

# PHYSICAL CHEMISTRY II

CORE XIII - PAPER XI

## UNIT-I

### Electrical properties of molecules

Electrical properties of molecules: Molar polarization, Orientation polarization and Distortion polarization polar and non-polar molecules. Determination of dipole moment of polar gases, liquids and solids, Applications of dipole moment in the study of simple molecules.

## UNIT - II

### Magnetic properties of molecules.

Magnetic properties of molecules: Molar polarization. Meaning of the terms magnetic susceptibility, Magnetic moment, diamagnetism, paramagnetism and ferromagnetism, Determination of magnetic susceptibility by Gouy's method. Application of magnetic properties in solving structural problems.

## UNIT - III

### Order and Molecularity of Reactions

Empirical laws and experimental aspects, Rate laws, Stoichiometry, Order and molecularity of reactions - Setting up and solving simple differential equation for first order, second

order, third order and zero order reactions.  
Characteristics of I, II, III and zero order reactions.  
Determination of order of reactions.

UNIT-IV

### Kinetics of Reactions

Experimental techniques involved in following kinetics of reaction, volumetry, manometry, polarimetry and colorimetry, typical examples for each of the techniques, Theoretical aspects, Effects of temperature on rate constant. The activation energy. The collision theory of reaction rates and its limitation. Lindemann theory of unimolecular reaction. The theory of Absolute reaction rates. Comparison of the collision theory with the Absolute reaction rate theory.

UNIT-V

### Photochemical Reactions

Thermal chain reaction  $H_2/Br_2$  reaction.

Kinetics of photochemical reactions. Absorption of light and photochemical process. The Stark-Einstein law of photochemical equivalence

photochemical chain reaction  $H_2/Br_2$  reaction.

Quantum yield of photochemical reactions.

Comparison of thermal & photochemical kinetics of  $H_2/Br_2$  reaction. Photosensitized reactions,

Fluorescence, phosphorescence and chemiluminescence.

Electric properties of molecules:

✓ polarisation of molecules in an electric field

\* An atom of a molecule is neutral it is composed of positively charged nuclei and negatively charged electrons.

Distortion polarisation:

\* When an atom or a molecule is placed in an electric field between two charged plates, the positively charged nuclei directed towards negatively plate and the electrons directed towards the positive plate. This is called electric distortion or polarization of the molecule.

\* Electric distortion causes an electric dipole i.e. positive charge at one end and negative charge at the other end.

\* This dipole is temporary because when the electric field is removed the molecules lost their dipole and comes to its "original state" this type of polarization is called induced polarization or distorted polarization.

Molar - polarization for non polar molecules!

✓ In the case of induced polarization the positive charge (+z) one end must be equal to the negative charge (-z) at the other end.

If 'd' or 'x' is the distance separating the two induced charges, the induced dipole moment.

$\mu_i$  is given by,

$$\mu_i = zL(\text{or}) \mu_i = zd \quad \text{--- (1)}$$

The magnitude of the induced dipole moment depends upon the strength of the electric field applied.

If 'E' is the strength of the electric field then

$$\mu_i = \alpha E \quad \text{--- (2)}$$

where  $\alpha$  is a constant called polarisability of the molecule. It is related to dielectric constant ( $\epsilon_r$ ) of the medium by the following equation.

$$\left( \frac{\epsilon_r - 1}{\epsilon_r + 2} \right) \frac{M}{\rho} = \frac{4}{3} \pi N_A \alpha \quad \text{--- (3)}$$

where M is the molar mass and  $\rho$

$\rho$  is the density of the substance

Molar polarization  
(Clausius - Mosotti introduced a quantity called molar polarization ( $p_m$ ) and <sup>H<sub>2</sub></sup> defined it as.

$$p_m = \left( \frac{\epsilon_r - 1}{\epsilon_r + 2} \right) \frac{M}{\rho} \quad \text{--- (4)}$$

Here the molar polarization is called induced molar polarization ( $p_i$ ) Hence.

$$p_i = \frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho} = \frac{4}{3} \pi N_A \alpha \quad \text{--- (5)}$$

This equation is known as Clausius - Mosotti equation. Equ (4) has the unit of m/e<sub>v</sub> volume [since  $\epsilon_r$  is more number]

Molar polarization for polar molecules orientation of polar molecules in an electric field.

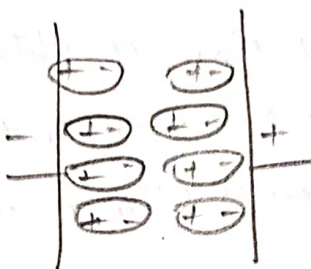
- \* polar molecules are permanent dipoles.
- \* The permanent dipoles are oriented in a random manner.

\* When polar molecules are placed in an electric field, the molecules rotate and orient themselves.

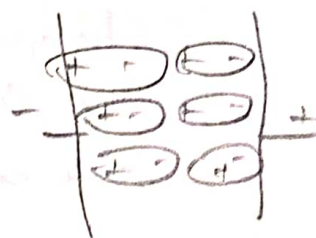
\* The perfect arrangement is resisted by thermal agitation of the molecules and hence the molecules are oriented in an intermediate position.



Orientation of electric dipoles in the absence of electric field.



Tendency of electric dipoles to rotate in an electric field.



Actual alignment of electric dipoles in an electric field.

In the case of molecules which do not have a permanent dipole (such as  $O_2, H_2, CH_2, CCl_4$ ) the molar polarization is only the induced polarization ( $p_i$ )

Orientation polarization: In the case of polar molecules ( $HCl, CH_3Cl, H_2O$ ) the molar polarization is the sum of  $p_i + p_o$  where  $p_i$  is the molar induced polarization and  $p_o$  is the molar orientation polarization.

$$P_m = \frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho} = p_i + p_o \quad \text{--- ①}$$

Debye showed that molar orientation polarization

$$P_o = \frac{4}{3} \pi N_A \left( \frac{\mu^2}{3kT} \right) \quad \text{--- ②}$$

where  $\mu$  is permanent dipole moment of the molecules.

$$p_i = \frac{4}{3} \pi N_A \kappa$$

Substituting the value  $p_i$  of  $P_0$  we get

$$P_m = \frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho} = \frac{4}{3} \pi N_A \kappa \frac{4}{3} \pi N_A \left( \frac{\mu^2}{3kT} \right)$$

This is known as Debye equation where  $\kappa$  &  $N_A$  are constant.)

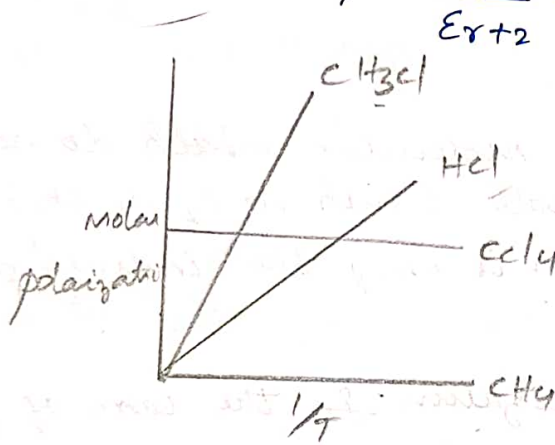
Non polar molecules  $P_m$  is independent of  $T$  (horizontal line is obtained)

Since  $P_m = p_i = \frac{4}{3} \pi N_A \kappa$

polar molecule:  $P_m$  is dependent on  $T$ .

$$P_m = p_i + P_0 = \frac{4}{3} \pi N_A \kappa + \frac{4}{3} \pi N_A \left( \frac{\mu^2}{3kT} \right)$$

$$P_m = A + \frac{B}{T} = \frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho} \text{ [straight line with a slope is obtained].}$$



### Application of dipole moment

- i) Dipole moment provides idea about the geometry of molecules.
- ii) It provides information about the electronegativity of atoms.
- iii) It gives idea about the geometry isomerism.
- iv) The presence of aromaticity is confirmed

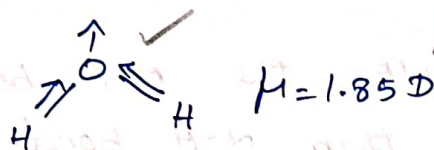
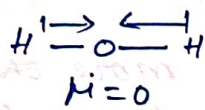
v) It is useful for the interpretation of solubility i.e. solvating power of a solvent.

vi) It is used to determine ionic character of a diatomic molecules.

vii) It's value gives the identification of s, m & p isomers. ) 5M

i) Geometry of the molecules:

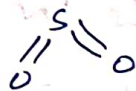
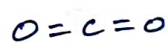
\*  $H_2O$  has a bent structure water molecule can have linear or boat structure



linear =  $\mu = 0$   
bend = something

Since water has a dipole moment 1.85 D its linear structure is ruled out. Thus water has a boat structure.

\*  $CO_2$  has a linear structure and  $SO_2$  has a bend structure



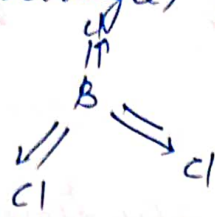
Carbon dioxide has no dipole moment  $\mu = 0$ . This is possible only if the molecule has a linear structure and the bond moment of two  $C=O$  unit cancel each other.

$SO_2$  has a dipole moment  $\mu = 1.63 \text{ D}$  here the individual dipole moment of the two  $S=O$  bond are not cancelled. Then the molecule has a bend structure.

\*  $BF_3$ ,  $BCl_3$  has a planar and  $NH_3$ ,  $NF_3$  a pyramidal structure.

The dipole moments of  $BF_3$ ,  $BCl_3$  molecules are zero, this is possible if the three B-X bonds.

arranged symmetrically around the boron atom in the same plane. i.e. the four atoms are coplanar the vector sum of  $\sigma$ -bond moments cancel each other. (i.e. equilateral triangle) Hence they have zero dipole moment



$$\mu = 0$$



$$\mu = 1.470$$



In  $\text{NF}_3$  the  $\text{N}-\text{F}$  bond is more than as polar as the  $\text{N}-\text{H}$  bond. Hence  $\text{NF}_3$  is expected to have larger  $\mu$ -value than that of ammonia. But actually it is reversed

Explain, N is more electronegative than hydrogen and therefore the  $\text{N}-\text{H}$  dipole is than hydrogen and therefore the  $\text{N}-\text{H}$  dipole is pointing towards 'N'

A lone pair of  $e^-$  is present on one side only and hence its other end becomes the negative end of dipole, the other end is positive

In  $\text{NH}_3$ , three  $\text{N}-\text{H}$  & one  $\text{N}-\text{LP}$  lone pair dipoles are in the same direction the  $\text{N}-\text{H}$  dipoles strengthen the lone pair dipole vector sum of the four members is high 1.460

In  $\text{NF}_3$  the  $\text{F}-\text{N}$  dipoles are opposed to the  $\text{N}-\text{LP}$  lone pair dipole i.e. the three  $\text{F}-\text{N}$  dipoles weaken the lone pair of  $\text{N}$  ~~the~~  $\text{F}-\text{N}$  dipoles the vector sum of four members becomes

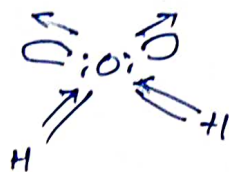


low has the value of 0.23 D. The lone pair moment is called orbital moment

### 2) Hybridisation of dipole moment:

Eg:  $H_2O$  the bond moments of water molecule contribute only to about one quarter of the total dipole moment. The lone pair moment provides the other three-quarters of its dipole moment.

Hybridization of lone pair must also be considered in arriving net dipole moment



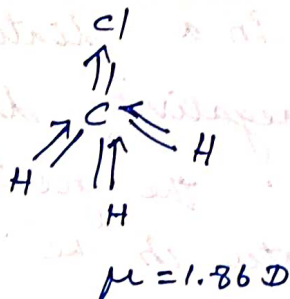
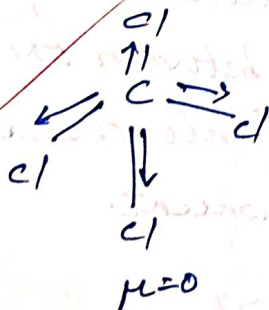
eg:  $C^+(sp^3) - C^-(sp^2)$  0.68 D

$C^+(sp^2) - C^-(sp)$  0.15 D

$C^+(sp^3) - C^-(sp)$  1.48 D.

### 3) $CCl_4$ , $CHCl_3$ tetrahedral:

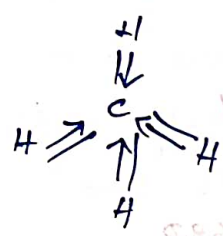
In  $CCl_4$  the bond moments are vectors of equal magnitude arranged tetrahedrally, their effects cancel and therefore vectors sum becomes zero



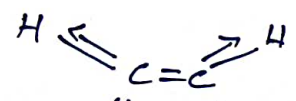
Tetrahedral  $CHCl_3$  than  $\mu = 1.86 D$ . This arises from highly polar carbon chloride bond

molecule	$\mu(D)$	molecule	$\mu(D)$
$BF_3$	0	$H_2S$	1.10
$CO_2$	0	$NH_3$	1.46
$CS_2$	0	$SO_2$	1.51
$CD_4$	0	$H_2O$	1.85
$NF_3$	0.23	$C_2H_5OH$	1.65
$CH_4$	0	$CF_4$	0
$C_2H_6$	0	$C_2F_4$	0

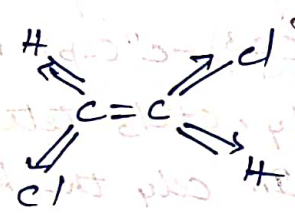
methane has symmetrical tetrahedral structure, Hence, it has zero dipole moment



4) Identification of cis & trans isomers:



cis dichloro ethylene  
 $\mu = 2.96 D$



$\mu = 0.0 D$

5) Dipole moment and electronegativity:

In a diatomic molecule the greater electronegativity difference between the bonded atoms, the greater is the ionic character and the greater is the dipole moment.

electronegativity  
dipole moment

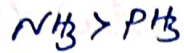
- $F > Cl > Br > I$
- $HF > HCl > HBr > HI$
- $IF > Br_2F > ClF$

High dipole moment  
HF

$\mu - 1.60 \ 1.29 \ 0.89 D$

$H_2O > H_2S > H_2SO > H_2Te$   
1.85 0.15 0.40 0.20 D

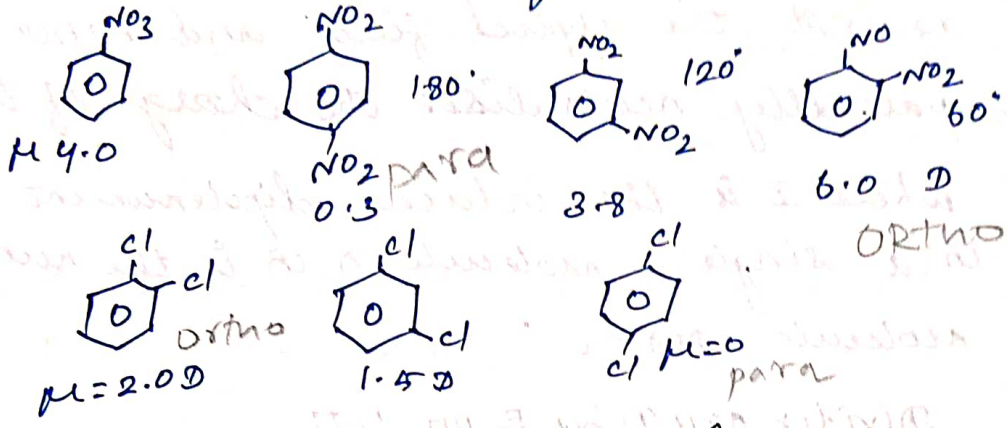
The greater the electronegativity difference between the bonded atoms, greater will be the charge separation and the degree of polarity



$$1.84 \text{ D} \quad 0.58 \text{ D}$$

### 6) Identification of ortho, meta and para isomers:

✓ The dipole moment value for dinitrobenzene increases progressively as the molecule becomes more and more unsymmetrical



### 7) Dipole moment and ionic character

✓ The magnitude of the dipole moment of a diatomic molecule determine its ionic character  $\mu_{exp} = 0.79 \text{ D}$

Eg: HBr

$$\begin{aligned} \mu_{ionic} &= e \times r \\ &= (4.8 \times 10^{-10} \text{ esu}) [1.41 \times 10^{-8} \text{ cm}] \\ &= 6.77 \text{ D} \end{aligned}$$

% of ionic character

$$\begin{aligned} &= \frac{\mu_{exp}}{\mu_{ionic}} \times 100 \\ &= \frac{0.79}{6.77} \times 100 \\ &= 11.67\% \end{aligned}$$

HBr = 12% ionic character

Gas, solid, liquid

Clausius Mosotti equation:

\* When an electric field is applied to two plates they get charged the strength of the uniform electric field produced between them is  $E_0$

\* If a non polar substance is placed between the plate, the strength of the electric field will be reduced to  $E$  because the induced dipole ~~is~~ called dielectric acts against the applied field and hence partially neutralises the charge of the plate

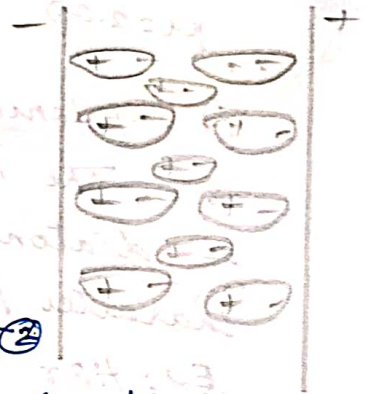
where  $I$  is the induced dipole moment in a single molecule  $N$  is the number of molecule per c.c.

Divide equ (1) by  $E$  on both sides by  $\epsilon_0$  putting

$E_0/E = D$  we get

Dielectric constant

$$D = 1 + \frac{4\pi N I}{E} \text{ or } (D-1)E = 4\pi N I \quad \text{--- (2)}$$



The electric intensity [intensity of electric field strength]  $\times$  has the contribution

(partial neutralisation of the charges on plates by the induced electric dipoles)

The charge induced on the surface of the spherical cavity =  $+\frac{4}{3}\pi I$

Induced molar polarisation and is represented by  $p_i$

$$p_i = \left[ \frac{D-1}{D+2} \right] \frac{M}{\rho} \rightarrow \text{Clausius-Mosotti equation}$$

The relationship between dielectric constant and polarisability of a substance.

## Debye equation :

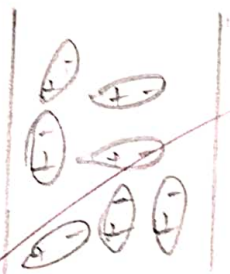
\* Molar polarisation value of compounds such as  $O_2$ ,  $CO_2$ ,  $N_2$  and  $CH_4$  are constant and independent of temperature.

\* Molar polarisation value of  $\epsilon_0$  for some other substance such as  $HCl$ ,  $CH_3Cl$ ,  $C_2H_5NO_2$  and  $CH_3Cl$  don't become constant but decrease with  $\frac{1}{T}$  (temperature)

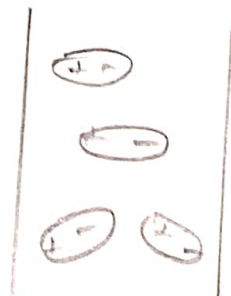
\* In the case of molecules such as  $HCl$ ,  $CH_3Cl$  etc. possess some dipole moment even in the absence of electric field. This is called permanent dipole moment

\* In the absence of electric field these permanent dipoles are oriented in a random manner

\* In the presence of electric field two distincting effects takes place.



i) In the absence of electric field



ii) In the presence of electric field.

\* These effects are

a) The electric field will tend to rotate and orient these dipoles in the direction of the field.

The total polarization will be the sum of the induced polarization  $p_{in}$  and the

$E_0/E = D$   
 $D = \frac{1}{3} \frac{N \mu^2}{E}$   
 $(D - \epsilon_0) = \frac{1}{3} \frac{N \mu^2}{E}$   
 $\frac{D - \epsilon_0}{\epsilon_0} = \frac{1}{3} \frac{N \mu^2}{E \epsilon_0}$

Orientation molar polarisation.

$$P_t = P_i + P_o \quad \text{--- (1)}$$

$$P_t = \left[ \frac{D-1}{D+2} \right] \frac{M}{\rho} = P_i + P_o$$

Induced polarisation is  $P_i = \frac{4}{3} \pi N \alpha$   
orientation molar polarisation is given by Debye.

$P_o = \frac{4}{3} \pi N \cdot \left( \frac{\mu^2}{3KT} \right)$  where  $(\mu)$  is the permanent dipole moment of the molecule &  $K$  is

Boltzmann substituting  $P_o$  &  $P_t$  values in the equ (1) we get

$$P_t = P_o + P_i \rightarrow \left( \frac{D-1}{D+2} \right) \frac{M}{\rho} = \frac{4}{3} \pi N \alpha + \frac{4}{3} \pi N \left( \frac{\mu^2}{3KT} \right)$$

This equ. is called Debye equations.