

# INORGANIC CHEMISTRY

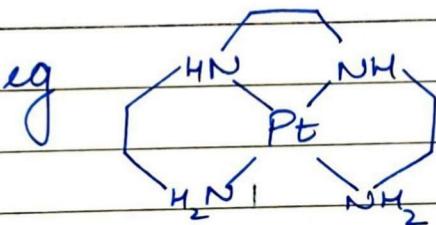
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## Chapter - 1 Coordination Compounds

### DEFINITIONS

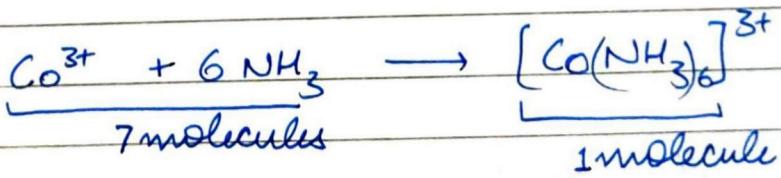
- a) **Coordination number** - The number of  $\sigma$ -bonds between ligands and the central atom.
- b) **Chelation** - Coordination of more than one non-contiguous  $\sigma$ -electron pair donor atom from a given ligand to the same central atom.
- A chelating agent ~~is~~ with 2 donor atoms forms bidentate chelation, ... and so on.
- eg  tetradeятate chelation.

NOTE

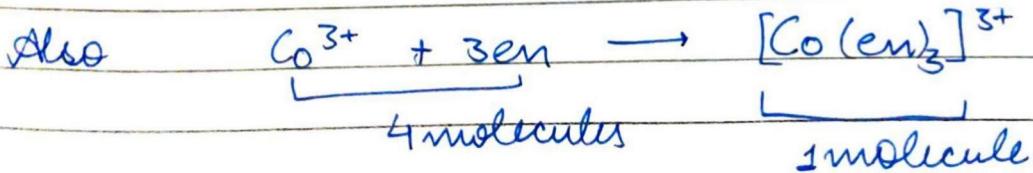
We know

$$\Delta G = \Delta H - T\Delta S$$

Consider rxn



∴ we can clearly see that  $\Delta S$  would be -ve  
∴  $\Delta H$  for this rxn must be highly negative for this reaction to occur



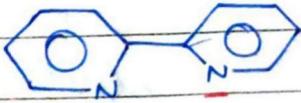
In the above rxn,  $\Delta S$  would be less negative than that in first reaction. It is more favourable.

c) Bridging: Chelation is when central atom is shared, bridging is when a ligand is shared by 2 metal ions. It is not a favourable process.



### SOME COMMON LIGANDS

NAME	NO. OF DONOR ATOMS	ABBREVIATION & STRUCTURE
1. Acetylacetone	2	(acac) <sup>-</sup>
2. Ammine	1	NH <sub>3</sub>
3. Aqua	1	H <sub>2</sub> O
4. 2,2' Bipyridine	2	bpy



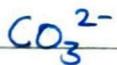
5. Bromido

1



6. Carbonato

1 or 2



(1 or 2 oxygen donor atoms)

7. Carbonyl

1

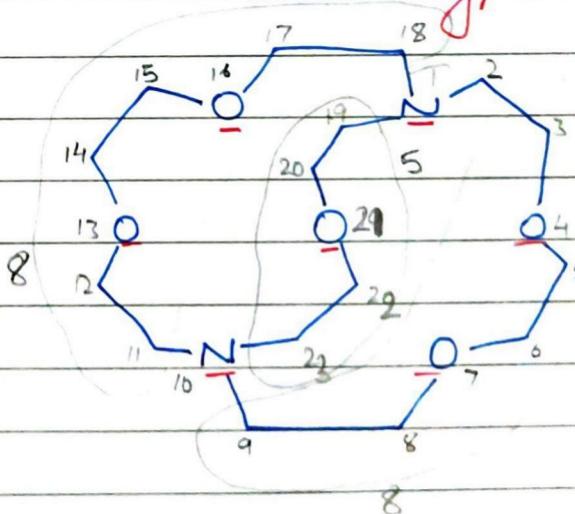


8.

9. 4,7,13,16,21-Pentaaza-1,  
10-diaya-bicyclo[8.8.5]  
tricosane

7

2.2.1 crypt



10. Cyanido

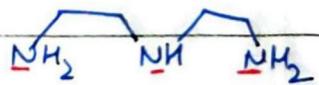
1



11. Diethylenetriamine

3

diene



12. Bis(diphenylphosphino)ethane

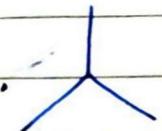
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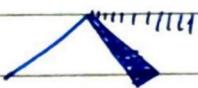
\*—Refer to slides—\*

## → Coordination number & geometry

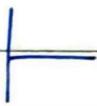
### 1. THREE COORDINATION



trigonal plane  
TP-3



trigonal pyramidal  
TPY-3



T-shape  
TS-3

### 2. FOUR COORDINATION

tetrahedron



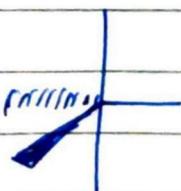
T-4

square plane

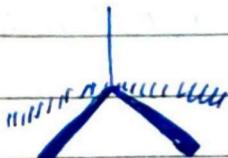


square pyramidal

### 3. 5 COORDINATION



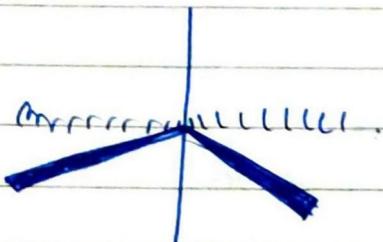
TBPY-5



SPY - 5

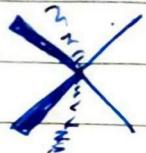
## 4. 6 COORDINATION

octahedron



OC - 6

trigonal prism



TPR - 6

## 5. 7 COORDINATION

pentagonal bipyramidal ; octahedron (face monocapped)

&amp; trigonal prism (square face monocapped)

NOTE: Refer to book/slides for structures & also for 8-coordination & 9-coordination.

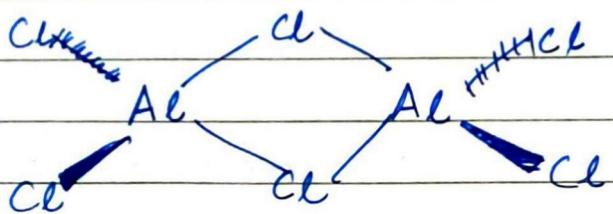
NOTE: 8-coordination geometries

1. Cube
2. Square antiprism
3. Dodecahedron
4. Pentagonal bipyramidal
5. octahedron, trans-bicapped
6. triangular face bicapped prism
7. square face bicapped prism

## → BRIDGING LIGANDS

- Form polynuclear species
- μ is a prefix to ligand formula or name

19-



$\text{di}-\mu\text{-chlorido - tetrachlorido - } 1 \text{ K}^2$

## → Metal - metal bonds



$\text{bis}(\text{tetrabromidorhenium})(\text{Re-Re})^{(2+)}$

Metal - metal bonds need to be shown  
in brackets (Re - Re)

## → Nomenclature of coordination compounds

- i) Ligand names first
- ii) no spaces for same coodrd " entity.
- iii)

## → NOMENCLATURE

- Refer to slides
- ( $\eta$ ) eta convention (hapticity): applied in cases where contiguous atoms are involved in electron donation to central atom.

## → ISOMERISM

Two types of isomerism are observed in coord<sup>n</sup> compounds

a) Structural : 5 types →

- i) Ionization
- ii) Hydratation
- iii) Coordination
- iv) Linkage
- v) Polymerization

b) Stereo : 2 types

- i) Geometrical
- ii) Optical

## → STRUCTURAL ISOMERISM

1. IONIZATION : They result from interchange of anionic ligand within the first coord<sup>n</sup> sphere with an anion outside the sphere. e.g. violet  $[\text{Co}(\text{NH}_3)_5\text{Br}_2]\text{SO}_4$  & red  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}_2$

The isomers are easily distinguished by IR spectroscopy. e.g. here free and coordinated sulfate ions give rise to one or three IR active SO stretching vibrations respectively.

NOTE : IR spectroscopy shows peak when vibrational energy of atoms matches the energy of radiations. IR spectroscopy will work only with IR active compounds bonds. The peaks observed will be different for different ligands

## 2. HYDRATION →

- Result from interchange of  $H_2O$  and another ligand b/w first coord<sup>n</sup> sphere and the ligands outside it.
- eg-  $CuCl_3 \cdot 6H_2O$ , actually  $[Cu(H_2O)_4Cl_2]Cl \cdot 2H_2O$  (yellow)  
 when this is dissolved in water, the chloride ions in complex are replaced by  $H_2O$  to give blue green  $[Cu(H_2O)_5Cl]Cl$  and finally violet  $[Cu(H_2O)_6]Cl_2$

NOTE: The colour of the solution slowly changes from slight yellow → violet.

## 3. COORDINATION →

- They are possible only for salts with both anions and cations as complexes. The isomers arise from change of ligands b/w two metal centres.
- eg- a)  $[Co(NH_3)_6][Cr(CN)_6]$  and  $[Cr(NH_3)_6][Co(CN)_6]$   
 b)  $[Co(NH_3)_6][Co(NO_2)_6]$  and  $[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_5]$

NOTE: Always write the cation first.

## 4. LINKAGE

- . Arises in ambidentate ligands when the atom of attachment with metal changesie when ligands can coordinate in more than one way.

- eg- linkage isomers of  $[\text{Co}(\text{NH}_3)_5 \text{NO}_2]^{2+}$  are

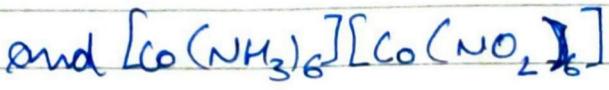
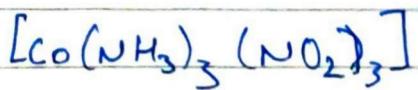
- Due to different atom linkages, IR spectroscopy can almost easily distinguish them in every case.

O-bonded characteristic absorption bands are b/w 1065 & 1470 cm<sup>-1</sup>

N-bonded characteristic absorption bands are b/w 1310 & 1340 cm<sup>-1</sup>

## 5. POLYMERIZATION

- Complexes with same empirical formula but different molecular masses.
  - e.g.  $[\text{PtCl}_2(\text{NH}_3)_2]$  and  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$



## → STEREOISOMERISM

### 1 GEOMETRICAL

- If 2 species have the same molecular formulae and same structural framework, but differ in spatial arrangement of different atoms or groups about a central atom or a double bond, then they are geometrical isomers.
- Seen in. square planar, octahedral and trigonal bipyramidal.
- Square planar - ~~one~~  $\equiv$  ~~two~~
- Octahedral - If atoms are present on a single face, then it is called facie arrangement in fac-isomer else meridional arrangement is mer-isomer
- Trigonal bipyramidal - In these species, geometrical isomerism arises

## 2. OPTICAL ISOMERISM

- It is concerned with chirality and some important terms relating to chiral complexes.
- ~~Enantiomers~~ Enantiomers are a pair of stereoisomers that are non-superimposable mirror images.
- Notations:

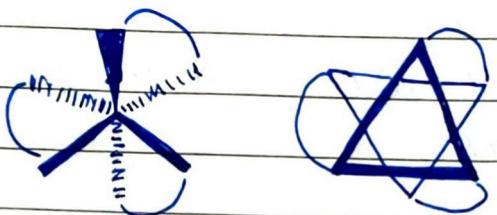
Several notations are used to denote optical isomerism.

- d & l notation - Dextrorotatory isomer ~~rotat~~ or d-isomer rotates light to right and Laevorotatory isomer or l-isomer rotates light to left.
- R and S notation - (Cahn - Ingold - Prelog notation). It is used for chiral organic ligands & tetrahedral complexes.

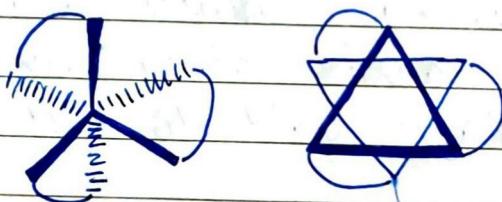
R (rectus) refers to clockwise and S (sinister) refers to anti-clockwise sequence of rotation of prioritised atoms from high to low.

### iii) $\Delta$ and $\Lambda$ prefixes

- Enantiomers of octahedral complexes containing 3 equivalent chelate ligands (tris-chelate complexes)
- Octahedron is viewed down a 3-fold axis and the chelates then define either a right or left handed helix



$\Delta$  notation



$\Lambda$  notation

### \* → SPATIAL ORIENTATION OF $\text{D}_{\pi}$ d-orbitals →

- In presence of ligands, d-orbitals split into groups of different energies, the type of splitting and magnitude of energy difference depending on the arrangement and nature of the ligands.

NOTE:  $[\text{Ni}(\text{CN})_5]^{3-}$  is  $\text{sp}^3\text{d}$ , square based pyramid.

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- The 'mixing' or 'blending' of atomic orbital to accommodate the spatial requirements in a molecule is known as hybridisation.

It occurs to minimize electron pair repulsions when atoms are brought together to form molecules.

2<sup>nd</sup> row elements:  $\text{sp}$   $\text{sp}^2$   $\text{sp}^3$

3<sup>rd</sup> row elements also have:  ~~$\text{sp}$~~   $\text{sp}^3\text{d}$

- Several theories explain electron interaction in coordination compounds.

### → VALENCE BOND THEORY

- It considers hybridisation of central metal acceptor.

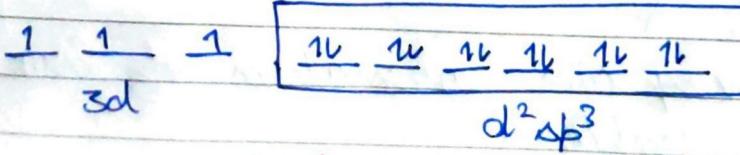
- Look at hybridisation chart in slides

- Consider

chromium (III): Octahedral



$\text{d}^2\text{sp}^3$  hybridisation formed.



High spin

- consider

$\text{Fe}^{3+}$  ion: Octahedral

1 1 1 1 1 — — — — —

Two orientations are possible

a) ↑ ↓ ↑

↑↑ ↑↑ ↑↑ ↑↑ ↑↑

$d^2 s^3$

Low spin  
Paramagnetic

b) ↑↑ ↑↑ ↑↑ ↑↑ ↑↑

↑↑ ↑↑ ↑↑ ↑↑ ↑↑

$s^3 p^3 d^2$

High spin  
Paramagnetic  
unrealistic

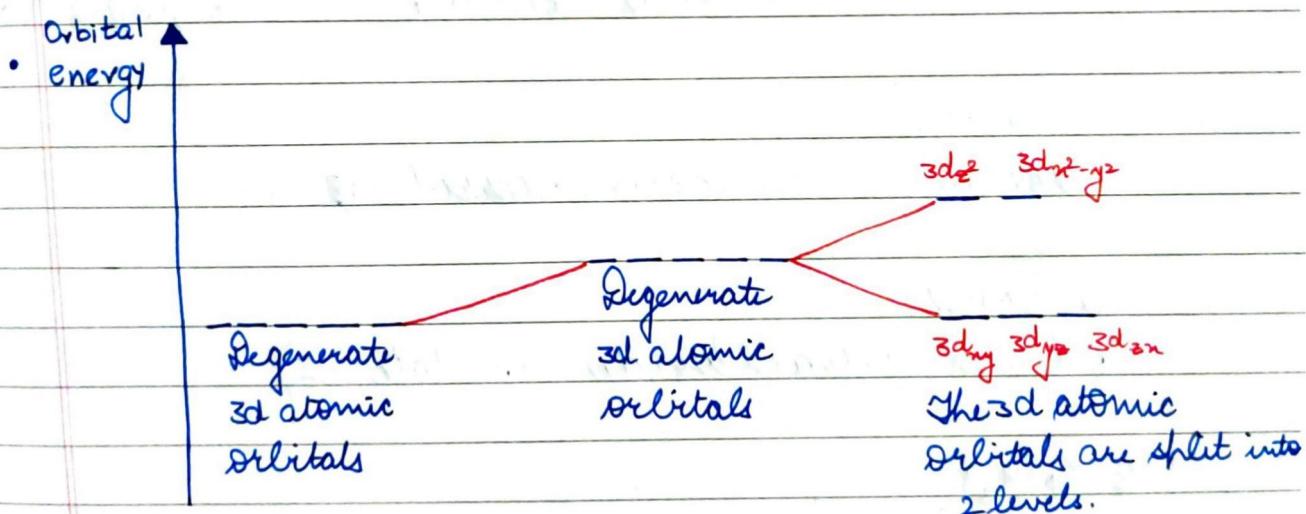
NOTE: Look at 2 more eg in slides

- LIMITATIONS

- i) It says nothing about electronic spectroscopic properties
- ii) Chemical reactivity can't be predicted.  
eg - kinetic inertness is a property of low spin  $d_6$  configurations.
- iii) Furthermore, it implies distinction b/w high & low spin complexes which is misleading
- iv) It can't explain formation of low and high spin complexes

## → CRYSTAL FIELD THEORY →

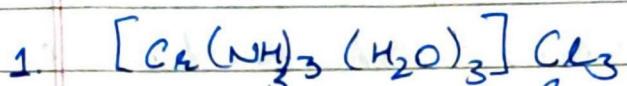
- This is an electrostatic model and simply uses the ligand electrons to create an electric field around the metal centre.
- Ligands are considered as point charges & no covalent interaction is considered.
- Predicts that the d-orbitals are not degenerate.



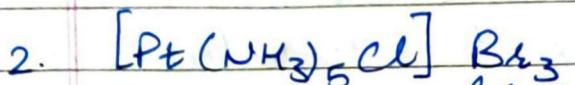
- We assume that when the ligands approach from in octahedral pattern, then they approach along x, y, z axis. d orbitals are symmetrical about  $d_{z^2}$  and we assume any octahedral approach of ligands across the metal along x, y, z direction.

## TUTORIAL

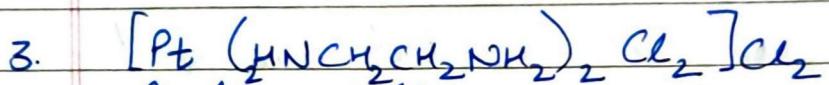
Q Write the IUPAC names of



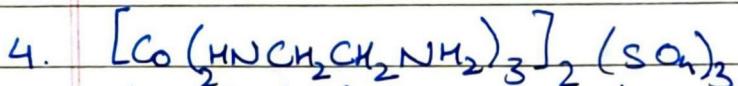
Triamminetriaquacobaltium (III) chloride



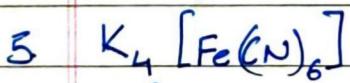
Pentaamminechloroplatinum (IV) bromide



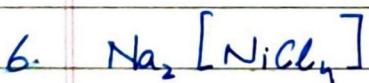
Dichlorodis-(ethylenediamine)-platinum (IV) chloride



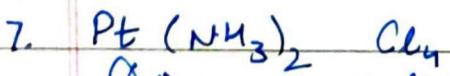
Tris-(ethylenediamine)-cobalt (III) sulphate



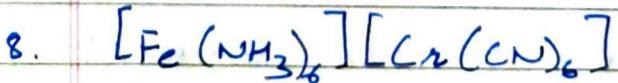
Potassium hexacyanoferrate (II) (II)



Sodium tetrachloronickelate (II)



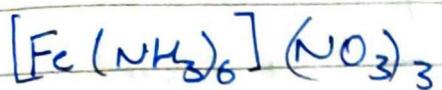
Diamminediplatinum Diaminetetrachloroplatinum (IV)



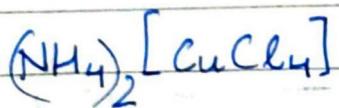
Hexaamminiron (II) hexacyanochromate (III)

Q:- Write the formula:-

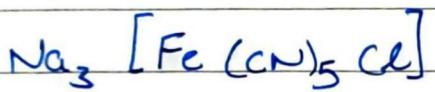
1. hexaammineiron (III) nitrate



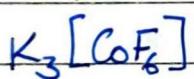
2. Ammoniumtetrachlorocuprate (II)



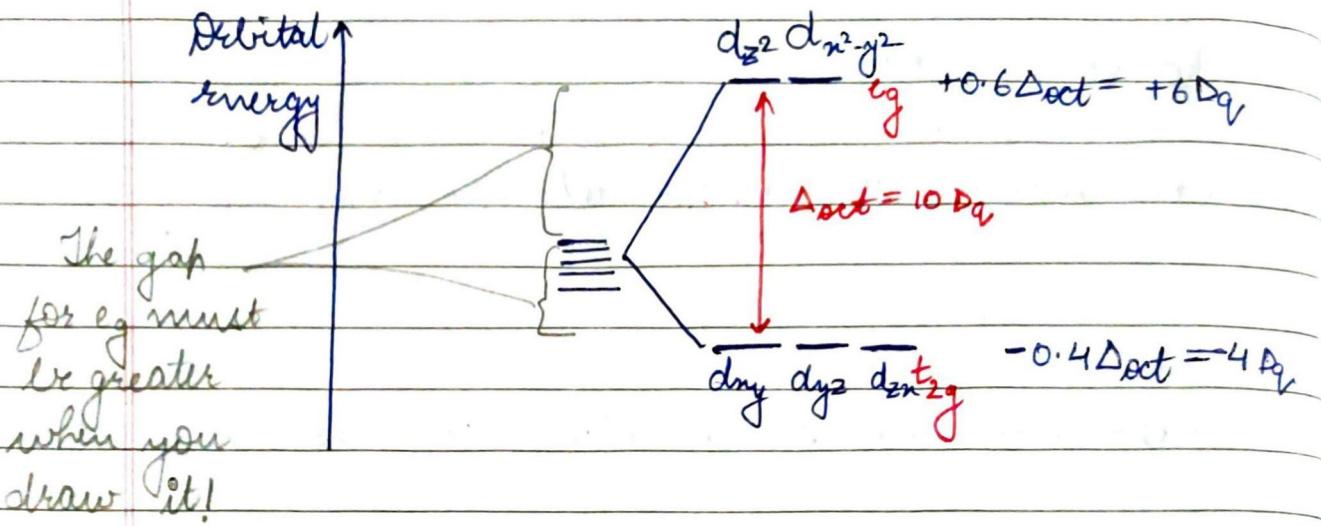
3. Sodium monochloropentacyanoferrate (III)



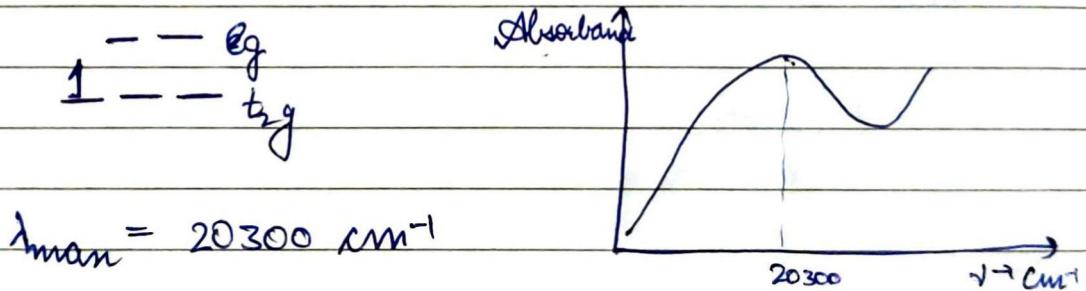
4. Potassium hexafluoridocobaltate (II)



- Splitting of d-orbitals in octahedral crystal field.



- Electronic spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

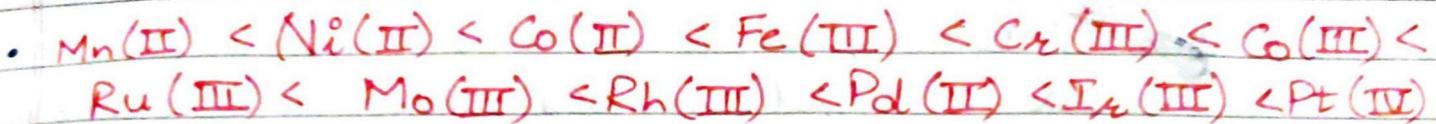
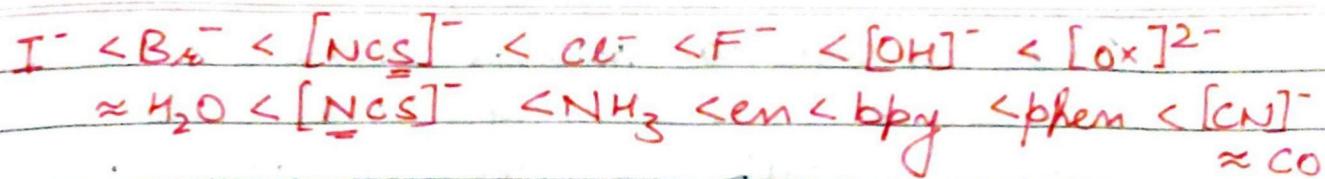


### → SPECTROCHEMICAL SERIES

- $\Delta_{\text{oct}} (\text{weak field}) < \Delta_{\text{oct}} (\text{strong field})$

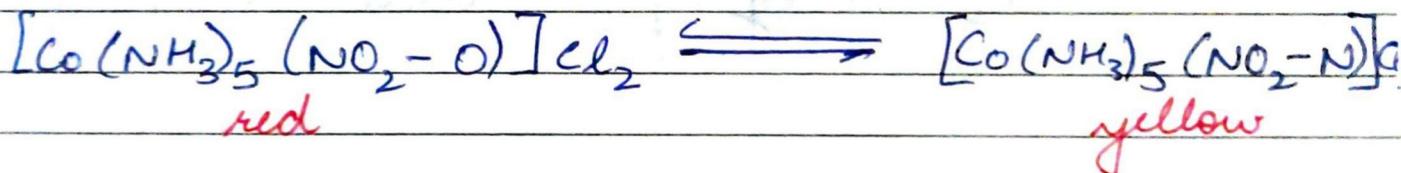
- The series is written as

weak field  $\xrightarrow{\text{increasing } \Delta_{\text{oct}}}$  strong field ligands



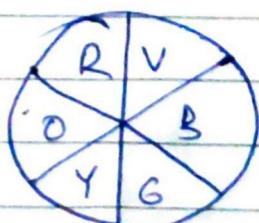
Increasing field strength.

Now remember the eq<sup>n</sup>



Red has larger  $\lambda$   $\therefore$  lower energy  $\therefore$  O atom is relatively weaker ligand.

We can also say that compound 1 absorbs green light and second one absorbs violet. Since violet has greater energy,  $\therefore$  N donor is relatively stronger as it increases  $\Delta_{oct}$  such that violet light is needed to excite an electron.



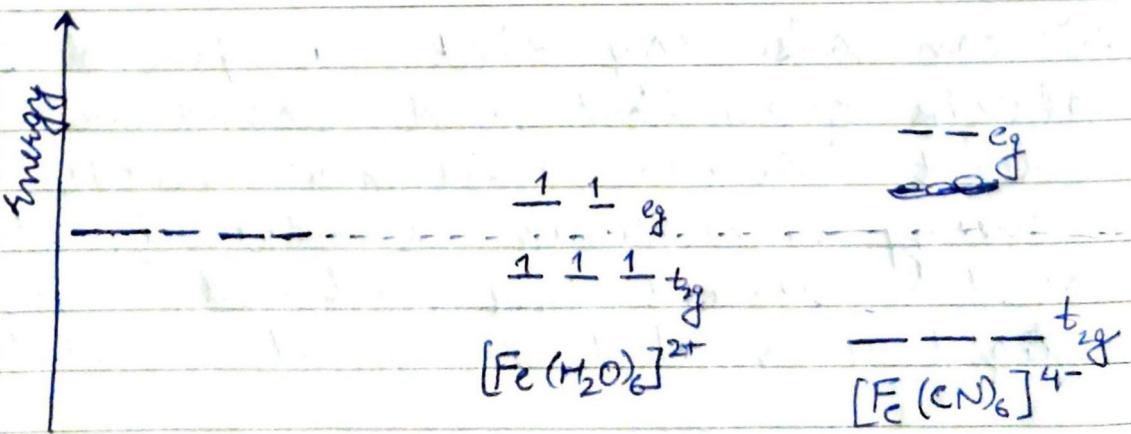
- High splitting occurs when electrostatic interaction is strong and weak in case of weak electrostatic interaction.
- Some amount of energy is ~~needed for~~ pairing of electrons in any orbital - Let us say that this energy is ' $P$ '

If  $P < \Delta_{\text{oct}}$ , electrons pair up and low spin complexes are formed.

If  $P > \Delta_{\text{oct}}$ , then the electrons take up  $\Delta_{\text{oct}}$  energy and occupy  $d_{z^2}$  or  $d_{x^2-y^2}$  i.e.  $t_{\text{eg}}$  orbitals : high spin comp.

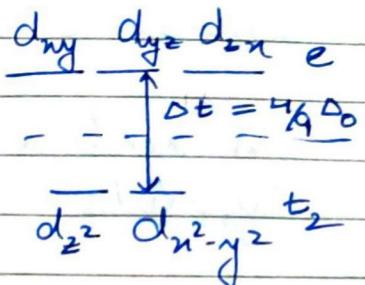
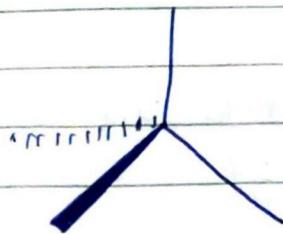
$\therefore P < \Delta_{\text{oct}}$  : low spin

$P > \Delta_{\text{oct}}$  : high spin



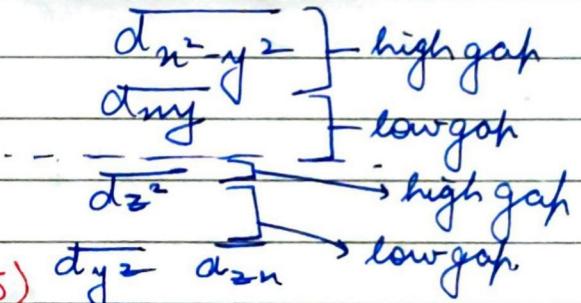
## CRYSTAL FIELD FOR OTHER TETRAKIEDRAL ARRANGEMENTS

TETRAHEDRAL (C.N. = 4)

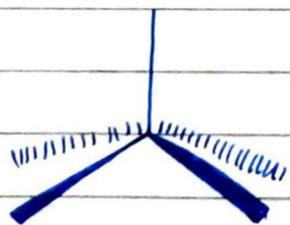


SQUARE PLANAR (C.N. = 4)

Square planar is basically 2 ligands removed from octahedral

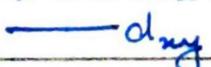
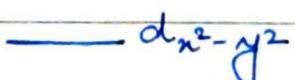


SQUARE PYRAMID (C.N. = 5)



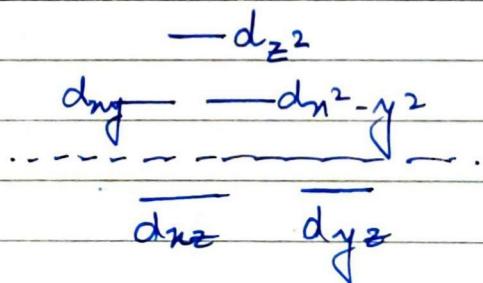
It is basically 1 ligand removed from octahedral

$\therefore$  we have

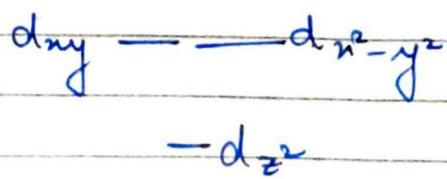


- PENTAGONAL BIPYRAMID ( $CN=7$ )

- we construct this from octahedral complex only
- In such a case  $d_{z^2}$  directly faces ligands  $\therefore$  highest energy.
- & neither  $d_{x^2-y^2}$  nor  $d_{xy}$  face ligands directly. However they are very close  
 $\therefore$  second place with equal energies.
- $d_{xy}$  &  $d_{zn}$  are the furthest from ligands  
 $\therefore$  lower energy.



- SQUARE ANTIPRISM ( $CN=8$ )



→ CFT uses and limitation

### \* → MOLECULAR ORBITAL THEORY (MOT) →

- considers covalent interactions b/w the metal centres & ligands as well.
- In MOT we begin with placing the nuclei of given molecule in their equilibrium positions and then calculate MO (ie regions of space spread over the entire molecule) that a single electrons might occupy.
- Each MO arises from interactions between orbitals of atomic centres in the molecule. Such interactions are:
  - a) allowed : if symmetries are compatible for atomic orbitals.
  - b) efficient : if region of overlap b/w the two atomic orbitals is significant
  - c) efficient : if the atomic orbitals are relatively close in energy.

info:

No. of molecular orbitals = number of participating atomic orbitals

- Interaction of 2 orbitals will form a bonding MO and an anti-bonding MO.

NOTE: When two orbitals combine, their in phase wave equations (quantum mechanical) combine to form a ~~one amplified~~ wave equation of ~~greater mag~~ a region where amplitude of electron wave is high. This region is called bonding MO. Similarly when orbitals out of phase combine, due to destructive interference, antibonding MO is formed.

- In MOT, electrons are not treated as properties of a bond b/w atoms, but are treated as moving under influence of nuclei.
- The  $\sigma$  label mean rotation of the orbital about the internuclear axis generates no phase change and
- The  $\pi^*$  label means that there is a nodal plane b/w the nuclei, and this plane is orthogonal to the internuclear axis

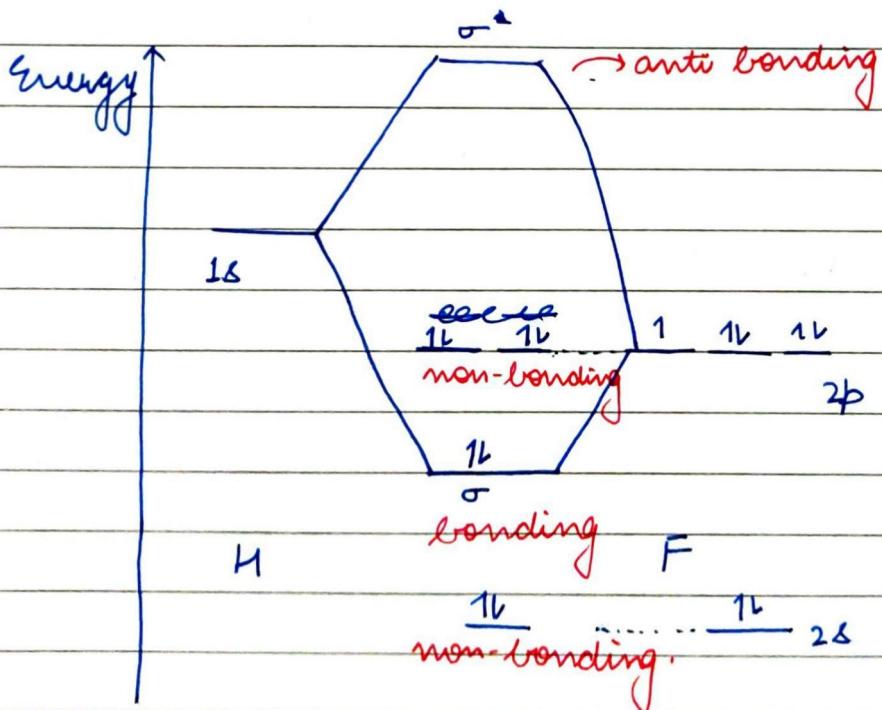
- the  $\pi$  label means that rotation of orbital about the internuclear axis generates a phase change

→ HOMONUCLEAR MO →

(slides)

→ HETERONUCLEAR MO

i) HF



PTO

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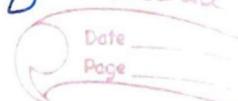
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NOTE: When showing splitting, show it from the very beginning

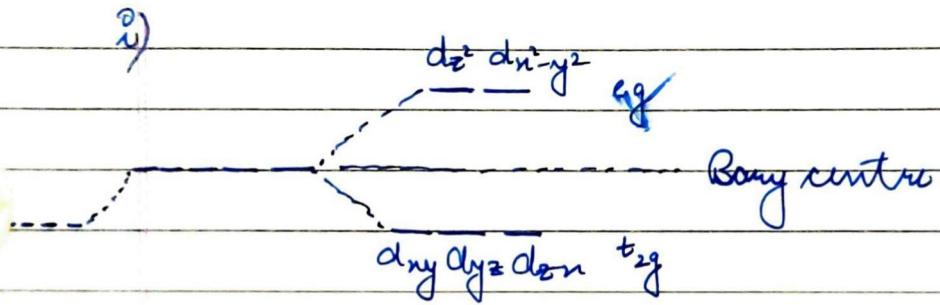


## TUTORIAL

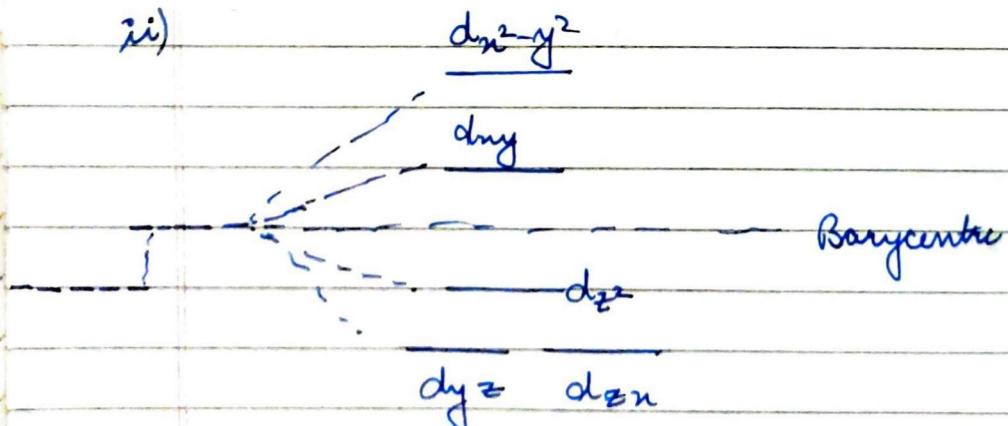
1. Draw the d-orbital splitting pattern in the presence of following diff geometries acc/ to CFT.
  - i) Octahedral ii) Square Planar iii) tetrahedral
  - iv) trigonal bipyramidal

Ans:

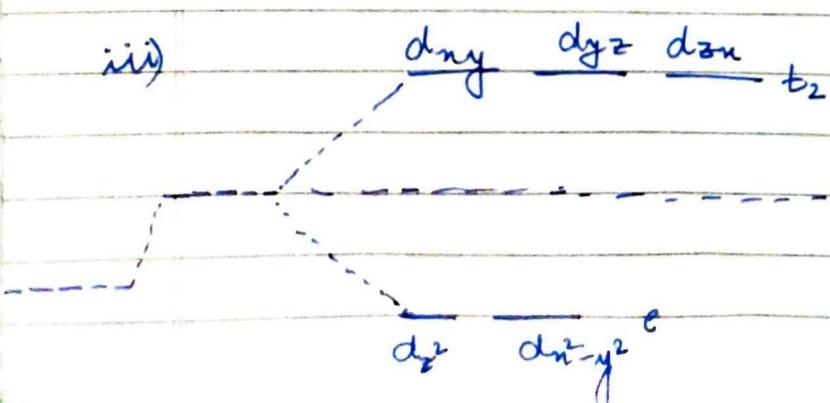
i)



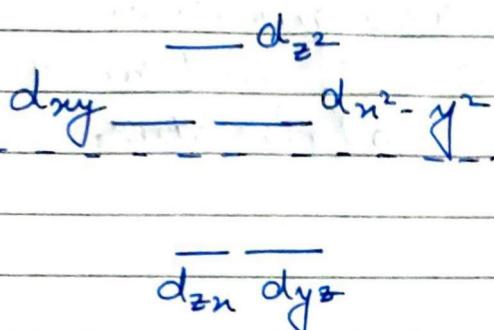
ii)



iii)

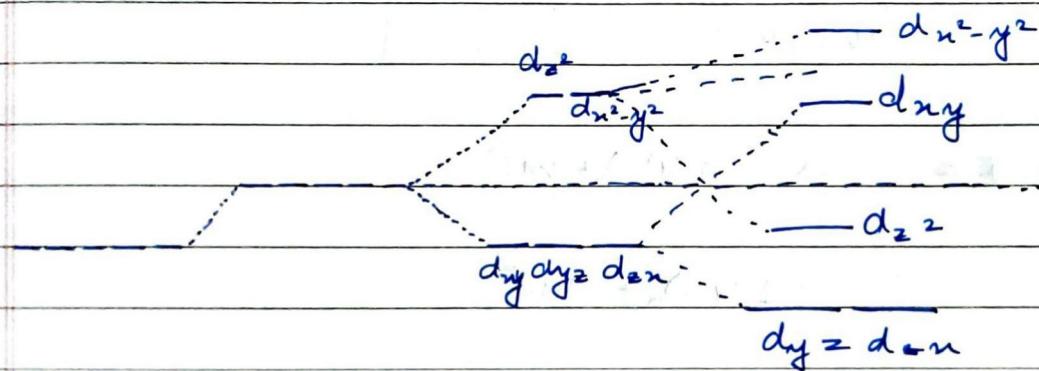


iv)

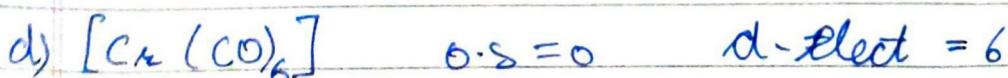
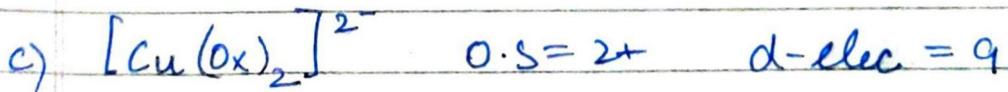


NOTE: Also show splitting through octahedral field

e.g. square planar



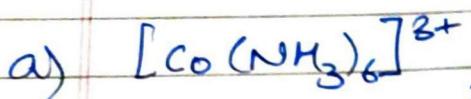
Q) Calculate the oxidation state of metal & no. of d-electrons in following complexes



NOTE: Octahedral LFSE =  $t_{2g} \text{ elec.} \times 0.4 + e_g \text{ elec.} \times 0.6$  Δ₀ + mP

Tetrahedral LFSE =  $[t_{2g} \text{ elec.} \times (0.4) + e_g \text{ elec.} \times (-0.6)]$  Δ₀ + mP

Q → Determine the configuration in form of  $t_{2g}^m$  &  $e_g^m$ , no. of unpaired  $c^-$  and ligand field stabilization energy: -



$$\text{Co}^{3+} \rightarrow \begin{array}{|c|c|c|c|c|} \hline \text{v} & \text{1} & \text{1} & \text{1} & \text{1} \\ \hline \end{array}$$

$$3\text{s}^2 \cancel{\text{ & }} 3\text{d}^7$$

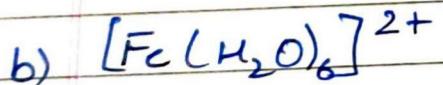
$$\text{d}^6$$

$\text{NH}_3 \rightarrow$  strong field.

$$\therefore \begin{array}{|c|c|c|} \hline \text{v} & \text{v} & \text{v} \\ \hline \end{array} \quad \begin{array}{|c|c|} \hline \text{v} & \text{v} \\ \hline \end{array}$$

$$\therefore \text{LFSE} = 6 \times (-0.4) \Delta_0 + mP$$

$$= -2.4 \Delta_0 + mP$$



$$\therefore \text{d}^6$$

$$\therefore \text{LFSE} = 4 \cancel{\text{ & }} \times (-0.4) + 2(0.6) + mP$$

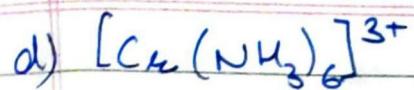
$$\text{LFSE} = -0.4 + mP$$



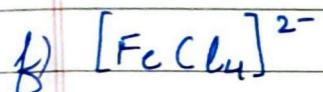
$$\therefore \text{d}^5$$

$$\text{LFSE} = 5 \times (-0.4) + 0 \times (0.6) + mP$$

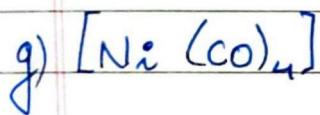
$$= -2 + mP$$



$$\text{LFSE} = (-0.4) \times 3 + 0 \times (0.6) + mP = -1.2 + mP$$



$\Delta^6$



## Chapter - 2

# Modern Techniques in Structural Elucidation of Compounds

### → SPECTROSCOPY →

- Spectroscopy is the study of the interaction b/w matter and electromagnetic radiation.
- UV or visible light have enough energy to cause electronic transitions.
- The order of MO energy is
 

$\sigma^+$	—
$\pi^*$	—
$n$	—
$\pi$	—
$\sigma$	—

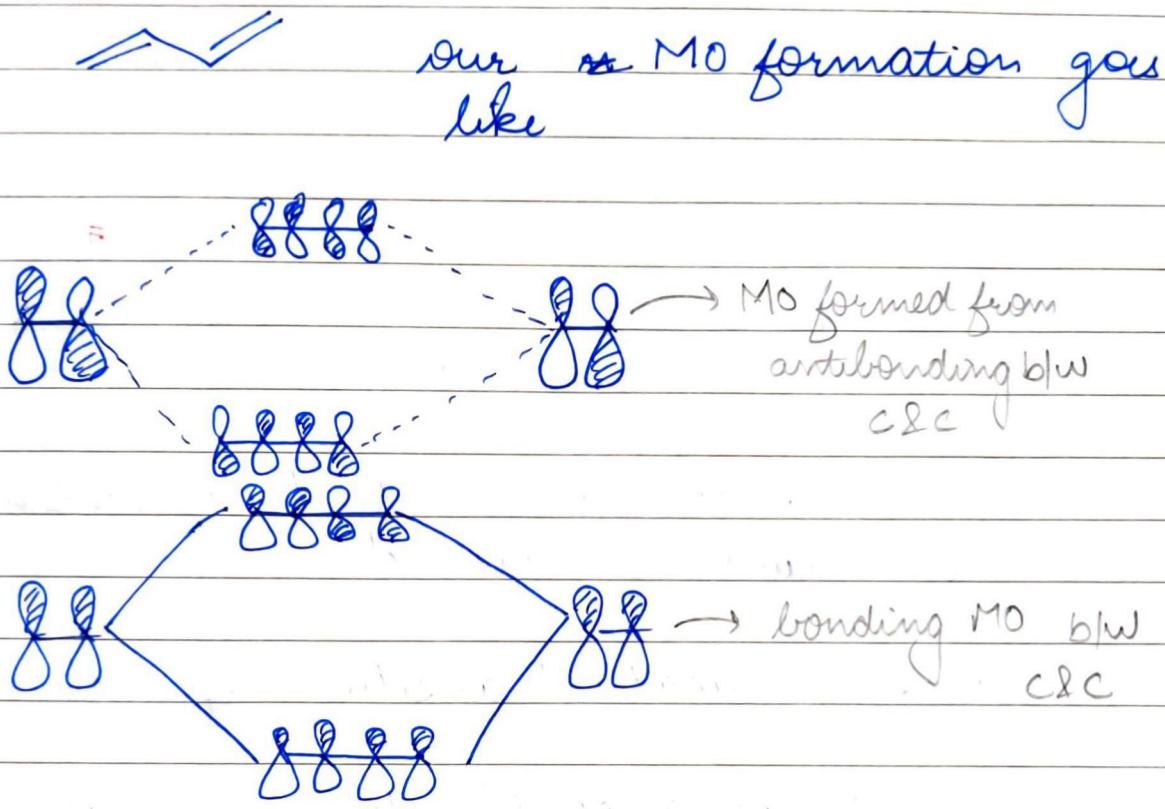
Electronic transitions b/w any of them are possible governed by Energy equation

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

### → UV - Visible Spectroscopy

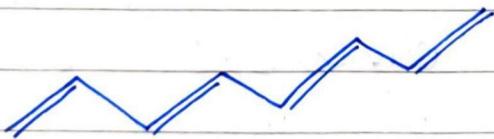
- Occurs in wavelength range 180 nm - 400 nm for UV & 400 nm to 800 nm for visible.
- It generally matches the energy of  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions.

- HOMO - LUMO and MO formations
- For

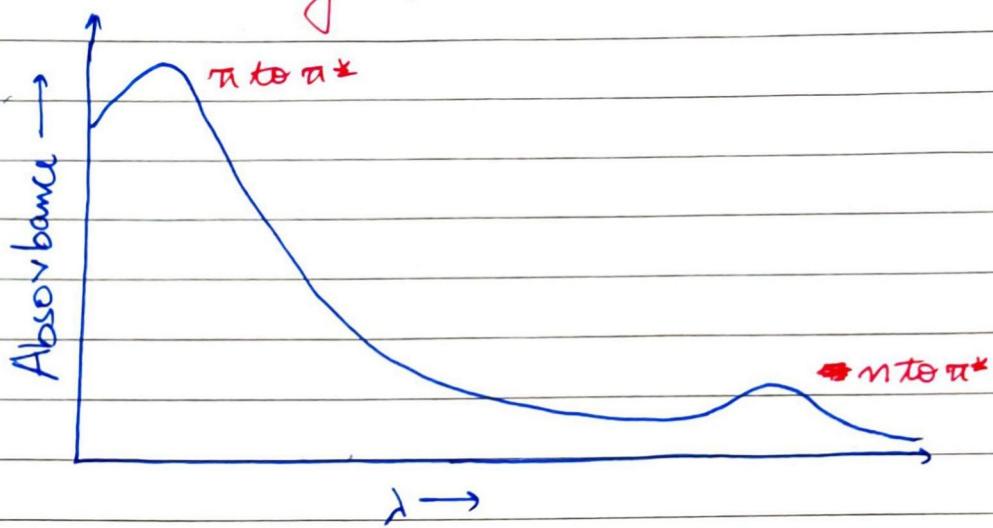


~~un  
right  
enam  
me  
ayoga~~

Draw MO structure for



- Absorbance graph



- Absorbance is the extent to which a  $\lambda$  light is absorbed.
- Peaks indicate transition of electrons
- The absorbance of  $n$  to  $n^*$  is greater than  $n$  to  $n^*$  i.e., more number of transitions occur since  $n$  to  $n^*$  is ~~symmett~~ symmetrically possible. But due to different symmetries,  $n$  to  $n^*$  is not possible.
- The absorbance graph should have been discontinuous, but it is continuous since even  $n$ ,  $n^*$  &  $n$  have further substates (vibrational states). And light is absorbed to transit b/w them.

NOTE: <sup>visible</sup> UV spectroscopy is only for molecules with  $\pi$  electrons.

### • BEER - LAMBERT LAW

- At a given  $\lambda$ , the absorbance of a sample depends on the amount of absorbing species that the light encounters as it passes through a sol<sup>m</sup> of the sample

$$A = \epsilon cl$$

$c$  = conc. of sample in mol/litre

$l$  = length of the light path through the sample in centimetres

$\epsilon$  = molar absorptivity

- molar absorptivity : absorbance for 1 M sol<sup>m</sup> in a cell with 1 cm path length. It is a const. characteristic of a compound at particular  $\lambda$ .

\* ~~examples~~

info

NOTE: As the conjugation increases, more and more number of MO's combine (as seen earlier) and the energy gap b/w the orbitals is reduced due to this. As such the  $\lambda$  for peak absorbance increases with conjugation. There are various eg. refer to slides for them.

## → IR SPECTROSCOPY

- Low energy light involved.
- each stretching and bending vibration of a bond in a molecule occurs with a charac. freq.
- when bombarded with radiation of similar frequency, radiation is absorbed
- An IR spectrum can be divided in two regions:
  - a) Functional group region. 4000 to  $1400\text{cm}^{-1}$  most of func. groups absorb the radiation.
  - b) Fingerprint region: All the rest of the IR spectroscopy band from  $600$  to  $1400\text{ cm}^{-1}$  is known as fingerprint region. It denotes the rest of the molecule bonds.

NOTE: a) no two <sup>different</sup> molecules will have same fingerprint region.

b) We plot transmission vs wavenumber graph.

## • POSITION OF ABSORPTION BANDS

- The amt of energy required to stretch a bond depends on strength of bond and masses of bonded atoms (reduced mass)

~~defn~~

$$\tilde{\nu} = \frac{1}{2\pi c} \left[ \frac{k(m_1 + m_2)}{m_1 m_2} \right]^{1/2}$$

$$\tilde{\nu} = 1/\lambda$$

$\tilde{\nu}$  depends on bond strength and interaction and  $c$  is speed of light.

- Thus the equation shows that stronger bonds and lighter atoms give rise to higher  $\nu$  (freq.) / wavenumbers.

~~don't  
seem eq-~~

Light atoms



$\sim 3000 \text{ cm}^{-1}$



$\sim 2200 \text{ cm}^{-1}$



$\sim 1100 \text{ cm}^{-1}$



$\sim 700 \text{ cm}^{-1}$

Strong bonds



$\sim 2200 \text{ cm}^{-1}$



$\sim 1600 \text{ cm}^{-1}$



$1100 \text{ cm}^{-1}$

OTE:

Resonance decreases bond order, thus decreasing bond strength. Due to this, the IR wavenumber is decreased as less energy is required for vibrations.

NOTE:

Q→

$\text{C}\equiv\text{C}-\text{H}$ ,  $\text{C}=\text{C}-\text{H}$ ,  $\text{C}-\text{C}-\text{H}$ . Write order of IR absorption wavenumbers.

Ans:

For  $\text{C}\equiv\text{C}-\text{H}$  we have sp carbon. Due to more s character, C-H bond length is smaller and bond is stronger. ∴ Due to this wavenumber for peak of  $\text{C}\equiv\text{C}-\text{H}$  is the greatest & similarly least for  $\text{C}-\text{C}-\text{H}$ .



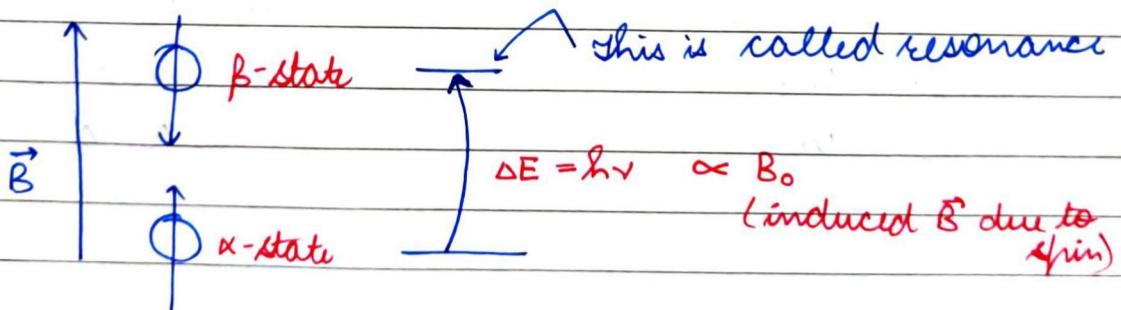
## NMR SPECTROSCOPY

- Nuclear Magnetic Resonance.
- The most advanced sort of spectroscopy.
- Electrons are charged, spinning particles with two allowed spin states:  $+1/2$  &  $-1/2$
- Certain nuclei also have allowed spin states of  $+1/2$  and  $-1/2$  and this property allows them to be studied by NMR. eg  $^1\text{H}$ ,  $^3\text{E}$ ,  $^{15}\text{N}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ .

- In general, if we bring a magnetic field to influence +ve and -ve ~~causen~~ charges, they are affected in a different way.
- In NMR spectroscopy, we target the spin states ( $+1/2$  and  $-1/2$ ) of electrons and nucleons and apply magnetic field to make them degenerate.

→ **TWO ENERGY STATES**

- Magnetic field of spinning nuclei will align with either external field or against the field.
- The photon with right amount of energy can be absorbed to flip the spinning of proton.



P.T.O

TUTORIAL

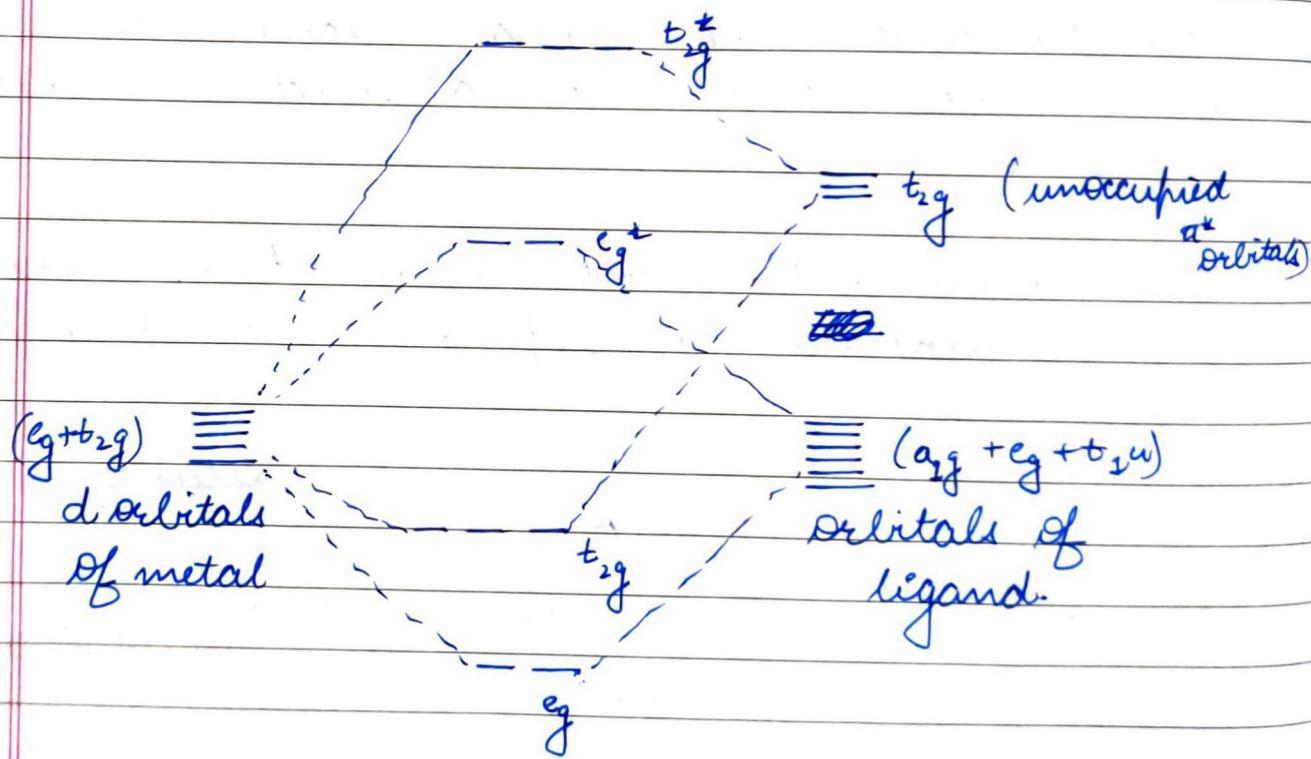
Q1: Draw MO of HF & O<sub>2</sub>

Ans: Do yourself.

~~Q2~~ Q2 →

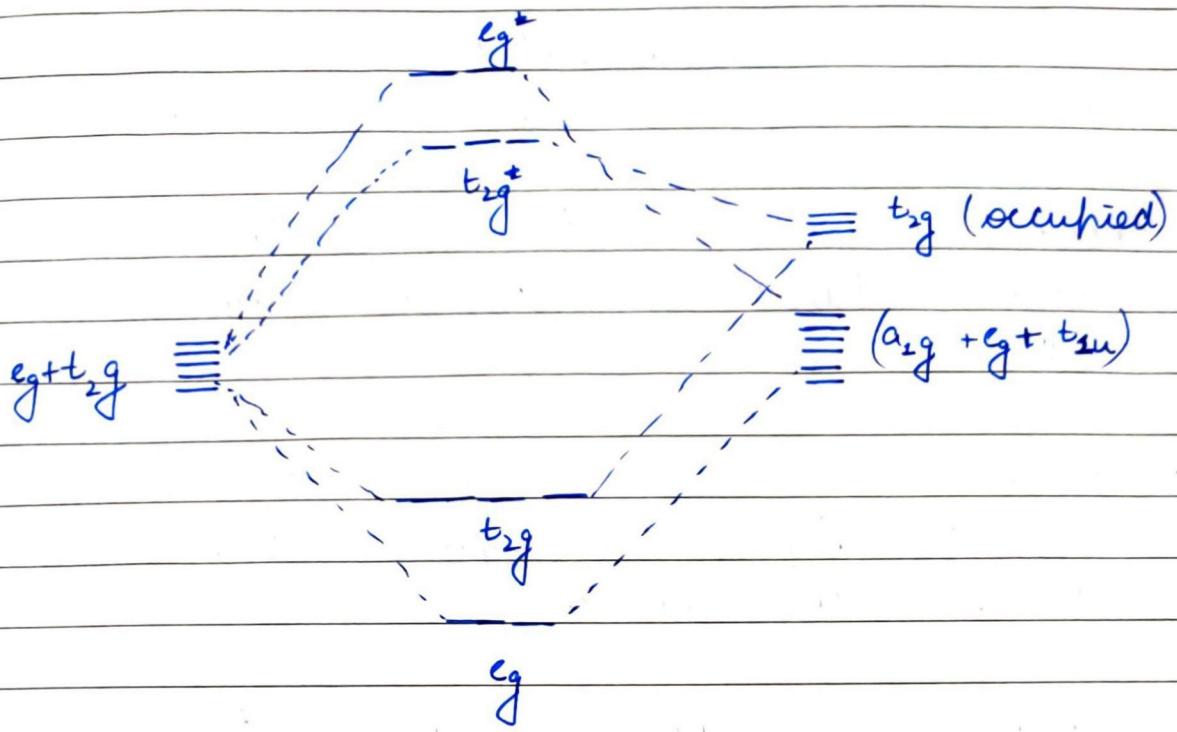
Draw MO diagram of a complex when ligand is

i)  $\pi$ -acceptor



$\pi_g$  - CO, CN<sup>-</sup>

ii)  $\pi$  donor



$\text{eg}^- \text{ I}^-, \text{Cl}^-, \text{Br}^-, \text{F}^-$

Q3: Draw MO diagram for CO.

## → MAGNETIC SHIELDING

- Protons are surrounded by electrons that shield them from external  $\vec{B}$ .
- circulating  $e^-$  creates an induced  $\vec{B}$  that opposes the external magnetic field.
- Protons in  $e^-$  rich environment sense low effective  $\vec{B}$ . Hence require less frequency to come to resonance.
- Protons in  $e^-$  poor environment sense high eff.  $\vec{B}$  and thus require more frequency to come to resonance.

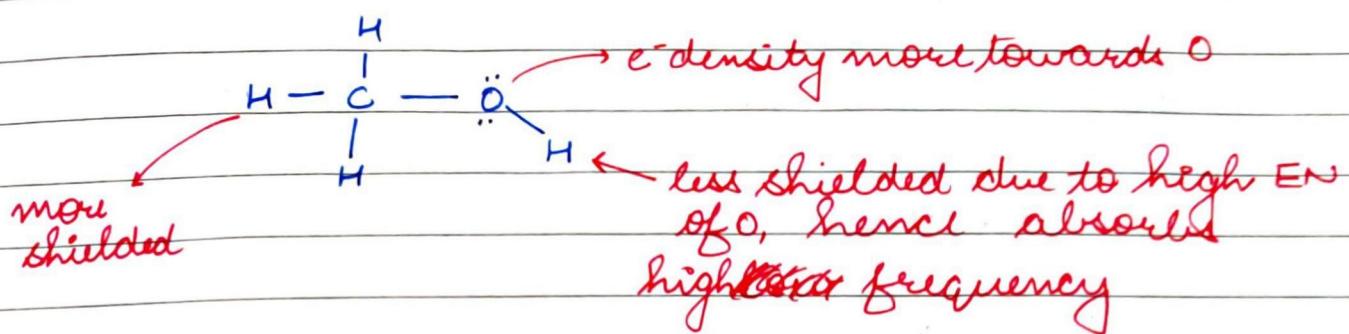
### NOTE:

External magnetic field introduces an energy gap between the two spin states. The more the eff.  $\vec{B}$ , the greater is the energy gap.  $\therefore$  more energy required to ~~get~~ transfer b/w 2 states.

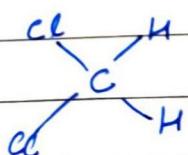
## → PROTONS IN A MOLECULE

- Depending on the chemical environment of protons, they are shielded by different atoms.

- consider



- $\rightarrow e^-$  poor environment



- Shielding  $\uparrow$ , eff  $\vec{B}$   $\downarrow$

### $\rightarrow$ NMR signals

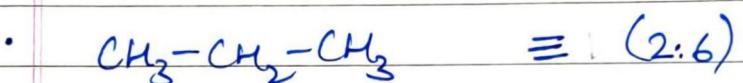
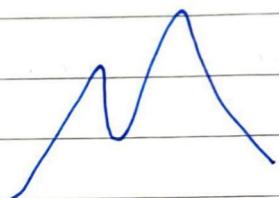
- Number of signals tells how many different kinds of protons are present.
- The location of signal shows how shielded or deshielded proton is
- The intensity of signal shows the no. of protons of that type.
- Signal splitting shows the proton on adjacent atom.
- Basically, in general we observe the signals obtained from hydrogen atoms. Same type of hydrogen atoms exhibit same signals.



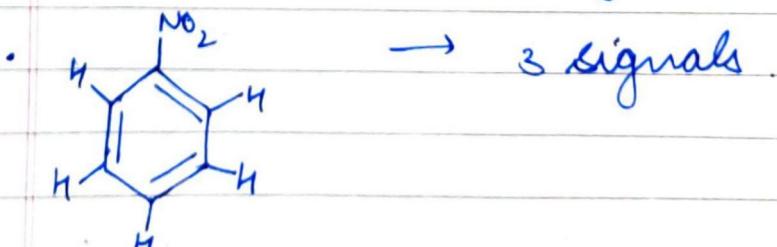
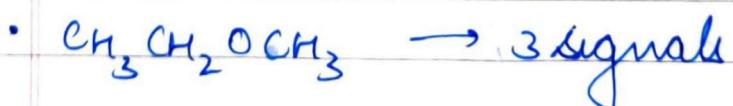
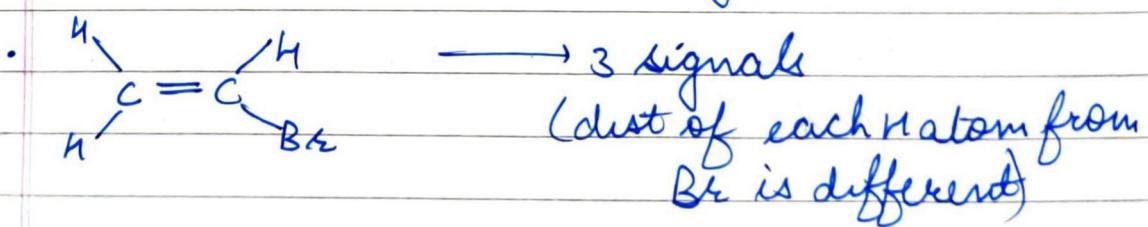
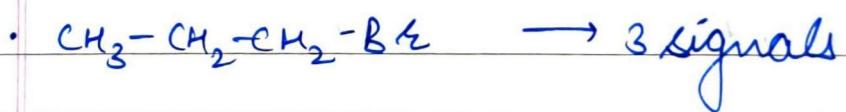
• 2 types of H atoms in ratio

$$\equiv (4:6)$$

∴ signal is of form



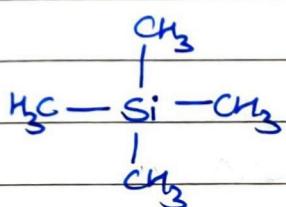
### → COUNTING CHEMICAL EQUIVALENT PROTONS



• Chlorocyclobutane has 5 signals.

## → CHEMICAL SHIFT

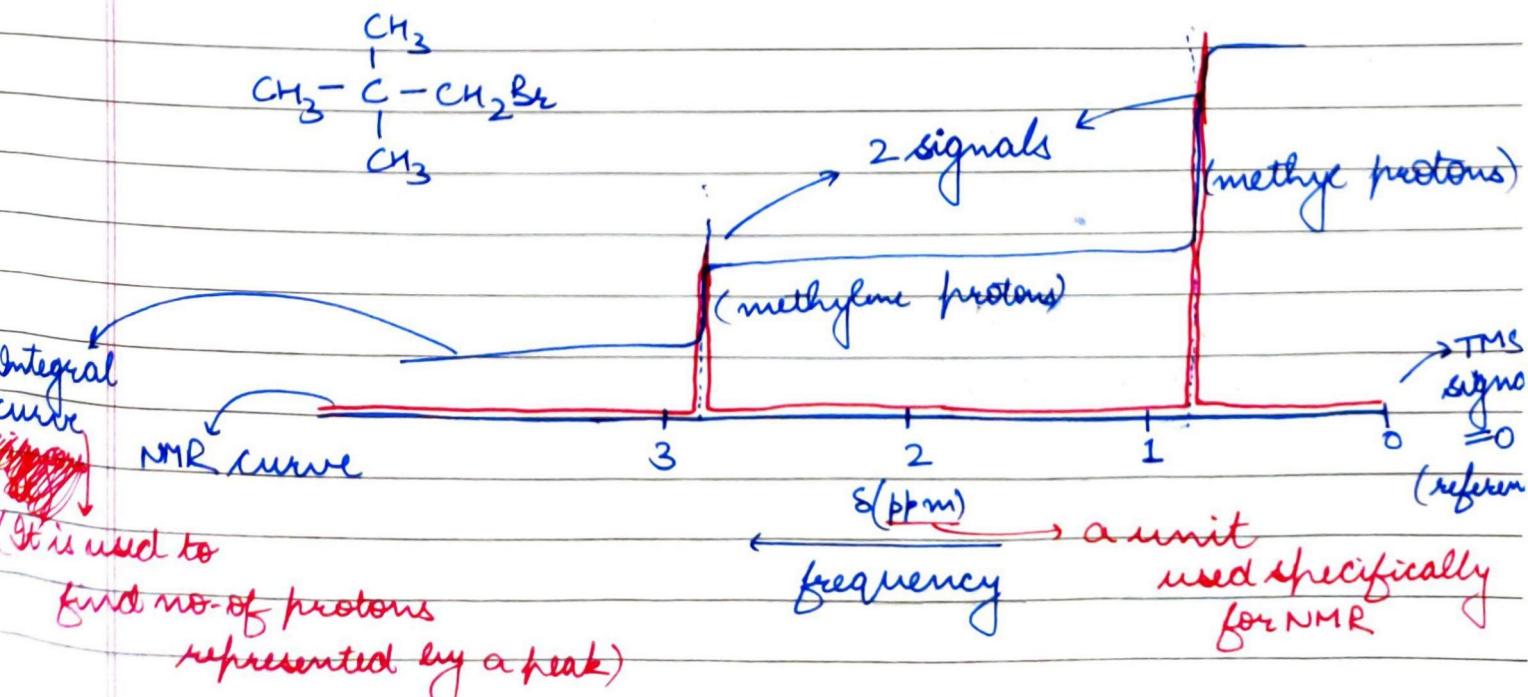
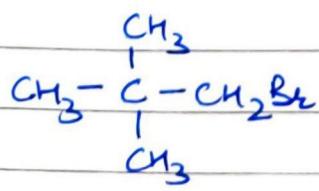
- The position of signals are defined according to how far they are from the signal of reference compound.
- Reference compound = TMS



Tetramethylsilane

- It's highly shielded
- Chemically inert
- There are 12 equivalent protons, so even small amount of TMS can help to get the field.

e.g-



NOTE:

In above example methylene protons are closer to Br which is highly electronegative. Due to this shielding on methylene protons is low. ∴ splitting is higher for it. ∴ more freq. absorbed

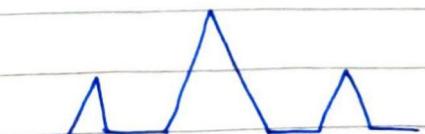
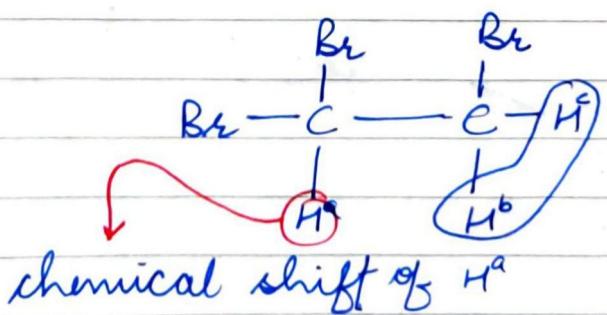
→ SPLITTING OF PROTON SIGNALS

For any particular type of protons, we have an NMR signal. But this signal might be further split into multiple peaks. This happens due to presence of protons nearby.

→  $N+1$  Rule :

- If a signal is split by  $N$  equivalent protons, it is split into  $N+1$  peaks
- e.g. if we only consider nearest (neighbouring) halogens.

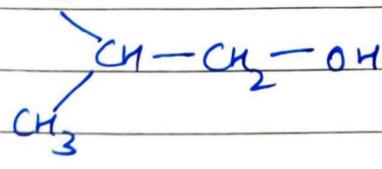
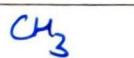
eg -



- There is a specific rule as to the areas under the splitted curves
- Relative peak intensities of symmetric multiplets

No. of eq; protons causing splitting	No. of peaks (multiplicity)	Area Ratios (Pascal's triangle)
0	1 (singlet)	1
1	2 (doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 1

- Consider

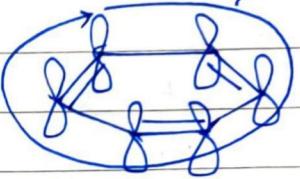


→ look at spectra and analyse it from sides.

### Note

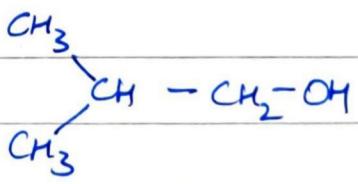
Alcoholic hydrogens may be placed around any frequency in the spectra. (explained later.)

## → MAGNETIC ANISOTROPY

- Alkenes and alkynes have electron density which causes some shielding whatever.
- In case of benzene,  current of moving electrons

due to this current, the  $\delta$  in benzene are very weakly shielded due to which the peaks are observed at

- Read from slides.
- Also focus on slide referring to compound



and then rest of structures.

NOTE: We may get an NMR peak in our spectra due to alcoholic proton. However, this peak may create confusion for us.  
 $\therefore$  we replace it by deuterium

NOTE: Integration refers to no. of protons

classmate

Date \_\_\_\_\_  
Page \_\_\_\_\_

Q: Refer to slides for NMR spectra of  $C_5H_{12}O$  and calculate structure given

1<sup>st</sup> peak  $\rightarrow$  0.9 ppm  $\rightarrow$  triplet  $\rightarrow$  integration = 3

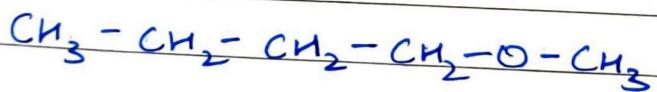
2<sup>nd</sup> peak  $\rightarrow$  1.4 ppm  $\rightarrow$  multiplicity = 6  $\rightarrow$  integration = 2

3<sup>rd</sup> peak  $\rightarrow$  1.6 ppm  $\rightarrow$  mul = 5  $\rightarrow$  integ = 2

4<sup>th</sup> peak  $\rightarrow$  3.3 ppm  $\rightarrow$  mul = 1  $\rightarrow$  integ = 3

5<sup>th</sup> peak  $\rightarrow$  3.4 ppm  $\rightarrow$  mul = 3  $\rightarrow$  int = 2

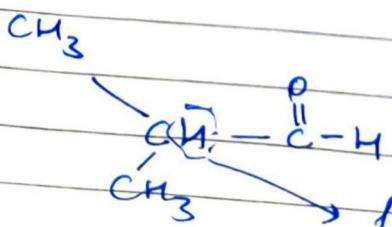
Ans:



$\rightarrow$  NMR for aldehydes

The NMR for 'H' in  $-C^{\ddagger}H$  is around 9.0 ppm due to very ~~heavy~~ <sup>low</sup> shielding.

Consider



for this hydrogen, pro

For the marked hydrogen, we must technically have multiplicity =  $7+1=8$  but the -CHO proton has different multiplicity arrangements. Due to this we get only 7 peaks each of which is split into two. We call it a doublet of septet or a doublet of multiplicity 7.

NOTE: Sometimes peaks for 2 different hydrogen types may lie in same range and may overlap to give irregular peak patterns.

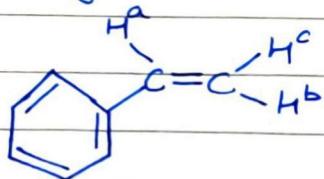
# Look at and observe structures for ketones and other functional groups

NOTE: Integration of NMR curves can also give us an idea of alcohols or keto form

PTO

## → COMPLEX SPLITTING

- Consider styrene

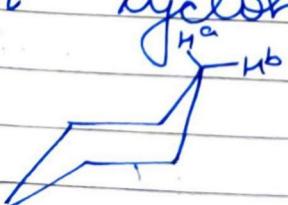


- For  $\text{H}^a$ , we ~~would~~ should have had a triplet but what we observe is that we have doublet of a doublet (i.e. 2 peaks further split into two) : this is because  $\text{H}^c$  &  $\text{H}^b$  are not equivalent (since  $\text{H}^c$  &  $\text{H}^b$  have different distance from aromatic ring)

NOTE

We can differentiate simple and complex splitting by comparing height of peaks. For simple splitting we have a specified pattern (Pascal's triangle) but for complex splitting we don't see that pattern.

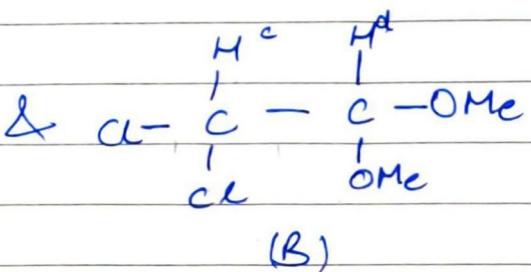
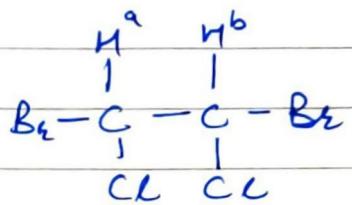
- Consider cyclohexane



$\text{H}^a$  &  $\text{H}^b$  are not equivalent but at room temp. they constantly interchange. Due to this only one peak is observed. But if we freeze the compound, then we can observe two peaks.

$\therefore$  1 peak at  $25^\circ\text{C}$   
2 peaks at  $-90^\circ\text{C}$

Q→



Show how would you differ b/w their NMR?

Ans: Compound (A) being non-chiral has equivalent protons. Due to this we will have only one peak split as a doublet. But for (B), due to non-symmetry we have 2 doublet peaks.

Q→ For  $\text{C}_9\text{H}_{10}\text{O}$ , we have 3 distinct peaks

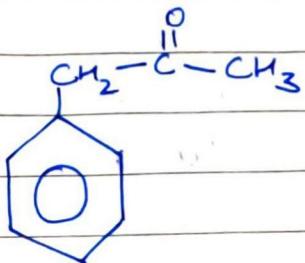
1<sup>st</sup> peak: 2.2 ppm  $\rightarrow$  singlet  $\rightarrow$  Int = 3

2<sup>nd</sup> peak: 3.5 ppm  $\rightarrow$  singlet  $\rightarrow$  Int = 2

3<sup>rd</sup> peak: 7.2 ppm  $\rightarrow$  multiplet  $\rightarrow$  Int's

Identify comp.

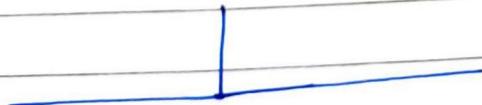
Ans



~~Ques~~ For aromatic hydrogens we should have 4 peaks for ortho - meta & para H but due to aromaticity they lie in same range & overlap creating a multiplet.

### → DIFFERENCES IN $^{13}\text{C}$ TECHNIQUE OF NMR →

- We won't see peaks for  $^2\text{H}$  due to cancellation of spins. But for  $^{13}\text{C}$  due to odd nucleon, spin may be observed.
- Natural abundance of  $^{13}\text{C}$  is around 1.1% due to which, the peaks observed have negligible area under them and have very very low intensity. We almost get lines in our graph.



- Integration can never give us an idea of number of carbons at a particular position.

- It is very very unlikely that in a molecule we would have adjacent  $^{13}\text{C}$  molecules.  $\therefore$  Splitting in  $^{13}\text{C}$  peaks is never seen.

NOTE For this chapter focus on slides else the chapter can be confusing.

CLASSMATE  
Date \_\_\_\_\_  
Page \_\_\_\_\_

## Chapter - 3 Organometallic Chemistry

### → IMPORTANCE

- It refers to chemistry b/w organic & inorganic
- It is responsible for homogeneous catalysis which is the method of choice for chemical & drug synthesis. *(provide easy catalyst)*
- Digestion of grass by herbivores to the blue colour of octopus's blood, everything comes under this topic.

NOTE: Blue colour is due to haemocyanin.

- Helps in synthesis of polymers & detergents.
- Helps to understand heterogeneous catalysis
- Synthesis of semiconductors.
- Involves transformation of organic compounds using metals.

NOTE:  $C_7^-$  = cycloheptadienyl

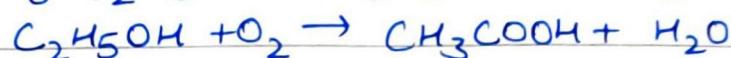
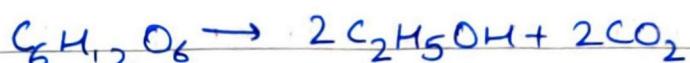
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- $CH_3COOH$  synthesis

Traditional :



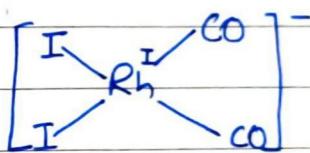
{

dirty and non-efficient process.

Industrial :



catalysed by Rhodium complex



→ HISTORY →

- Read from slides

- Important topics : Ferrocene, zeigler - natta, Schrock catalysis & grubbs catalysis (2005 Nobel), C-H activation.

## → LIGANDS IN ORGANOMETALLIC CHEMISTRY

- Cationic  $2e^-$  donor:  $\text{NO}^+$  (nitrosoyl)
- Neutral  $2e^-$  donor:  $\text{PR}_3$ ,  $\text{CO}$ ,  $\text{R}_2\text{C}=\text{CR}_2$ ,  $\text{RC}\equiv\text{CR}$ ,  $\text{N}\equiv\text{CR}$ .
- Anionic  $2e^-$  donors:  $\text{X}^-$ ,  $\text{CH}_3^-$ ,  $\text{CH}_2^-$  etc.
- Anionic  $4e^-$  donors:  $\text{C}_3\text{H}_5^-$  (allyl),  $\text{NR}_2^+$  (imide) etc.
- Anionic  $6e^-$  donors:  $\text{Cp}^-$ ,  $\text{O}^{2-}$
- **Ligands:** Don't bring  $c-$  to metal ( $\text{BR}_3$ ,  $\text{AlR}_3$ )

## → 18 electron rule

- All stable organometallic complexes follow this. They have 9 valence orbitals which must have 18 electrons.
- After this, they almost become noble-gas like and thus don't act like catalysts (as they are not open for activation)

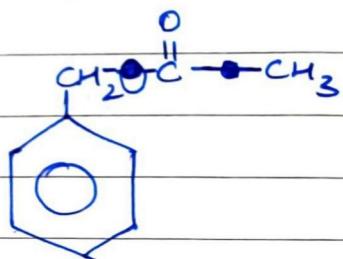
TUTORIAL

Q: NMR data for a compound: multiplet near 7.3 ppm (5 protons) & singlets at 5.1 (integ = 2 protons) & 2.1 ppm (3 protons). General formula:  $C_9H_{10}O_2$ . Reconfirmed presence of acid / esters.

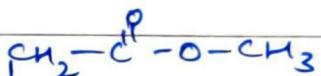
Ans.

$$DOU = C+1 - \frac{H}{2} - \frac{X}{2} + \frac{N}{2}$$

$$= 5$$

NOTE:

We can't have



since in the case 3H would have low shielding & ∵ higher v, but that is not the case.

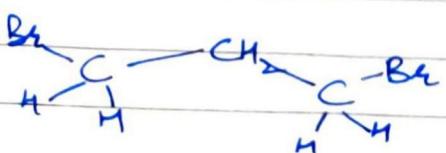
Q:

NMR data: triplet near 3.7 ppm (int: 4 protons) & pentet at 2.4 (int: 2 protons). Gen formula:  $C_3H_6Br_2$ . Identify it.

Ans.

$$DOU = 4 - 3 - 1 = 0$$

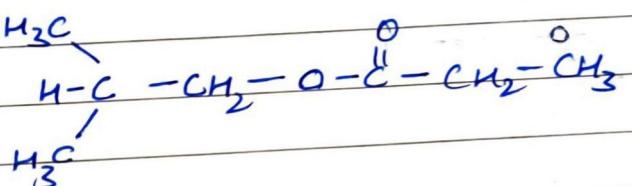
~~ABAB (tetraethylbenzene)~~



~~intr~~~~30:~~

NMR data: Doublet near 3.8 ppm (int: 2 protons), quartet at 2.4 ppm (int: 2 protons), multiplet at 1.9 ppm (integration 1 proton), triplet at 1.2 ppm (integration 3 protons), doublet 0.9 ppm (integration 6). General formula:  $C_7H_{14}O_2$ . Identify the compound.

Ans.: DOU = 8 - 7 = 1



NOTE: Refer to slides for details on the chapter.

classmate

Date \_\_\_\_\_

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## Chapter - 4 Bio Inorganic Chemistry

### → IMPORTANT ROLES OF METALS IN BIOCHEMISTRY

1.  $\text{Na}^+$  and  $\text{K}^+$  help in regulatory actions through nerve signals & muscle impulses.
2.  $\text{Ca}^{2+}$  &  $\text{Mg}^{2+}$  provide strength in bones.
3.  $\text{Fe}^{3+}$  acts as oxygen carrier in form of haemoglobin.

### → STRUCTURE OF METALLO PROTEIN

- We have 2 forms of protein: Spiral ( $\alpha$  helix) & beta ( $\beta$  pleated sheet)
- Prosthetic group: A metal complex positioned in a crevice.

(READ IN DETAIL FROM SLIDES)

NOTE : glutamic Acid is present in chain form in the RBC's. But sometimes, naturally, glutamic acid chains may have valine as substituents. Due to this, there is deformation in RBC's (due to hydrophobic nature of valine) and this disease is called sickle-cell anaemia.

### → PROTEIN STRUCTURE →

- Read structures from slides.

NOTE: When we boil an egg, the hydrogen bonds in the secondary, tertiary & quaternary structures get destroyed. Also there are many hydrophobic interactions which get destroyed & when they are re-established, they don't get connected in same way (since they are non-selective). ∴ we can't get egg back from omelette 😊.

### → INORGANIC ACTIVE SITE (PROSTHETIC GROUP)

- In molecular biology, the active site, is the location where all the substrate bind with and a specific function is carried out.

NOTE: Look at video ~~of~~ on cellular respiration (electron flow chain) on youtube.



• However, the active site is only able to perform its function when it is surrounded by respective protein - eg - Fe can permanently bind with  $O_2$  otherwise.

NOTE: Haemoglobin has  $Fe^{3+}$  and chlorophyll has  $Mg^{2+}$ , rest they have literally the same structure !!.

## Chapter - 5 Stereochemistry

### → STEREOCHEMISTRY

- Refers to 3-D properties of molecules
- Compounds of same molecular formula are called isomers.
- If they have same connectivity, then they are stereoisomers else constitutional isomers.

### → STEREOISOMERS

- 2 types:  
*configurational* , *conformational*
- *Configurational* →  
2 types: geometric, Optical.

### → OPTICAL ISOMERISM →

### → CIP Priority Rules (For R-S config. determination)

- Higher Z precedes lower
- Higher atomic mass precedes lower
- Ci precedes trans & R precedes S.

- To look at R or S config, put the lowest priority atom/group away from you & then look at the precedence of rest of atoms. If clockwise increasing priority then type is R type else S type.

NOTE: Always remember that R & S is just a convention to represent molecules on paper. Practically it has no meaning. Practically any compound (chiral) is either (+) dextrorotatory or (-) laevorotatory.

### → PPL ROTATION →

- Dextrorotatory - rotates light in (+) direction (in clockwise direction)
- Saevorotatory - rotates light in (-) direction (in anticlockwise direction)

NOTE: Look at formulas for specific rotation, ~~optical~~ optical purity & enantiomeric excess in slides

NOTE: In more than 2 one chiral centre, erythro means substituents are on same side & threo means they are on opposite sides.

NOTE: Look at <sup>slides for</sup> diastereomers, meso compounds and separation of ~~enantiomers~~ enantiomers.

## Chapter - 6 Green Chemistry

### → GREEN CHEMISTRY

- Technologies that are energy efficient, minimise or preferably eliminate the formation of waste, avoid the use of toxic and/or hazardous solvents and reagents and, where possible, utilise renewable raw materials.
- goal: Sustainability : meeting our needs but not hampering the needs of future generations
- Green Chemistry involves →
  - a) waste minimisation at source
  - b) use of catalysts in place of Reagents
  - c) using non-toxic reagents.
  - d) Use of Renewable Resources
  - e) Improved atom efficiency ( $\text{rxn}$  efficiency)
  - f) use of solvent free or recyclable environmentally Benign solvent systems (since we generally use excess of ~~solvent~~ <sup>absence of</sup> solvent for even small amounts of reagent)

→ Read from slides 700 →

→ THE E-FACTOR →

- It is the actual amount of waste formed in the process including solvent losses, acids etc

## → BIOCATALYSIS

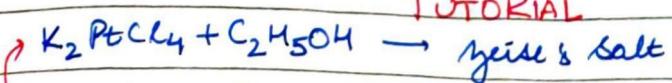
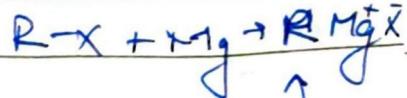
- mild conditions: ambient temp. and pressure and physiological pH.
- Fewer steps (avoids protection/deprotection steps)
- Largely avoids toxic / hazardous reagents & solvents.
- eg - look in slides

## → BIODEGRADABLE PLASTICS : Polyhydroalcanoates (PHAs)

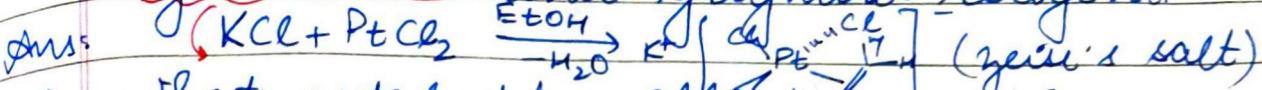
- Sunlight → crop → sugar sol<sup>n</sup> → fermentation  
↓  
Biodegradable ← Plastic product → PHA  
to CO<sub>2</sub> & H<sub>2</sub>O

NOTE:

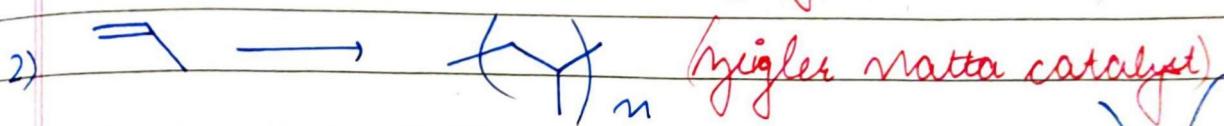
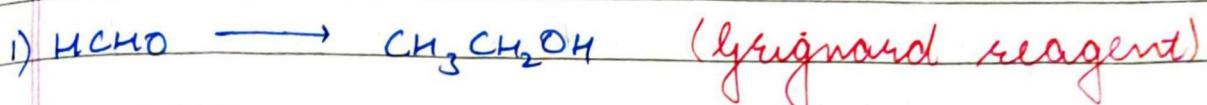
Biodegradable plastics are not the best choice for long-term storage since they decompose. For such purposes, we must use recyclable plastics.

TUTORIAL

Q1 Write the structure and synthesis of Geise's salt and Grignard reagent.



Q2 What catalyst/vessel will you use in reagent?



Q3: NMR : Molecular Formula =  $C_7H_{14}O_2$

doublet at 3.8 ppm (2H)

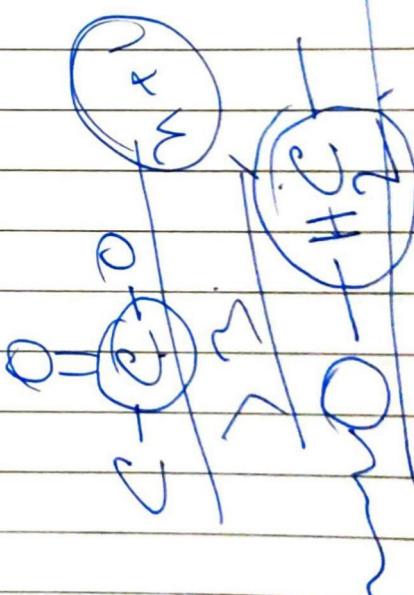
quartet at 2.4 ppm (2H)

multiplet (q) at 1.9 ppm (1H)

triplet at 1.2 ppm (3H)

doublet at 0.9 ppm (6H)

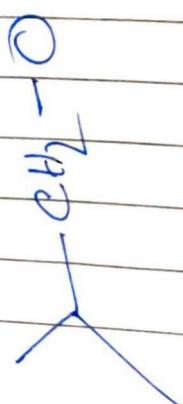
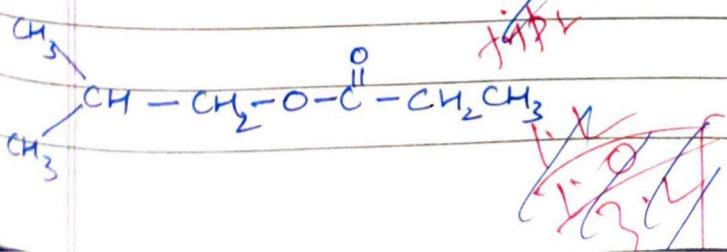
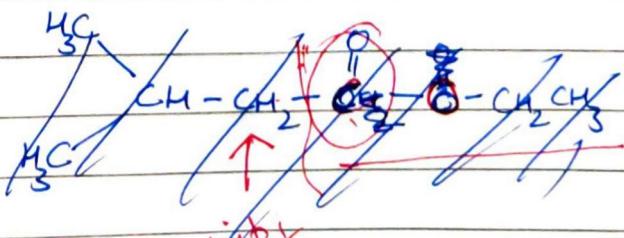
I  
C



Ans: DOU =  $C + H - \frac{H}{2} - \frac{X}{2} + \frac{N}{2}$

$\Rightarrow DOU = 7 + 1 - \frac{14}{2} = 1$

~~degree~~



4Ques: what metals are present in following system?

- a) Haemoglobin Fe
- b) Cytochrome c Fe

5Ques: what is fate of oxygen in living system.

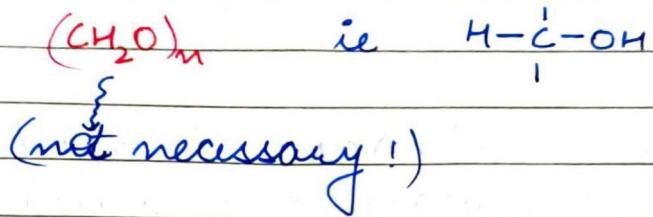
6Ques: Define cofactor and prosthetic group with one example.

NOTE: Informative chapter : read from slide *classmate* *date* *Page*

## Chapter-7 Carbohydrates

### → CARBOHYDRATES

- Carbohydrates (glycans) have the following basic composition:

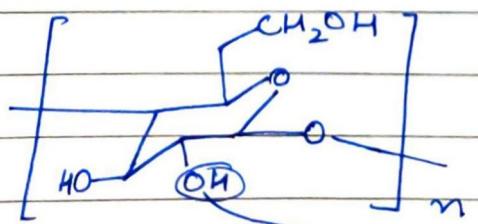


### → CLASSIFICATION

- **Monosaccharides:** simple sugars with multiple -OH groups.
- **Disaccharides:** 2 monomeric sugar structures attached together.
- **Disaccharides:**
- **Polysaccharides:**

NOTE:

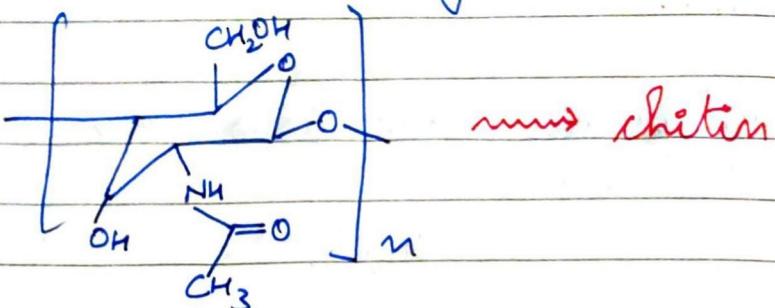
Cellulose is



is stable in water, but  
temporarily.

However if we just replace this group

by  $-\text{NH}-\overset{\text{O}}{\underset{\text{C}_2\text{H}_5}{\text{C}}}-\text{CH}_3$ , we get the component present in shells of organisms like snails, which is very stable in water.



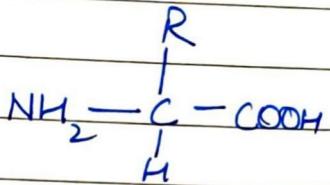
If we replace the group by  $-\text{NH}_2$ , we get chitosan, a renewable polymer which can be used to make a variety of biomedical substances.

## chapter - 8

# Amino Acids, Peptides and Proteins

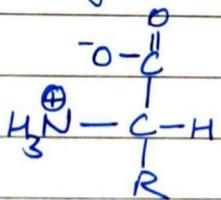
### → AMINO ACIDS

- Building blocks of proteins.
- 20 standard amino acids ( $\alpha$ -amino acids)
- general structure



### → ZWITTER IONS →

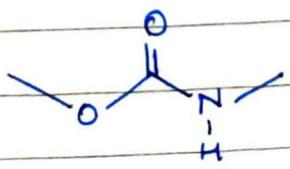
- Both  $\text{NH}_2$  and  $\text{COOH}$  groups in an amino acid undergo ionization in water.
- They are generally at physiological  $\text{pH} = 7.4$



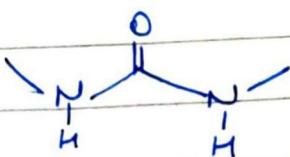
### → CLASSIFICATION

- a) POLAR    b) NON-POLAR    c) AROMATIC ....

NOTE:



→ urethane



→ urea or carbamide

## Chapter -9 Thermodynamics

### → SYLLABUS

- Definition and Introduction to Thermodynamics terms
- Different systems and processes
- Reversible and Irreversible transformation
- 1<sup>st</sup> Law of Thermodynamics
  - enthalpy
  - Heat and work
- 2<sup>nd</sup> Law of Thermodynamics
  - statements of Thermodynamics
  - entropy
  - Carnot cycle and its efficiency
  - Gibbs Free Energy
  - ~~Bellard's~~ Helmholtz Free energy
  - Clausius Inequality
- Phase Transition of matter
- 3<sup>rd</sup> Law of Thermodynamics
  - Introductory

NOTE: In the IR spectra of water, we observe a peak of low intensity due to the hydrogen bond in water. This arises due to vibrations in H-bond called librations.

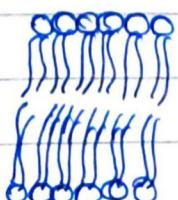
## → DEFINITIONS

1. **SYSTEM**: The entity under observation is called a system.
2. **SURROUNDINGS**: everything in the universe apart from system is called surroundings.

System + Surroundings = Universe

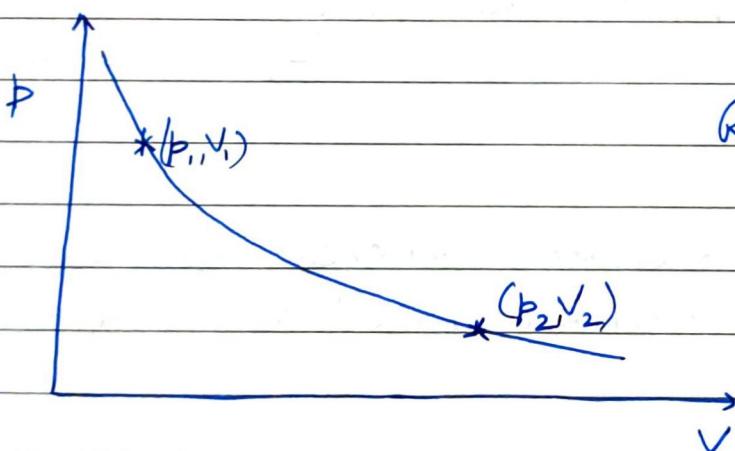
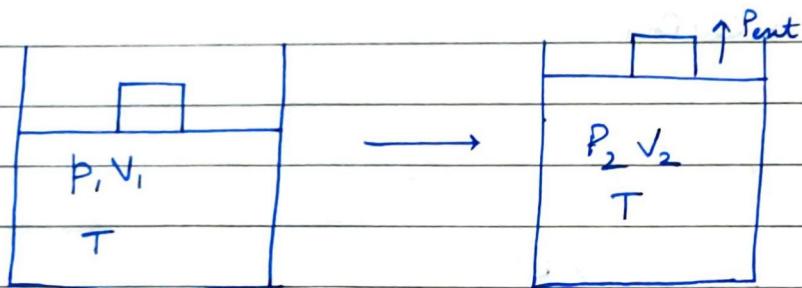
3. **Isolated System**: A system preventing any sort of mass or energy transfer. Practically can't be engineered.
4. **Closed System**: A system preventing mass transfer but allowing energy transfer. eg- vacuum flask etc.
5. **Open Cell**: A system allowing both mass and energy transfer. eg ~~human~~ cells etc.

**NOTE:** The semi-permeable membrane in cell membrane is phospholipid bilayer



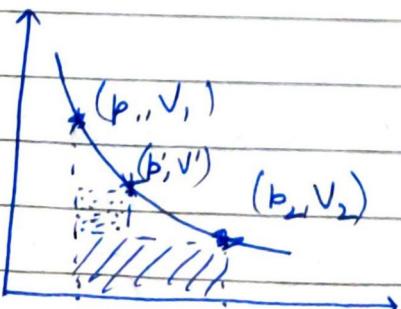
6. Reversible processes: These processes are the ones which occur in infinitesimal ~~steps~~ changes ie they have infinite steps. They can be reversed back.

Consider



Rectangular  
hyperbolic  
graph

If we carried this change in a single step (irreversibly): (ie we directly changed point to  $P_2$ ), then,



$$\therefore W_1 = P_2 (V_2 - V_1)$$

If we carried it out in 2 steps (first to  $P'$  then to  $P_2$ ) then  $W_2 = P' (V' - V_1) + P_2 (V_2 - V')$

$$\therefore \Delta W = (P' - P_2) (V' - V_1)$$

If we carried out infinite steps,

$$W_{\infty}^e = \int p dV \xrightarrow{\text{expansion}}$$

$$\Rightarrow W_{\infty}^e = nRT \ln \frac{V_2}{V_1} \xrightarrow{\text{external work done by gas}}$$

For compression

$$W_{\infty}^c = p_i (V_1 - V_2)$$

$$W_{\infty}^c = nRT \ln \frac{V_1}{V_2}$$

$$W_{\infty}^c = nRT \ln \frac{V_1}{V_2} \xrightarrow{\text{external work done by gas}}$$

NOTE: In a reversible process, the system is in quasi-equilibrium situation at every step.

→ LAWS OF THERMODYNAMICS →

→ ZEROTH LAW OF THERMODYNAMICS →

- If there are 3 bodies : A, B and C such that A and B are in thermal eqm and B & C are in thermal eqm, then A and C are in thermal eqm.

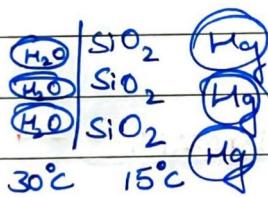
- eg - Thermometer



The glass is in eq<sup>m</sup> with surroundings and the mercury is in eq<sup>m</sup> with the surroundings.

- molecular picture of thermal eq<sup>m</sup>.

Due to molecular collisions, the thermal eq<sup>m</sup> is attained.



collisions b/w sheet<sup>molecules</sup>, makes them attain thermal eq<sup>m</sup>.

Temperature of any substance is dependent on the KE of its particles. The equation linking them is given by equipartition principle

$$\frac{1}{2}mv^2 = \frac{3}{2}K_b T$$

The H<sub>2</sub>O molecule have all vibrational, rotational & translational degree of freedom. However, SiO<sub>2</sub> only has vibrational (majorly) & Hg has translational

- These conversion b/w modes while attaining eq<sup>m</sup>. This takes time ∵ thermal eq<sup>m</sup> is not attained immediately.

NOTE:

Thermal eq<sup>m</sup> requires contact. It is attained only when KE of 2 bodies is equal.

eg - A chalk in environment is in thermal eq<sup>m</sup> with environment but chalk has no translational KE.

the vibrational KE of chalk = Trans + rot + vib. KE of air molecules surrounding (overall KE of air molecules)

### → FIRST LAW OF THERMODYNAMICS →

- For a cyclic process the amount of heat absorbed by the system is equal to the work done by the system to the surrounding.

$$\oint dq = \oint dw$$

$$\Rightarrow \oint (dq - dw) = 0$$

$$\Rightarrow \oint d(q-w) = 0$$

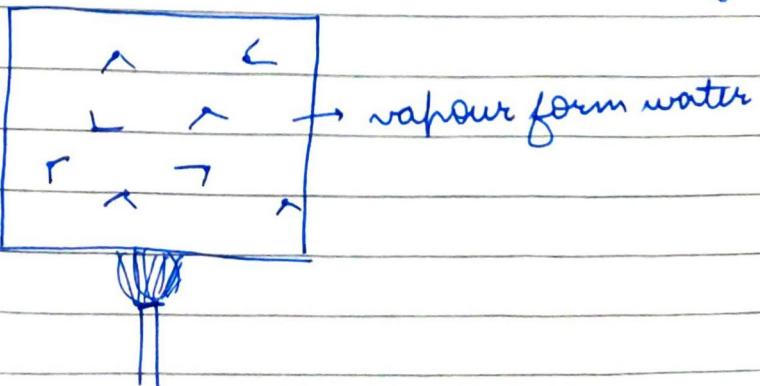
$$\oint d(q_i - w) = \oint du \quad \text{where } u \text{ is any state function}$$

$$\Rightarrow dq = du + dw$$

NOTE: State and Path function:

$q$  is a path function. This is because, we know that we get different work on different paths (from earlier) and thus using first law,  $q$  also changes.  $\therefore q$  is a state function.

- Here, we know  $\oint$  state func = 0  $\therefore$  we replace 0 by any state function  $u$ . As of now, we don't know what is  $u$ . But now we will try and analyse  $u$ .
- For analysis of  $u$ , consider an expandable container which we are heating



This increases the temperature and

## TUTORIAL

Ques: Calculate the final volume of 1 mol of an ideal gas, which was initially at 0°C and 1 atm pressure. The gas has absorbed 2000 calories of heat during reversible isothermal expansion. (STP given)

Ans:

$$W = -nRT \ln \frac{V_2}{V_1}$$

$$1 \times V = n \times R \times T$$

$$V = \cancel{n} \times 0.0821 \frac{\cancel{T}}{273}$$

$$\Delta U = 0$$

$$q = 2000 \text{ cal}$$

$$\Rightarrow V = 22.4133 \text{ l}$$

$$\therefore W = 2000 \text{ cal}$$

$$W = 2000 \times 4.184 \text{ J}$$

$$\Rightarrow RT \ln \frac{V_2}{V_1} = 2000 \times 4.184$$

$$\Rightarrow 8.314 \times 273 \times \ln \frac{V_2 \times 10^3}{22.4133} = 2000 \times 4.184$$

$$\Rightarrow \ln \frac{V_2}{22.41 \times 10^{-3}} = 3.6868$$

$$\Rightarrow V_2 = 0.894 \text{ m}^3$$

2Ques: Prove mathematically that work is a path function.

Ans:

$$dw = pdV$$

$$\delta V = f(T, P)$$

3Ques: Show mathematically that the magnitude of the work in a reversible expansion of an ideal gas from pressure and volume  $V_1$  to pressure  $P_2$  & volume  $V_2$  is larger than the corresponding work involved in an irreversible expansion against constant pressure  $P_2$ .

4Q: Show that pressure is a state function for gas obeying:

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

5Qn: For an ideal gas  $PV = nRT$ . Taking  $V = f(n, P, T)$  verify that  $dV$  is an exact differential.

## → HEAT CAPACITY →

- In first law, we can write work as

a

$$dW = dW_{\text{mech}} + dW_{\text{chem}}$$

But mostly we don't consider  $W_{\text{chem}}$  because no chem rxn is involved generally.  $\therefore dW = P \text{ext} dV$

NOTE:  $dW$  and  $dq$  are exact differential

- The amount of heat required to increase the temp of a system by  $1^\circ\text{C}$  is called the **heat capacity of the system**.

  
**TE:**  $\text{H}_2\text{O}$  has a relatively very high \* heat capacity when compared to molecules of similar radii. (water has radii  $\approx 1.5\text{\AA}$ )

- Molecular picture:

The atoms/molecules have to increase their kinetic energy to get the temperature increased.

- The greater the size, more friction is provided to motion of molecules and thus greater is the heat capacity (molar)

- H-bonding increases heat capacity.

NOTE: In case of water, each molecule may have either 1, 2, 3, 4, 5 or 6 hydrogen bonds. On an average each  $H_2O$  molecule has ~~on an ave~~ 3.6 hydrogen bonds. ∴ For increasing kinetic energy, very large amount of heat is required.

### • Expression for heat capacity

$$C = \lim_{\Delta T \rightarrow 0} \frac{dq}{\Delta T}$$

where  $C$  = heat capacity  
 $q$  = heat taken

$$\Rightarrow C = \boxed{\frac{dq}{dT}}$$

### • Heat capacity at constant volume

$$\underset{\text{int}}{C} = \left( \frac{\partial q_v}{\partial T} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V$$

since

$$dq = dU + dw$$

$$\Rightarrow dq = dU + PdV$$

$$\Rightarrow \left( \frac{\partial q_v}{\partial T} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial P}{\partial T} \right)_V dV$$

### • Heat capacity at constant pressure

$$C = \left( \frac{\partial q_p}{\partial T} \right)_P$$

Now

$$dq = dU + PdV$$

$$\Rightarrow dq + VdP \neq = dU + PdV + VdP$$

$$\Rightarrow dq_v + VdP = d(U + PV) \quad - (ii)$$

From this,  
we define

$$H = U + PV$$

where  $H$  could be anything for now

From (i)

$$dq_v + VdP = dH$$

$$\Rightarrow \left(\frac{\partial q_v}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$\therefore$   $C = \left(\frac{\partial q_v}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$

## TUTORIAL

Ques: Prove mathematically that work is a path function

Ans: For a function  $Z = f(x, y)$  to be a state function, it must satisfy

$$\left( \frac{\partial}{\partial y} \left( \frac{\partial z}{\partial x} \right)_y \right)_x = \left( \frac{\partial}{\partial x} \left( \frac{\partial z}{\partial y} \right)_x \right)_y$$

For work

$$W = PdV$$

$$V = f(T, P)$$

$$V = f(T, P)$$

$$dV = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP$$

$$W = PdV = P \left( \frac{\partial V}{\partial T} \right)_P dT + P \left( \frac{\partial V}{\partial P} \right)_T dP$$

now taking work  
Now we check

$$\left( \frac{\partial}{\partial P} \left( \frac{\partial W}{\partial T} \right)_P \right)_T = P \left( \frac{\partial^2 V}{\partial T^2} \right)_P dT + \left( \frac{\partial}{\partial P} \left( \frac{\partial V}{\partial P} \right)_T \right)_T$$

$$\left( \frac{\partial}{\partial T} \left( \frac{\partial W}{\partial P} \right)_T \right)_P = \left( \left( \frac{\partial}{\partial P} \left( \frac{\partial V}{\partial T} \right)_P \right)_T \right)_P$$

$$\left(\frac{\partial w}{\partial T}\right)_P = P \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial x}{\partial T}\right)_P^0 + P \left(\frac{\partial v}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_P^0$$

$$\Rightarrow \left(\frac{\partial w}{\partial T}\right)_P = P \left(\frac{\partial v}{\partial T}\right)_P$$

$$\left(\frac{\partial}{\partial P} \left(\frac{\partial w}{\partial T}\right)_P\right)_T = \frac{\partial}{\partial P} \left[P \left(\frac{\partial v}{\partial T}\right)_P\right]_T$$

$$= \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_T^0 + P \left(\frac{\partial}{\partial P} \left(\frac{\partial v}{\partial T}\right)_P\right)_T$$

$$= \left(\frac{\partial v}{\partial T}\right)_P + P \left[\frac{\partial}{\partial P} \left(\frac{\partial v}{\partial T}\right)_P\right]_T - (i)$$

$$\left(\frac{\partial w}{\partial P}\right)_T = P \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial x}{\partial P}\right)_T^0 + P \left(\frac{\partial v}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_T^0$$

$$\Rightarrow \left(\frac{\partial w}{\partial P}\right)_T = P \left(\frac{\partial v}{\partial P}\right)_T$$

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial w}{\partial P}\right)_T\right)_P = \left(\frac{\partial P}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_P^0 \left(\frac{\partial v}{\partial P}\right)_T + P \left[\frac{\partial}{\partial T} \left(\frac{\partial v}{\partial P}\right)_T\right]_P$$

$$= P \left[\frac{\partial}{\partial T} \left(\frac{\partial v}{\partial P}\right)_T\right]_P - (ii)$$

$(i) \neq (ii)$

$\therefore$  work is a path function

Ques: Show that pressure is a state function for a gas obeying.

$$\Rightarrow \left( P + \frac{a}{V_m^2} \right) (V_m) = RT \quad [V_m = \text{molar vol}]$$

Ans:

$$P = \frac{RT}{V_m} - \frac{a}{V_m^2}$$

$$\cancel{Q} \quad \cancel{\frac{\partial P}{\partial V_m}}_T = -\frac{RT}{V_m^2} + \frac{2a}{V_m^3}$$

$$\frac{\partial}{\partial T} \left[ \cancel{\frac{\partial P}{\partial V_m}}_T \right] = -\frac{R}{V_m^2} \cancel{+ \frac{2a}{V_m^3}}_T + 0 \quad -(i) \rightarrow \text{LHS}$$

~~$\frac{\partial P}{\partial T}$~~  now,

$$\left( \frac{\partial P}{\partial T} \right)_{V_m} = \frac{R}{V_m}$$

$$\frac{\partial}{\partial V_m} \left[ \left( \frac{\partial P}{\partial T} \right)_{V_m} \right]_T = -\frac{R}{V_m^2} \quad (ii) \Rightarrow \text{RHS}$$

LHS = RHS: Hence Proved.

**NOTE**

$U = f(V, T)$  and  $H = f(P, T)$

for general gas you can use  $dU = nC_V dT$  and  $dH = nC_P dT$  only in case of const. vol.

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const. press.

Q: 10 dm<sup>3</sup> of O<sub>2</sub> at 101.325 kPa and 298 K is heated to 348 K. Assume ideal behaviour and calculate the heat absorbed, over enthalpy ΔH, ΔU of this process at (a) constant pressure (b) const. vol.

$$C_P = C_V + R$$

given  $C_P (J \text{ K}^{-1} \text{ mol}^{-1}) = 25.72 + 0.013 T/\text{K}$   
 $- 3.86 \times 10^{-6} (T/\text{K})^2$

Ans: In both cases

~~$\Delta H = \int nC_P dT$~~

~~$\Delta U = \int nC_V dT$~~

wrong  
 since  $\Delta H$  and  $\Delta U$  are state functions  
 therefore these formulae are valid  
 everywhere (since it doesn't matter  
 what path we choose for a change)

~~$\Delta H = \Delta U + P\Delta V + \cancel{\Delta P}^0$~~ 

work done

~~$\therefore \Delta H = \Delta U$~~

a)  $\Delta H = \int nC_P dT$

$$\Delta H = \Delta U + \cancel{P\Delta V} + \cancel{y\Delta P}^0$$

work

$\therefore \Delta H = q$

NOTE:  $U = f(T)$  and  $H = f(T)$   
for ideal gas

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$$w + \Delta U = q$$

$$\Rightarrow \Delta U = q - w$$

$$\Rightarrow \Delta U = q_v - P(V_2 - V_1)$$

calculate  $V_2, V_1$ , and put here.

b)  $\Delta U = \int n C_V dT$

$$\Delta U = 0 \quad \therefore w = 0$$

$$\therefore \Delta U = q$$

For  $\Delta H$ ,

$$\Delta H = \Delta U + P\Delta V + V\Delta P$$

find this using  
 $PV = nRT$ .

- Relation b/w  $C_p$  and  $C_V$ :

$$C_p - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V - (ii)$$

Now,

$$U = f(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\therefore \left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad (ii)$$

Using (ii) in (i)

$$C_p - C_v = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$\Rightarrow C_p - C_v = \left(\frac{\partial U}{\partial T}\right)_P \left[ \left(\frac{\partial U}{\partial V}\right)_T + P \right] \quad - (iii)$$

NOTE

### HERMODYNAMIC EQUATION OF STATE →

~~U P  
V T~~

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P} \rightarrow \text{remember}$$

∴ in (iii) using thermodynamic eq<sup>n</sup> of state,

$$\Rightarrow C_p - C_v = T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V \quad - (iv)$$

\* ~~C<sub>p</sub> - C<sub>v</sub> = CP - CV~~

$$\therefore \boxed{C_p - C_v = T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V}$$

- general relation  
(valid even  
for solid)

For ideal gas using PV = nRT

$$C_p - C_v = \cancel{T \frac{mR}{P}} \rightarrow \times \frac{mR}{P}$$

$$\therefore \boxed{C_p - C_v = mR} \rightarrow \text{for ideal gas}$$

TUTORIAL

1Q. Show mathematically (not with graph) that the magnitude of work in a reversible isothermal expansion of an ideal gas from pressure  $P_1$ , volume to pressure  $P_2$  and volume  $V_2$  is larger than that in irreversible isothermal expansion against pressure  $P_2$ .

$$\text{Ans. } W_{\text{rev}} = \int P dV$$

$$W_{\text{rev}} = nRT \ln \frac{V_2}{V_1} = nRT \ln \left( \left( \frac{V_2}{V_1} - 1 \right) + 1 \right)$$

$$W_{\text{irr}} = P_2 (V_2 - V_1) = P_2 V_1 \left( \frac{V_2}{V_1} - 1 \right)$$

Ans

$$nRT = P_2 V_1$$

$\therefore$  we need to prove inequality of  $\frac{V_2}{V_1} - 1$  and  $\ln \left( \frac{V_2}{V_1} \right)$

$$\text{Let } \frac{V_2}{V_1} - 1 = n$$

$\therefore$  we have curves  $\ln(1+n)$  and  $n$ .  
And acc. que  $n > 0$   
At 0

$$\ln(1+n) = n$$

But for  $n > 0$ ,  
Differentiating 2 curves

$$\frac{1}{1+n}$$

{ decreases

&amp;

↓ const

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$\therefore$  slope of  $\ln(1+n)$  is  $< 1$  beyond  $n$  than  $n$  for  $n > 0$

$\ln(1+n) < n ; n > 0$

Q.: For an ideal gas  $PV = nRT$ , taking  $V = f(n, P, T)$  verify that  $dV$  is an exact differential

Ans.:

$$V = f(n, P, T)$$

To prove:

$$dV = \left(\frac{\partial V}{\partial n}\right)_{P,T} dn + \left(\frac{\partial V}{\partial P}\right)_{n,T} dP + \left(\frac{\partial V}{\partial T}\right)_{P,n} dT$$

For proof,

$$\frac{d}{dP} \left[ \left( \frac{\partial V}{\partial n} \right)_{P,T} \right] = \frac{d}{dn} \left[ \left( \frac{\partial V}{\partial P} \right)_{n,T} \right]$$

&

$$\frac{d}{dT} \left[ \left( \frac{\partial V}{\partial P} \right)_{P,n} \right] = \frac{d}{dT} \left[ \left( \frac{\partial V}{\partial T} \right)_{P,n} \right]$$

&

$$\frac{d}{dT} \left[ \left( \frac{\partial V}{\partial n} \right)_{P,n} \right] = \frac{d}{dn} \left[ \left( \frac{\partial V}{\partial T} \right)_{P,n} \right]$$

Prove it.

Q.: A gas contained in a cylinder with a movable piston on which a heavy block is placed. Suppose the region outside the chamber is evacuated and the total mass of the block and the movable piston is 102 kg. When 2140 J heat flows into the gas, the internal E of gas increased by 1580 J. What is the distance S through which piston rises. (Ans: 0.54 m)

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NOTE:

Isothermal compressibility  $\rightarrow$   
compressibility at const.  $T$

$$K_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

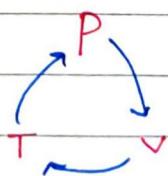
Thermal expansion coefficient  $\rightarrow$   
expansion capacity at const.  $P$

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

Together, these 2 coefficients determine  
thermodynamic state of a system.

→ CYCLIC RULE →

- For interdependent state variables like  $P, V$ , and  $T$ , we can write



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

$$\left[ \left( \frac{\partial P}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial T}{\partial P} \right)_V + 1 = 0 \right]$$

look at  
proof in  
KL Kapoor.

NOTE:  $z = f(x, y)$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

ruler's reciprocity rule

$\left(\frac{\partial z}{\partial x}\right)_y$	$= \frac{1}{\left(\frac{\partial x}{\partial z}\right)_y}$
--	--

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∴ from cyclic rule,

$$\left(\frac{\partial P}{\partial T}\right)_V = - \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad (i)$$

• coming back to  $C_p, C_v$  relation

$$C_p - C_v = T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$$

From (i)

$$C_p - C_v = -T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$\Rightarrow C_p - C_v = -T \frac{\left[\left(\frac{\partial V}{\partial T}\right)_P\right]^2}{\left(\frac{\partial V}{\partial P}\right)_T}$$

$$\Rightarrow C_p - C_v = \frac{\sqrt{T} \propto^2}{K_T}$$

for any ~~given~~ material (solid, liq, gas)

And  $\sqrt{T}, \propto^2$  and  $K_T$  are all positive ∴  $C_p$  is always greater than  $C_v$

cubical exp = thermal exp.

Q→ The coefficient of cubical expansion  $\alpha$  of a metal at 293 K is  $21.3 \times 10^{-6} \text{ K}^{-1}$  and compressibility coefficient  $K_T = 1.56 \times 10^{-1} \text{ Pa}^{-1}$  the molar mass of metal is  $M = 63.55 \text{ g mol}^{-1}$  and density  ~~$\rho = 0.97 \text{ g/cm}^3$~~

calculate  $C_p - C_v$  of the metal at 293 K (for 1 mol) (Ans:  $0.558 \text{ J mol}^{-1} \text{ K}^{-1}$ )

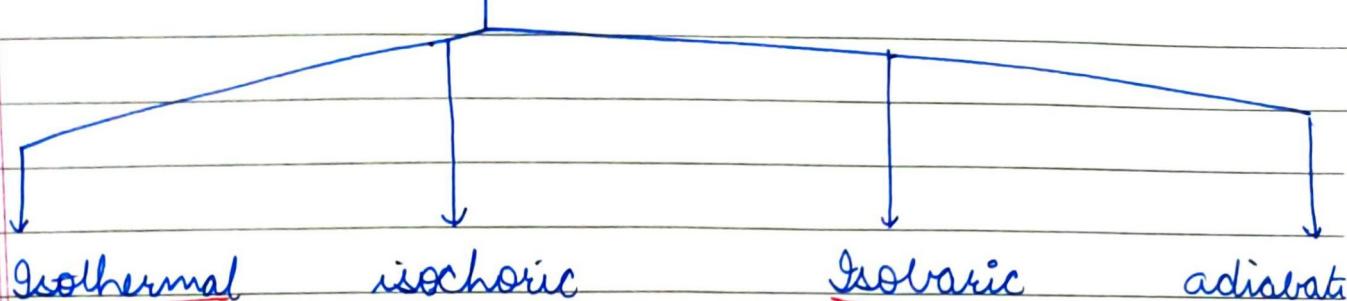
$$\text{Ans: } C_p - C_v = \frac{V T \alpha^2}{K_T}$$

$$\therefore V = \frac{63.55 \times 0.97}{0.97} \text{ cm}^3$$

→ SUMMARY OF PROCESSES IN FIRST LAW →

(for ideal gases)

REVERSIBLE



$$\Delta U = 0$$

$$W = nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$q = nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta H = 0$$

$$\Delta U = nC_V \Delta T$$

$$W = 0$$

$$q = nC_V \Delta T$$

$$\Delta H = \Delta U + V \Delta P$$

$$\Delta U = nC_V \Delta T$$

$$W = P(V_2 - V_1)$$

$$q = \Delta U + W$$

$$\Delta U = -W$$

$$q = 0$$

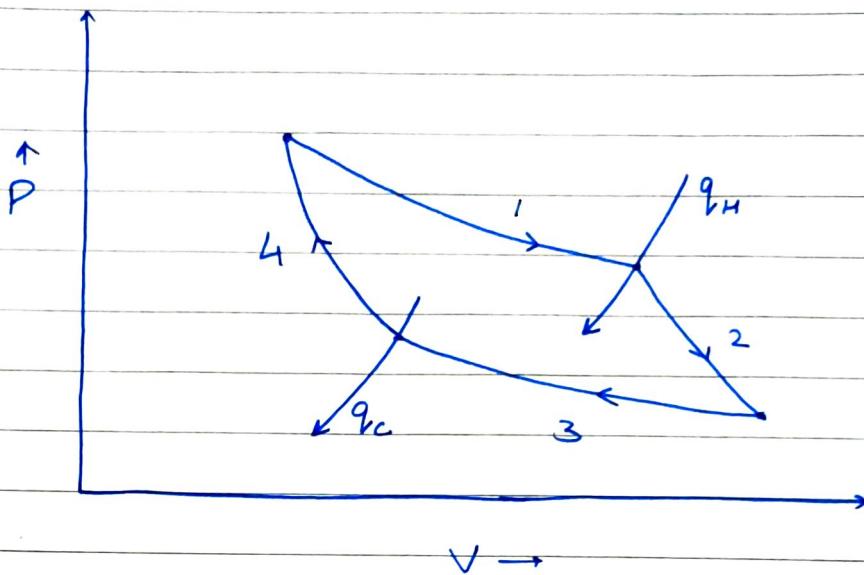
$$\Delta H = nC_p \Delta T$$

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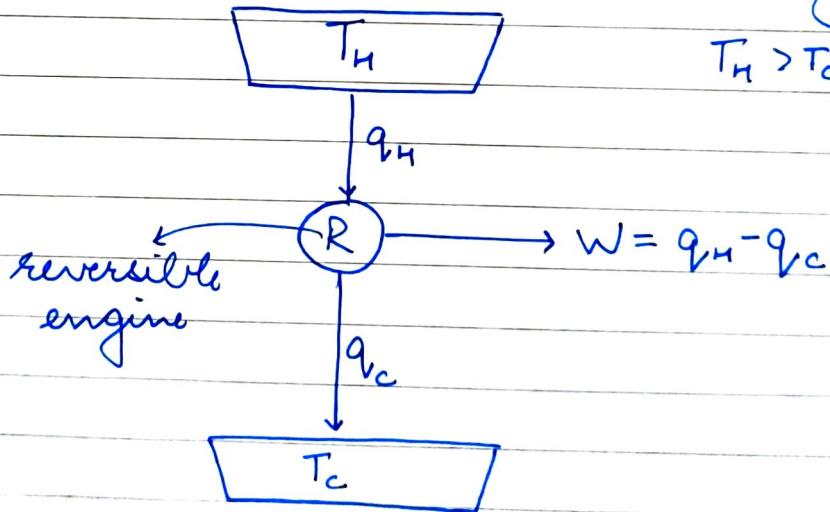
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## \* → CARNOT ENGINE



- We call a system following Carnot cycle a Carnot Engine or Carnot System.
- Representation of Carnot engine



$$\eta = \frac{q_H - q_C}{q_H} = \frac{T_H - T_C}{T_H}$$

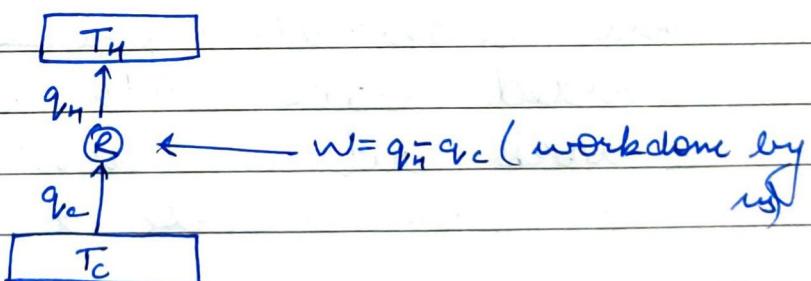
- Kelvin - Planck statement:

It is impossible for a system / engine operating in a cycle and connected to a single heat reservoir to produce a positive amount of work on the surroundings.

- Clausius statement:

It is impossible for a cyclic process to convert heat into work without simultaneous transfer of heat from a body of higher temp. to lower temp. or vice versa.

NOTE: In a refrigerator, we reverse the direction of heat flow



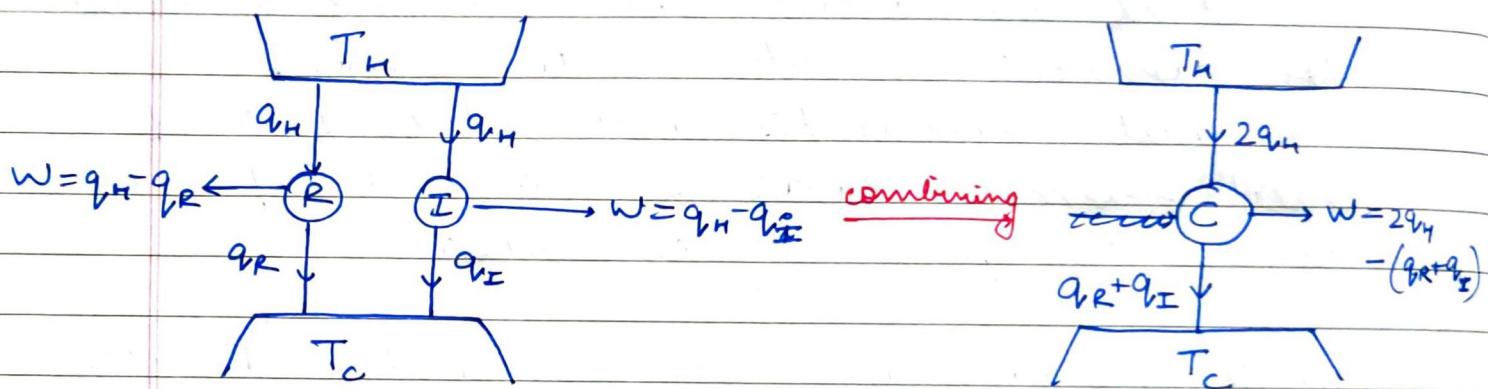
→ COMPARISON B/W REVERSIBLE & IRREVERSIBLE CARNOT ENGINE →

- A reversible process has a differentiable and continuous graph of individual steps
- Even if a single step in the cycle is irreversible, the whole cycle is irreversible.

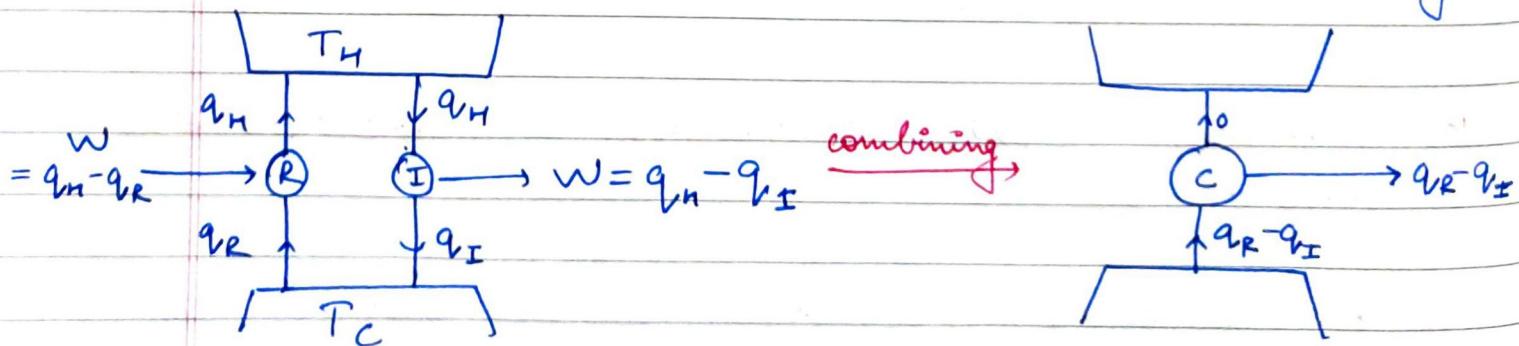
NOTE:

Irreversible denotes that the amount of work obtained on a change of state is different from the amount of work needed to bring it back to initial position.

- Consider a rev. & irr. system (engine) working b/w the same reservoirs.



Now a reversible ~~process~~<sup>cycle</sup> can be exerted back with same amount of work but an irreversible cycle can't.  
∴ we now reverse the reversible engine



According to Clausius statement, we know that all heat from a single reservoir can never be converted into work.

∴ if we carefully see above,

$$q_R < q_I$$

(i)

if we look at the efficiencies of reversible and irreversible process as above,  
we needed to prove

$$\eta_R > \eta_I$$

$$\Rightarrow \frac{w_R}{q_H} > \frac{w_I}{q_H}$$

$$\Rightarrow w_R > w_I$$

$$\Rightarrow q_H - q_R > q_H - q_I$$

$$\Rightarrow q_R < q_I$$

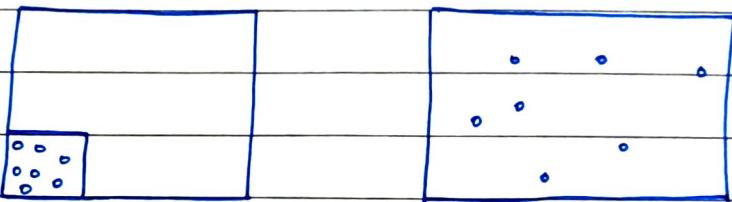
as written in (i)

Hence proved.

PTO:

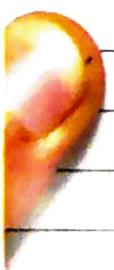
→ ENTROPY →

- Entropy is a measure of number of possible microstates of a system.
- Consider 7 molecules in 2 boxes. In box 1, it ~~is~~ is confined to a specific volume.



NOTE: **Phase Space:** It is a six dimensional space for a system consisting of 6 coordinates (independent of each other)  
 $\equiv (x, y, z, p_x, p_y, p_z)$

- For any system, the greater the extent of phase space, greater is the entropy. e.g. - in above case, the phase space for box 2 is surely greater than box 1. ∴ entropy is greater.



NOTE: Entropy can be calculated absolutely as in

$S = k_B \ln \sigma$  → this is a part of 2nd law  
 where  $\sigma$  is probability of getting a specific microstate in phase space.

e.g. lets say for a dice,

$$S = -k_B \ln (\frac{1}{6})$$

## • Defining entropy

$$\eta_{rev} = \frac{W}{q_H} = \frac{T_H - T_C}{T_H}$$

For reversible Carnot cycle

$$\Rightarrow \frac{q_H - q_C}{q_H} = \frac{T_H - T_C}{T_H}$$

$$\Rightarrow \frac{q_H}{T_H} = \frac{q_C}{T_C}$$

$$\Rightarrow \frac{q_H}{T_H} + \left( \frac{q_C}{T_C} \right) = 0 \quad ]$$

$$\Rightarrow \oint \frac{dq}{T} = 0$$

This step comes from the fact that reversible Carnot cycle can be divided into infinite Carnot cycles with the same equations as valid.

- For irreversible process, we can write

$$\eta_I = \frac{w}{q_H} = \frac{q_H - q_C}{q_H} = 1 - \frac{q_C}{q_H}$$

$$\eta_R = \frac{T_H - T_C}{T_H} = 1 - \frac{T_C}{T_H}$$

& we know

$$\eta_R > \eta_I$$

$$\Rightarrow 1 - \frac{T_C}{T_H} > 1 - \frac{q_C}{q_H}$$

NOTE:

$T_C$  &  $T_H$  for rev. & irrev. process are same

$$\Rightarrow \frac{T_C}{q_C} < \frac{T_H}{q_H}$$

$$\Rightarrow \frac{q_H}{T_H} + \left( -\frac{q_C}{T_C} \right) < 0$$

$\therefore \boxed{\int \frac{dq_I}{T} < 0}$  *Clausius inequality*

- Consider a general process of conversion from  $A \rightarrow B$  (irreversibly) & we

$A \xrightarrow{\text{Irreversible, } B}$

$\xleftarrow{\text{Reversible}}$

$$\int \frac{dq_I}{T} = \int_A^B \frac{dq_{A \rightarrow B}}{T} + \int_B^A \frac{dq_{B \rightarrow A}}{T} < 0$$

↓ rev      ↓ rev

Clausius Ineq.

$$\int_A^B \frac{dq_{VA \rightarrow B}}{T} < \int_A^B ds$$

$$\Rightarrow \Delta S > \int_A^B \frac{dq_{VA \rightarrow B}}{T}$$

for rev                          for irreversible

For an isolated system,  $\underline{q=0}$

~~implies~~

$$\therefore \boxed{\Delta S > 0}$$

i.e. entropy of an isolated system is always increasing

## → CONDITIONS OF SPONTANEITY AND EQUILIBRIUM →

- To find out what characteristics distinguish irreversible & reversible transformation, we begin by asking what relation exists b/w entropy change in a transformation & the irreversible heat flow that accompanies it.
- In a reversible trans. at every stage the system departs from equilibrium only infinitesimally but in irreversible trans., at no point the system exists in equilibrium. ∴ irrev. transformation is a spontaneous trans. while reversible transformation is basically equilibrium
- For a spontaneous process,

$$Tds > dq \quad (\text{as seen earlier})$$

$$\Rightarrow Tds - dq > 0$$

$$\Rightarrow Tds - dU - dW > 0 \quad \text{thus spontaneous}$$

$$\Rightarrow Tds - dU - dw_m - dw_{av} > 0$$

[  $dw_m$  = mechanical work ]

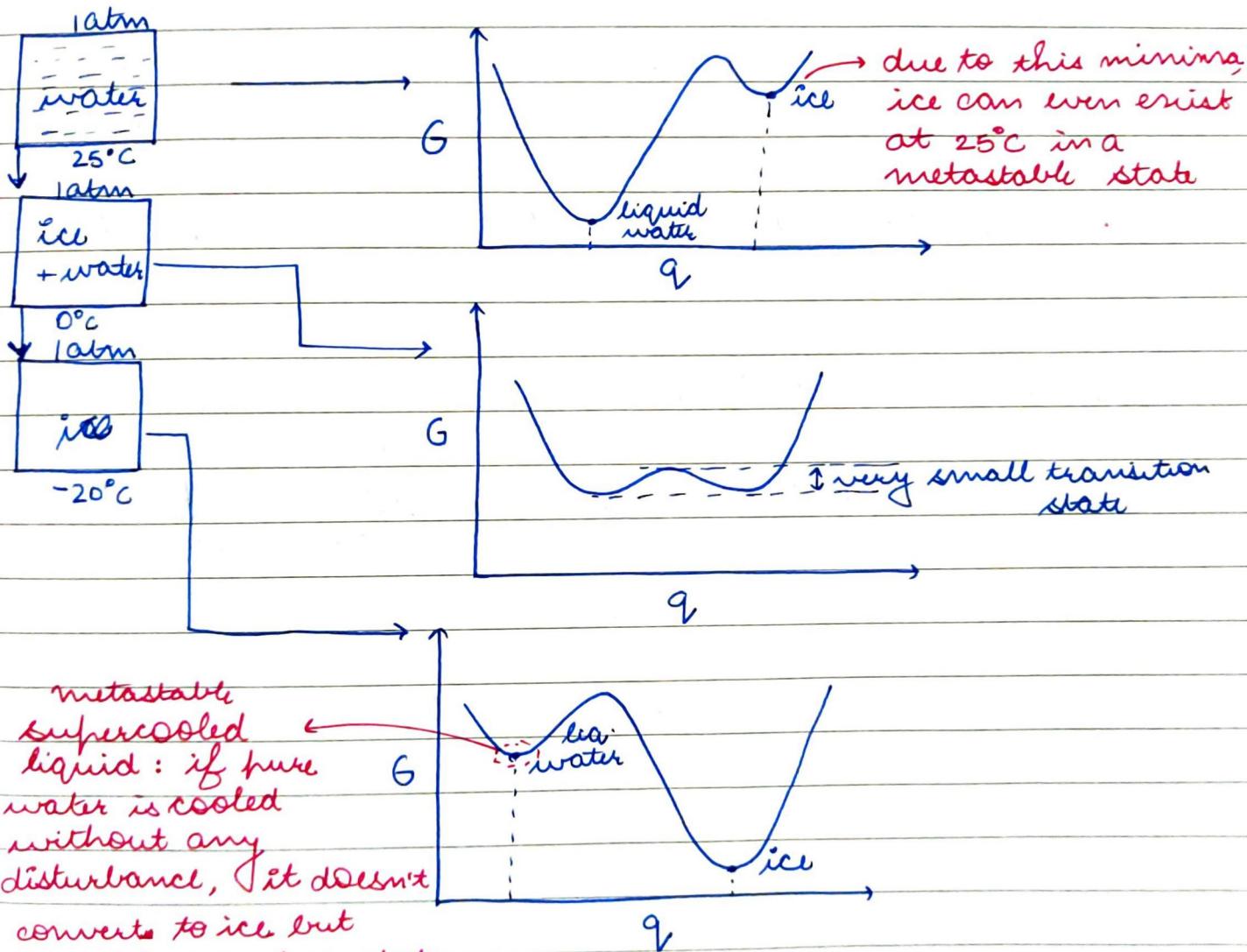
$dw_{av}$  = available work }

for any general process,

$$\therefore TdS - dU - dW_m - dW_{av} \geq 0$$

$>$  for spont.  
 $=$  for reversible

- Consider phase transition in water



Here  $q$  is tetrahedral order parameter, a parameter which can distinguish b/w water & ice. (ice has a higher tetrahedral arrangement than water (liq))

NOTE

- Here criteria of spontaneity is  $\Delta G$  but remember that  $\Delta G$  is a parameter only at const.  $T$  and  $P$ .
- But the general condition of spontaneity is what we had written earlier.

$$TdS - dU - dW_m - dW_{av} \geq 0 \quad (i)$$

- Spontaneity conditions (all derived from i)

### 1. for Isolated System:

$$dU = 0 \quad (\text{since } dT = 0, dV = 0)$$

$$dW = 0 \quad (\text{since } dP = 0, dQ = 0) \\ \text{isolated system}$$

$$\therefore TdS \geq 0$$

$$\Delta S \geq 0$$

## TUTORIAL

Ques:

Show mathematically that the magnitude of the work in reversible expansion of an ideal gas from  $P_1$  pressure and volume  $V_1$  to pressure  $P_2$  and volume  $V_2$  is larger than the corresponding work involved in an irreversible expansion against a constant pressure  $P_2$ .

~~Ans.~~Ans:

Since nothing about the process is given, we take the equation for process to be

$$PV^n = \text{const.} \Rightarrow V = \frac{C}{P^{1/n}}$$

$$\therefore \cancel{\int dP} + nV^{n-1} P dV = 0$$

$$\Rightarrow \cancel{nV^{n-1} P dV} = - \cancel{V^n dP}$$

$$\Rightarrow P dV = - \frac{V^n dP}{n}$$

~~W = C ∫ P dV~~

$$\therefore W = - \int \cancel{\frac{V^n dP}{n}} = - \int \cancel{\frac{C^{1/n}}{nP^{1/n}}} dP = - \frac{1}{nC^{1/n}} \left[ P^{n+1} \right]_{P_1}^{P_2}$$

$$\therefore W = - \frac{1}{nC^{1/n}} \left( P_2^{n+1} - P_1^{n+1} \right)$$

$$w_{\text{ext}} = \int P dV = \int \frac{C}{V^n} dV = \frac{C}{1-n} \left( V_2^{1-n} - V_1^{1-n} \right) = \frac{P_2 V_2 - P_1 V_1}{1-n}$$

$$w_{\text{ext}} = P_2 (V_2 - V_1)$$

$n > 1$	$n = 1$	$n < 1$

Ques: The coefficient of cubical expansion  $\alpha$  of a metal at 293 K is  $21.3 \times 10^{-6} \text{ K}^{-1}$  and the compressibility coeff.  $K_T = 1.56 \times 10^{-11} \text{ Pa}^{-1}$ . The molar mass of metal is  $63.55 \text{ g/mol}^{-1}$  and its density is  $0.97 \text{ g/cm}^3$ . Calculate  $C_p - C_V$  at 293 K.

Ans.

$$C_p - C_V = \frac{V_m T \alpha^2}{K_T}$$

$$V_m = \frac{63.55}{0.97} \text{ cm}^3 = 65.5154 \times 10^{-6} \text{ m}^3$$

$$\therefore C_p - C_V = \frac{65.5154 \times 293 \times (21.3)^2 \times 10^{-18}}{1.56 \times 10^{-11}}$$

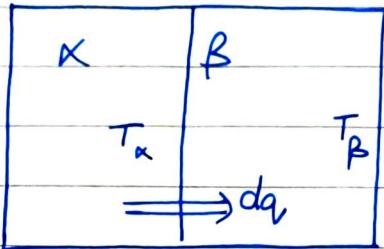
$$= 0.5583 \cancel{\text{J}}$$

Ques:

Derive T - V equation for adiabatic expansion of van der waal's gas.  
[KL Kapoor Vol 2 page 94]

- for an isolated system,  
 $\Delta S > 0$

Consider a box with 2 compartments and let's say  $dq$  heat gets transferred



$$dS \text{ for } x \quad dS_x = -\frac{dq}{T_x}$$

$$dS \text{ for } B \quad dS_B = \frac{dq}{T_B}$$

$$dS_{\text{total}} = dS_x + dS_B = -\frac{dq}{T_B} - \frac{dq}{T_x}$$

For spontaneity

$$\frac{dq}{T_B} - \frac{dq}{T_x} > 0$$

$$\frac{1}{T_B} - \frac{1}{T_x} > 0$$

$$\therefore T_x > T_B$$

2. for constant  $T$  (isothermal)

we write for spontaneity

$$\text{with } TdS - dU - dW_m - dW_{\text{ext}} \geq 0$$

Since temp is constant, we can rewrite it as

$$-d(U-TS) - dW \geq 0$$

$$\Rightarrow d(U-TS) + dW \leq 0$$

$$\Rightarrow \boxed{dA + dW \leq 0}$$

where

$A = \underline{\text{Helmholtz}}$

Free energy

$$\Rightarrow dA \leq -dW$$

condition  
of spontaneity at const.  $T$

when  $w=0$

$$\Rightarrow \boxed{dA \leq 0}$$

condition of spontaneity  
at const  $T$  and zero  $w$

e.g. in a pressure cooker (closed vessel), during phase transition,  $T$  is constant and  $P$  is ~~const~~ not. Also  $w=0$ .  $\therefore dA \leq 0$  is criteria of spontaneity there.

3. for constant  $T$  and  $P$  (general condition in any phase transition)

we write for spontaneity

$$TdS - dU - dW_m - dW_{\text{ext}} \geq 0$$

$$\Rightarrow TdS - dU - pdV - dW_{\text{ext}} \geq 0$$

since  $P$  is const. &  $T$  is const., we can write it as

$$-d(U-TS) - d(pV) > dW_{av}$$

$$\Rightarrow d(U-TS+pV) \leq -dW_{av}$$

$$\text{Since } U+pV = H$$

$$\Rightarrow d(H-TS) \leq -dW_{av}$$

$$\Rightarrow dG \leq -dW_{av}$$

$G$  = Gibbs free energy

If  $W_{av} = 0$

$$\Rightarrow dG \leq 0$$

condition of spontaneity  
when  $T$  &  $P$  are constant

condition of spontaneity  
at const.  $T$  and  $P$  and  
 $W_{av} = 0$

- ∴ Our equations for spontaneity

- $TdS - dU - dW_m - dW_{av} > 0 \rightarrow$  Parent/master eq'
- $dS > 0$   $\xrightarrow{(B_1)}$  Isolated
- ~~$dA \leq 0$~~   $\xrightarrow{(B_2)}$  const  $T$   $A = U - TS$
- $dG \leq 0$   $\xrightarrow{(B_3)}$  const  $T$  and  $P$   $G = H - TS$

2 classes missed



## → CONDUCTANCE IN ELECTROLYTE SOLUTION

- \* **Current (I):** quantity of electric charge that passes through a point in unit time
- \* **Current density (J):** quantity of electric charge that passes a point in unit time in unit area  
 also called electric flux

$$I = \frac{q}{t}$$

and

$$J = \frac{I}{A}$$

(i)

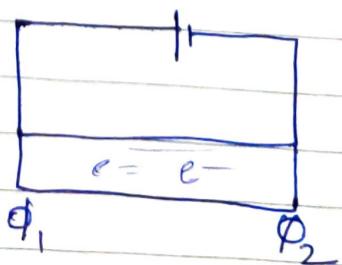
### NOTE:

Consider water flowing from a higher point to a lower point, then the current density of water (amount of water / time / area) will depend on the difference in heights of 2 points, i.e. its dependent on the pot. diff. b/w 2 points as:

- For conductors →

$$J \propto -\frac{d\phi}{dx} \rightarrow \text{potential}$$

Same is the case here.



$$\phi_1 > \phi_2$$

$$J \propto -\frac{d\phi}{dx}$$

$$\Rightarrow J = -K \frac{d\phi}{dx}$$

where  $K$  is a constant called conductivity

$$\Rightarrow J = KE$$

electric field

$$\Rightarrow J = K \frac{\Delta \phi}{l} \rightarrow \text{heat diff.}$$

(ii)

From (i) & (ii)

$$J = K \frac{\Delta \phi}{l} = \frac{I}{A}$$

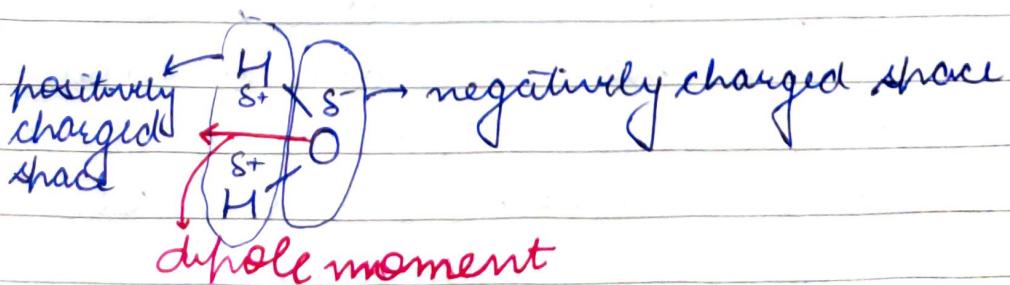
$$\Rightarrow \Delta \phi = \frac{I}{K} \frac{l}{A}$$

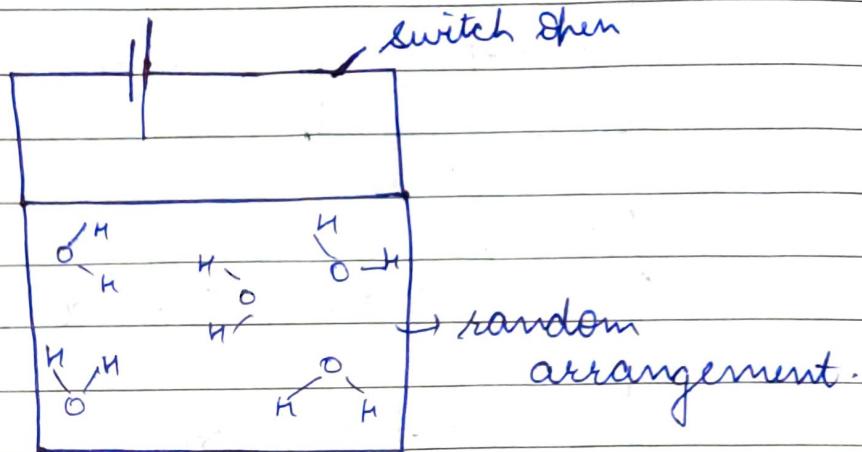
$$\Rightarrow \Delta \phi = I \frac{l}{A}$$

$$\Rightarrow \boxed{\Delta \phi = IR}$$

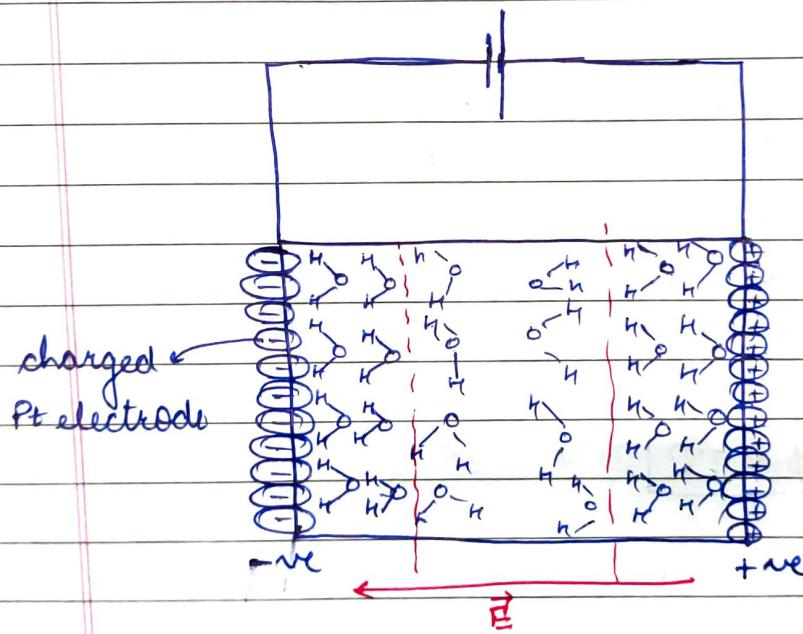
• For electrolytes →

• consider pure water in an electrolytic cell →



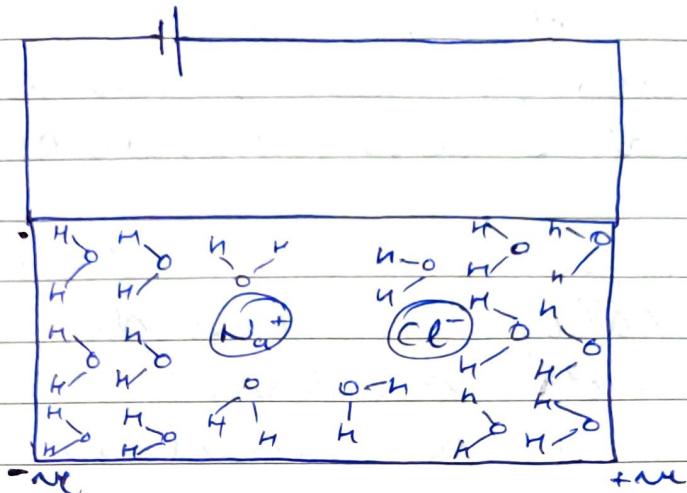


when we close the switch,



*note:* We see above that upto two layers of water molecules is in perfect alignment acc. to the charges on electrodes. But the inner layers have random arrangement. This is due to the screening effect of the <sup>aligned</sup> layers of water. The electric field weakens in the middle region. The reason for this randomness is entropy -

- now consider we add a solute to water,



For conductors we have  $I = \frac{\Delta\phi}{R}$

but it's not valid for electrolytes.

For electrolytes,  $I$  certainly increases with  $\Delta\phi$ , but there are a lot of resistive factors as:

- friction in ion's movement due to solvent for +ve solvent friction emanates from the water surrounding it
- Attraction b/w opposite charges (eg-  $\text{Na}^+$  and  $\text{Cl}^-$ )
- Friction because of Brownian motion (random walk)

The natural tendency of the ions is to move randomly.

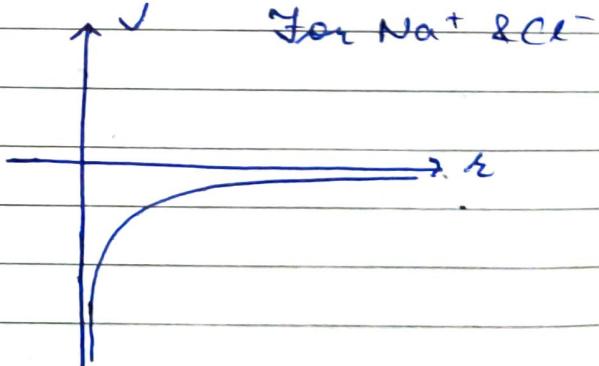
## → KÖLRAUSCH'S LAW OF INDEPENDENT MIGRATION

- It states that the total conductivity of the electrolyte soln is the sum of individual ions' conductivities.
- \* Applicable for infinitely diluted solution  
(Theoretically we consider it to be  $1: 6 \times 10^{23}$  dilution)  
we do this to neglect the interaction b/w ions
- Consider  $\text{Na}^+$  &  $\text{Cl}^-$  in aq. soln. Then they have an attractive potential

$$\nabla = \frac{q_1 q_2}{4\pi \epsilon_0 r}$$

$$\nabla = \frac{q_1 q_2}{r}$$

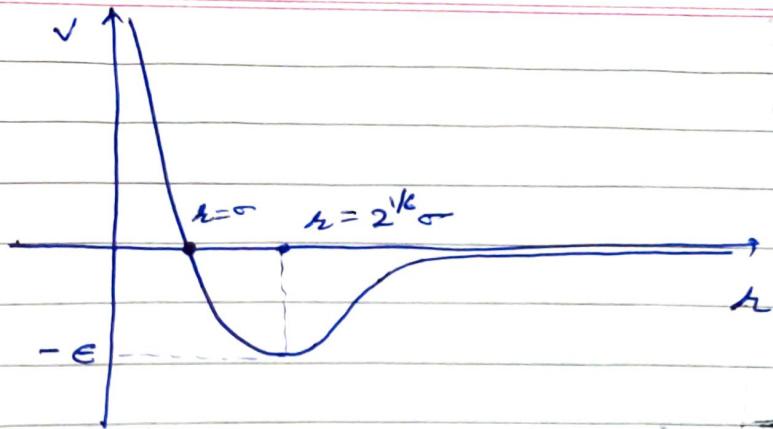
take  $\epsilon_0$  as 1 for vacuum (relatively)



- If we take any general molecule, it has interactions between atoms (due to electrons governed by Lennard Jones potential)

$$\nabla_{ij} = 4e \left[ \left( \frac{r}{r_0} \right)^{12} - \left( \frac{r}{r_0} \right)^6 \right]$$

If we plot it, we get,



NOTE: Lennard Jones is derived from quantum mechanical model of atomic interactions.

- Also apart from electrostatic interactions, we have ion dipole interaction

$$V = \frac{\mu q_1}{r^2}$$

but this potential is in general very small (negligible)

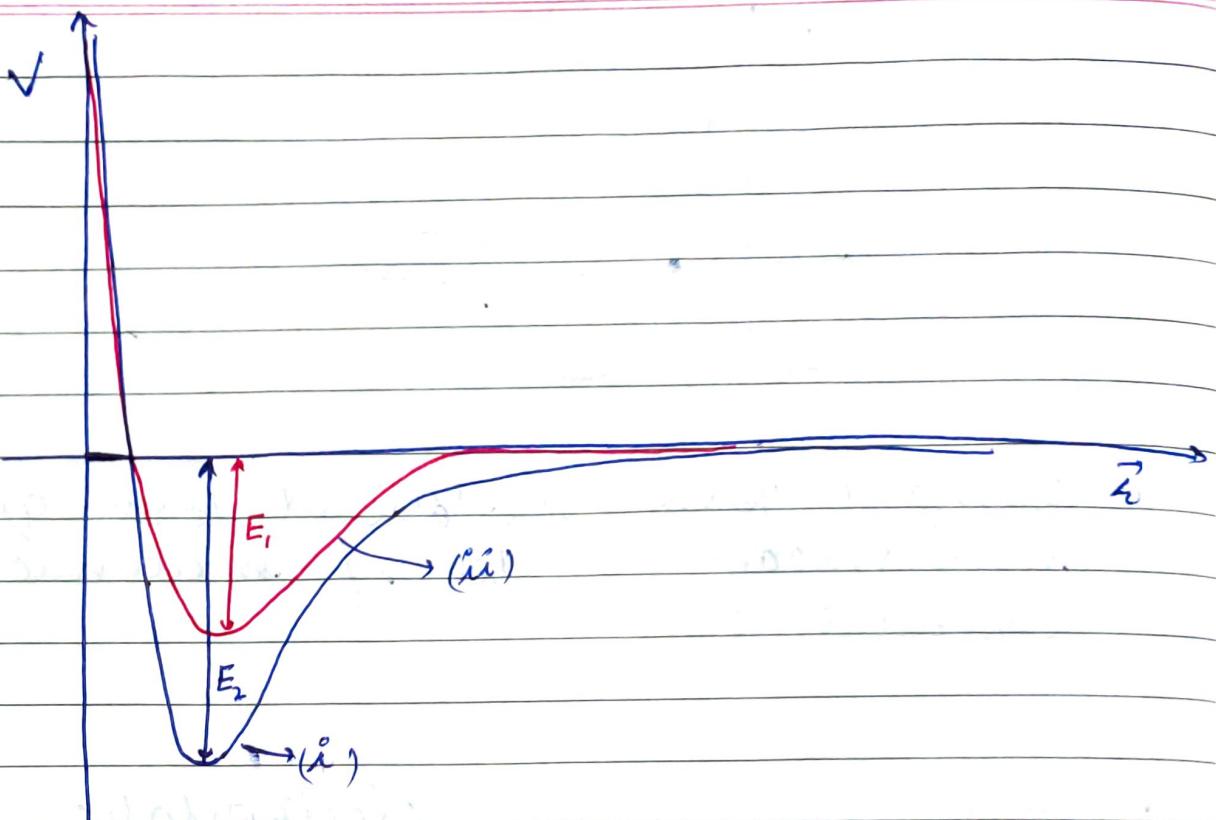
- ∴ total V governing  $\text{Na}^+$  &  $\text{Cl}^-$  interac.

$$V = \frac{q_1 q_2}{r} + 4\epsilon_{\infty} \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad \text{-(i) without water}$$

$$V = \frac{q_1 q_2}{\epsilon r} + 4\epsilon_{\infty} \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad \text{-(ii) in water (neglecting ion dipole interaction)}$$

is close to 80

If we plot these two, we get



$E_1$  = energy to separate  $\text{Na}^+$  &  $\text{Cl}^-$  in  $\text{H}_2\text{O}$

$E_2$  = energy to separate  $\text{Na}^+$ ,  $\text{Cl}^-$  otherwise

Since water decreases the  $E$  to such an extent,  $\therefore$  the  $\text{Na}^+$  &  $\text{Cl}^-$  easily dissociate in water & remain separated.

- Now note carefully that if we have a high conc. of salt in water, there will be some atomic interaction involved b/w  $\text{Na}^+$  &  $\text{Cl}^-$  atoms as per the graph above.  $\therefore$  Kohlrausch's law won't hold there. But for infinite dilution, it's almost equivalent to the case where we have  $\text{Na}^+$  &  $\text{Cl}^-$  individually in water.  $\therefore$  in such case, we can

Simply add their conductivities.



$$(\gamma_+)(z+) + (\gamma_-)(-z) = 0$$

electrolytic neutrality

- we write ~~conductivity~~ <sup>conductance</sup> as:

$$K = N_+ u_+ z_+ e + N_- u_- z_- e$$

→ velocity of cations  
 ↓ no. of cations/vol      ↓ no. of anions/vol  
 ↓ no. of cations/vol      ↓ charge on each cation.

where

$$N_+ = N_A \gamma_+ C$$

→ stoichiometry  
 → concentration  
 ↓ avogadro's number

$$N_- = N_A \gamma_- C$$

$$\Rightarrow K = (\gamma_+ u_+ z_+ + \gamma_- u_- z_-) \cdot F \cdot C$$

where  $F = e N_A$

↓ eq<sup>n</sup> for Kohlrausch's law

- we can also write the molar ~~conductivity~~ <sup>conductance</sup>

$$\Lambda = \frac{K}{C}$$

**A**

$$\Lambda = (\gamma_+ u_+ z_+ + \gamma_- u_- z_-) F$$

$$\Rightarrow \Lambda = \gamma_+ (u_+ z_+ F) + \gamma_- (u_- z_- F)$$

↓  
molar  
conductance  
of cations

↓  
molar  
conductance of  
anions

$$\Rightarrow \Lambda^\circ = \underbrace{\gamma_+ \lambda_+^\circ}_{\text{cation}} + \underbrace{\gamma_- \lambda_-^\circ}_{\text{anion}}$$

### $\rightarrow$ TRANSFERENCE NUMBER

- It is denoted by ' $t_k$ ' where 'k' is ~~an ion~~ an ion.
- It is the fraction of current carried by constituent ions.

If  $\Lambda$  is the molar conductance of electrolyte soln., then

$$t_+ = \frac{\lambda_+}{\Lambda}$$

$$t_- = \frac{\lambda_-}{\Lambda}$$

We could have taken  $\gamma_+ \lambda_+$  but here we are calculating  $t$  for an ion so we take  $\frac{\lambda_+}{\Lambda}$  which would give us the value of fraction in per mol of ion.

If we take  $t$  for all cations / anions,

$$t_+ = \frac{\gamma_+ \lambda_+}{\zeta}$$

$$t_- = \frac{\gamma_- \lambda_-}{\zeta}$$

$$\delta \lambda_r = F u_r z_r$$

$$\therefore t_+ = \frac{\gamma_+ z_+ u_+}{\gamma_+ z_+ u_+ + \gamma_- z_- u_-}$$

$$t_- = \frac{\gamma_- z_- u_-}{\gamma_+ z_+ u_+ + \gamma_- z_- u_-}$$

In many cases

$$|\gamma_+ z_+| = |\gamma_- z_-|$$

$$\Rightarrow t_+ = \frac{u_+}{u_+ + u_-}$$

$$\& t_- = \frac{u_-}{u_+ + u_-}$$

NOTE: In  $\text{NaCl}(\text{aq.})$ ,  $\text{H}_2\text{O}$  molecules transfer hindrance to the motion of  $\text{Na}^+$  &  $\text{Cl}^-$  since  $\text{H}_2\text{O}$  molecules don't move towards electrodes. But in molten  $\text{NaCl}$   $\text{Na}^+$  &  $\text{Cl}^-$  both move towards electrodes & rather lower resistance is provided  $\therefore$  higher conductivity.

NOTE:

Brownian motion is governed by certain rules. Research still goes on in this field. Brownian motion increases conductivity. Einstein gave an eq<sup>n</sup> governing ~~is~~ Brownian motion

$$D = \frac{K_B T}{6\pi \eta a}$$

Einstein Stokes equation.

Diffusion coefficient

Greater the D greater is the conductivity.