

$K = \frac{1}{2} I \omega^2 = \frac{1}{2} \omega^2 \frac{I^2}{I} = \frac{1}{2}\frac{(I\omega)^2}{I}$

$K = \frac{1}{2}\frac{L^2}{I}$ $\{L = I\omega\}$

$L = \sqrt{J(J+1)}\ \dfrac{h}{2\pi}$ $J =$ Rotational Quantom no.
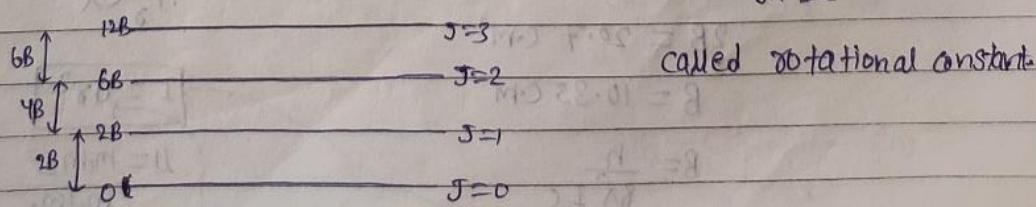
$K = \dfrac{h^2}{8\pi^2 I} J(J+1)$ Joule. $\boxed{I = \mu r^2}$ $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$

$E = \dfrac{h^2}{8\pi^2 I} J(J+1)$

$\bar{V} = \dfrac{E}{hc} = \dfrac{h}{8\pi^2 I c} J(J+1)$ m^{-1} or cm^{-1}

$\mathcal{E}_J = \dfrac{h}{8\pi^2 I c} J(J+1)$ cm^{-1}

$\mathcal{E}_J = BJ(J+1)\ cm^{-1}$ where $B = \dfrac{h}{8\pi^2 I c}$ and is

called rotational constant.

```
 12B ─────────────────        J=3
6B↓                            J=2
 4B↑ 6B ─────────────
 2B↓ 2B ─────────────         J=1
2B↓ 0 ────────────────        J=0
```

Que $^4_{35}HCl$ has a force constant value $480\ Nm^{-1}$. calculate the fundamental frequency its. wave number.

$$H - Cl$$

$$V = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{1 \times 35}{(1+35)} = \frac{35}{36} \times \frac{1}{6.022 \times 10^{23}} \times \frac{1}{10^3}\ kg$$

$$= 0.16 \times 10^{-26}\ kg$$

$$V = \frac{1}{2\pi}\sqrt{\frac{480 \times 10^{90}}{0.16 \times 10^{-27}}}$$

$$V = \frac{C}{\lambda}$$

$$V = \frac{1}{2\pi}\sqrt{3 \times 10^{29}}$$
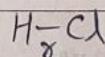
$$\bar{V} = \frac{1}{\lambda} = \frac{V}{C}$$

$$V = 8.7 \times 10^{13}$$

$$\bar{V} = \frac{8.7 \times 10^{13}}{3 \times 10^8}$$

$$\bar{V} = 2.9 \times 10^5$$

Que microwave spectrum of gaseous HCl molecule exihibits of gaseous HCl molecule exhibits a series of equally spaced lines . speparate by a distance $20.7\ cm^{-1}$. calculate the intermolecular distance.

$$H - Cl$$

$$2B = 20.7\ cm^{-1}$$

$$B = 10.35\ cm^{-1}$$

$$\boxed{I = \mu r^2}$$

$$B = \frac{h}{8\pi^2 IC}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{35.5}{36.5} \times \frac{1}{6.022} \times 10^{23} \times 10^{-3}$$

$$10.35 = \frac{h}{8\pi^2 IC} \to 3 \times 10^{10}\ cm/s$$

$$\mu = 1.66 \times 10^{-27}\ kg$$