DIELECTRICS

Electric dipole moment is the measure of the polarity of the system. It is the separation of positive charge and a negative charge by a distance. The SI unit of electric dipole moment is Coulomb-meter. The simplest example is a pair of electric charges of two opposite signs and equal magnitude separated by distance.

Net electric dipole moment = Σ(induced dipoles + permanent dipoles + ionic dipoles)
electronic   orientation   ionic bond

$$\vec{p} = \vec{p_e} + \vec{p_o} + \vec{p_i}$$

Dielectric polarization is the term given to describe the behaviour of a material when an external electric field is applied on it.

In an electric field the alignment of the dipoles layer of charge on each surface of the dielectric surface charge density σ_{bound} ($\sigma_{induced}$) – these bound charges are not free to move as they are bound to the molecules. In the interior of the dielectric, the net dipole moment is zero because of the cancellation of the charges. This phenomenon is called **polarization** and the material is said to be **polarized**. This is the reason why a charged object can attracts a neutral object

Net polarization= Σ(electronic polarization + orientation polarization + ionic polarization)

$$\vec{P} = n\,\vec{p} = \vec{P_e} + \vec{P_o} + \vec{P_i}$$

Interfacial Polarization

Interfacial or space charge polarization occurs when there is an accumulation of charge at an interface between two materials or between two regions within a material because of an external field. This can occur when there is a compound dielectric, or when there are two electrodes connected to a dielectric material. This type of electronic polarization is different from orientation and ionic polarization because instead of affecting bound positive and negative charges i.e. ionic and covalent bonded structures, interfacial polarization also affects free charges as well. As a result interfacial polarization is usually observed in amorphous or polycrystalline solids.

Orientation Polarization

Orientation polarization arises when there is a permanent dipole moment in the material. Materials such as HCl and H_2O will have a net permanent dipole moment because the charge distributions of these molecules are skewed. For example, in a HCl molecule , the chlorine atom will be negatively charged and the hydrogen atoms will be positively charged causing the molecule to be dipolar. The dipolar nature of the molecule should cause a dipole moment in the material, however, in the absence of an electric field, the dipole moment is canceled out by thermal agitation resulting in a net zero dipole moment per molecule. When an electric field is applied however, the molecule will begin to rotate to align the molecule with the field, causing a net average dipole moment per molecule

Ionic Polarization

Ionic polarization is a mechanism that contributes to the relative permittivity of a material. This type of polarization typically occurs in ionic crystal elements such as NaCl, KCl, and LiBr. There is no net polarization inside these materials in the absence of an external electric field because the dipole moments of the negative ions are canceled out with the positive ions.

However, when an external field is applied, the ions become displaced, which leads to an induced polarization.

Response of a molecule to an electric field

We can assume the electric dipole moment and polarization are proportional to the electric field experienced by the molecule (local electric field). Taking into account the three contributions:

Electric dipole moment $\qquad p = (\alpha_e + \alpha_o + \alpha_i)E_{loc} = \alpha\, E_{loc}$

$\qquad$ Polarization $\qquad\qquad P = n(\alpha_e + \alpha_o + \alpha_i)E_{loc} = n\,\alpha\, E_{loc}$

$\quad \alpha \qquad$ polarizability
$\quad \alpha_e \qquad$ electronic or molecular polarizability
$\quad \alpha_o \qquad$ orientation polarizability
$\quad \alpha_i \qquad$ ionic polarizabiltiy

Macroscopic view (homogeneous electric field and ε_r independent of E)

$$P = \chi_e\, \varepsilon_0\, E = (\varepsilon_r - 1)\varepsilon_0\, E \qquad E \text{ is the electric field within the dielectric}$$

We are now in a position to relate the macroscopic quantities, the electric susceptibility and the dielectric constant to a property of the molecules, the polarizability.

E_{loc} – **The local (inner) field**
$\qquad$ – **Electric field acting upon a molecule within a dielectric**

Dielectric – not continuous – composed of molecules

What is the local (inner) field E_{loc} that acts upon an individual molecule within the dielectric?

Consider dielectric between the plates of a parallel plate capacitor.

The local electric field at the point O consists of 4 parts:

1 Field at O due only to the charged plates

$$E_1 = \frac{\sigma_f}{\varepsilon_0}$$

2 Polarization of the charges on the surface of the dielectric

$$E_2 = -\frac{\sigma_b}{\varepsilon_0} = -\frac{P}{\varepsilon_0}$$

3 Polarization of charges on the surface of S which would be formed if the spherical section of the dielectric was removed

$$E_3 = \frac{P}{3\varepsilon_0}$$

4 $\quad$ Polarization from the polar molecules within the spherical section, E_4
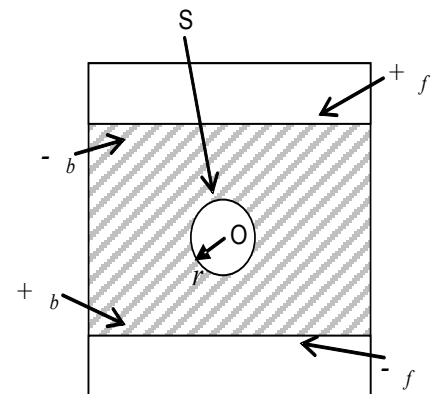
$$E_4 = K_4 \frac{P}{\varepsilon_0}$$

K_4 some constant

Usually, E_4 can't be calculated exactly.

$$E_{loc} = E_1 + E_2 + E_3 + E_4$$

$$E_{loc} = \frac{\sigma_f}{\varepsilon_0} - \frac{P}{\varepsilon_0} + \frac{P}{3\varepsilon_0} + K_4 \frac{P}{\varepsilon_0}$$

$$E_{loc} = \frac{D - P}{\varepsilon_0} + \frac{P}{3\varepsilon_0} + K_4 \frac{P}{\varepsilon_0}$$

$$E_{loc} = E + \frac{P}{3\varepsilon_0} + K_4 \frac{P}{\varepsilon_0}$$

$$E_{loc} = E + K \frac{P}{\varepsilon_0}$$

Electric field inside dielectric

K is some positive constant.

$$E = \frac{D - P}{\varepsilon_0}$$

This equation gives the electric field E_{loc} that acts upon a single molecule of the dielectric.

For dielectrics with $E_4 \approx 0$, the total local electric field at O is

$$E_{loc} = E + \frac{P}{3\varepsilon_0}$$

This equation is applicable to:

Cubic crystals $\qquad\qquad$ $E_4 = 0$ $\quad$ $K_4 = 0$ $\quad$ $K = 1/3$

Gases and dilute solutions $\quad$ $E_4 \approx 0$

Calculation of E_3

Assumed spherical section removed.
E_3 found by summing the contributions to the field of all ring elements of polarization charge on the surface S.

The charge density σ_s on the spherical surface is given by the component of the polarization normal to S

$$\sigma_s = -P\cos\theta$$

Surface area of the ring element is

$$dS = 2\pi\, r\sin\theta\, r\, d\theta$$

The charge on the surface element dS that lies between θ and $\theta + d\theta$ is

$$dq = (-P\cos\theta)(2\pi\, r\sin\theta\, r\, d\theta)$$

By symmetry, all components of the field that are not normal to the capacitor plates cancel each other, therefore the electric field at O due the charge dq is

The area of the shaded ring between and $+ d$ is equal to

$$dE_3 = \frac{-1}{4\pi\,\varepsilon_0}\frac{dq}{r^2}\cos\theta = -\frac{P}{2\varepsilon_0}\cos^2\theta\sin\theta\, d\theta$$

The resultant field at the centre of the sphere is obtained by integrating over $\theta = 0 \rightarrow \pi$

$$E_3 = \int_0^\pi \frac{-P}{2\varepsilon_0}\cos^2\theta\sin\theta\, d\theta$$

$$E_3 = \frac{P}{3\varepsilon_0}$$

Dielectric constant of monatomic gases

We will consider the rare gases such as helium and argon because of the simple theoretical model that can be used, although for most practical purposes it is not very useful.

Simple model of a single atom (*gives results that are correct to an order of magnitude*)
  Positive nucleus: $+Ze$ and electrons: $-Ze$
  Atomic nucleus: diameter $\sim 10^{-10}$ m   nuclear diameter $\sim 10^{-15}$ m
  Nucleus point charge and electron cloud of charge $-Ze$ distributed homogeneously throughout a sphere of radius $a \approx 10^{-10}$ m

When the atom placed into external electric field E ($E = E_{loc}$)
Nucleus and electron cloud move in opposite directions to create an induced electric dipole. Equilibrium established with the nucleus shifted slightly relative to the centre of the electron cloud by a distance d.

$$d \ll a$$

$$E$$
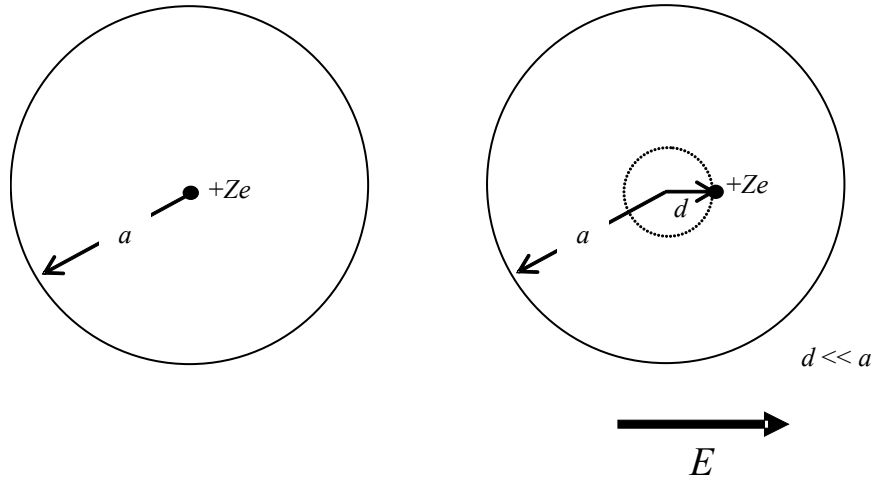
The nucleus will experience a force in the direction of the electric field F_E

$$F_E = Ze\,E$$

and an opposing force F_G due to the electric field of the charge located within the sphere of radius d and concentrated at the centre of the electron cloud - by Gauss's Law electric field at edge location of nucleus due to electrons within sphere of radius d is

$$E_G\left(4\pi\,d^2\right) = \frac{-Z\,e\,(d^3/a^3)}{\varepsilon_0}$$

$$\left|F_G\right| = Ze\,E_G = \frac{Z^2\,e^2\,d}{4\pi\,\varepsilon_0\,a^3}$$

$$\left|F_G\right| = \left|F_E\right| \quad \Rightarrow \quad d = \frac{4\pi\,\varepsilon_0\,a^3}{Z\,e}E$$

The displacement distance d is proportional to the external electric field E.

For the single atom $E_{loc} = E$, the molecular (electronic) polarizability of a monatomic gas is

$$\alpha = \alpha_e$$

$$p = \alpha\,E_{loc} = \alpha\,E = (Ze)\,d = (Ze)\frac{4\pi\,\varepsilon_0\,a^3}{Ze}E$$

$$\alpha_e = \alpha = 4\pi\,\varepsilon_0\,a^3$$

The electronic (molecular) polarizability is proportional to the volume of the electron cloud (a^3). The larger the atom, the greater the charge separation and the greater the induced dipole moment.

Now we consider a rare gas containing n molecules.m^{-3} and we can neglect any interactions between the induced dipoles in the atoms (good approximation for a gas).

The polarization of the gas P is

$$P = n\,p = n\,\alpha\,E$$

The polarization from the macroscopic point of view is

$$P = \chi_e \, \varepsilon_0 \, E = (\varepsilon_r - 1) \varepsilon_0 \, E$$

Therefore we can relate the microscopic molecular polarizability α with the macroscopic dielectric constant ε_r

$$\varepsilon_r = 1 + \frac{n\alpha}{\varepsilon_0} = 1 + 4\pi \, n \, a^3$$

We have obtained a relationship between the measurable quantity ε_r and the microscopic quantities α and a. *How good is our simple model?*

He gas at 0 ºC 1 atm $T = 300$ K $\varepsilon_r = 1.0000684$

$$pV = NkT$$

$$a = \left(\frac{\varepsilon_r - 1}{4\pi \, n} \right)^{1/3} = 6 \times 10^{-11} \text{ m}$$

→ $n = 2.5 \times 10^{25}$ atoms.m⁻³ →

10^{-40} F.m²	He	Ne	A	Kr	Xe
α	0.18	0.35	1.43	2.18	3.54

bigger the atom → the larger α

We can estimate the relative shift d between the nucleus and the centre of the electron cloud

$$E \sim 10^5 \text{ V.m}^{-1} \quad a \sim 10^{-10} \text{ m} \quad Z \sim 2 \quad \rightarrow \quad d \sim 10^{-17} \text{ m}$$

very small – very slight perturbing influence of the applied electric field on the atom

Dielectric constant of elemental dielectric solids

Insulators: one kind of atom eg diamond, phosphorus
No permanent dipole moments or ions
Polarization due to relative displacement of electron clouds and nuclei
Local electric field same for all atoms

For the special case when $K = 1/3$ (no polar molecules $E_4 = 0$ $K_4 = 0$) - applicable only to cubic crystals, gases and dilute solutions , gives

$$\alpha = \alpha_e$$

$$P = n \, p = n \, \alpha \, E_{loc}$$

$$E_{loc} = E + \frac{P}{3\varepsilon_0} \qquad P = (\varepsilon_r - 1)\varepsilon_0 \, E$$

$$\alpha = \frac{3\varepsilon_0}{n} \frac{(\varepsilon_r - 1)}{(\varepsilon_r + 2)} \qquad \textbf{Clausius-Mossotti relationships}$$

$$\frac{(\varepsilon_r - 1)}{(\varepsilon_r + 2)} = \frac{n\alpha}{3\varepsilon_0}$$

The distance between atoms in a solid is affected only slightly by temperature and therefore, n, α, K and ε_r are in a first approximation independent of the temperature.

For a solid, a typical value for the number density is $n \sim 5 \times 10^{28}$ m^{-3}.

The dielectric constant for three solids with a diamond structure are:

$\quad\quad \varepsilon_r(C) = 5.68 \quad\quad \varepsilon_r(Si) = 12 \quad\quad \varepsilon_r(Ge) = 16$

The dielectric constant for the gases are very close to 1 eg $\varepsilon_r(H_2) = 1.000132$.

??? Why is the dielectric constant for a solid much greater than for a gas?

$$\varepsilon_r = 1 + \frac{n\alpha}{\varepsilon_0}$$

If ε_r very close to 1 $\rightarrow$ $\varepsilon_r + 2 \approx 3$ $\rightarrow$ $\quad$ same equation for monatomic gases

Dielectric constant of polyatomic gases containing polar molecules

Consider a gas containing n molecules.m^{-3}. Assume that each molecule has a permanent electric dipole moment p.

The polarization is due to the electronic polarization P_e (nucleus shifted slightly relative to the centre of the electron cloud) and the ionic polarization P_i (ionic nature of bond between atoms) and the orientation polarization P_o (rotation and alignment of the polar molecules in the external electric field).

P_e and P_i are essentially independent of the temperature but P_o is very temperature dependent.

At a temperature T and zero external electric field, the molecules will be randomly oriented $\rightarrow$ zero polarization.

When there is an external electric field, the molecules will try to align with the field. Each polar molecule can be considered to be a simple dipole. The force on the dipole provides the torque to rotate the molecule so that they will be in the lowest state where they are parallel to the field. If there were no thermal motion, all dipoles would line up along the external field direction.
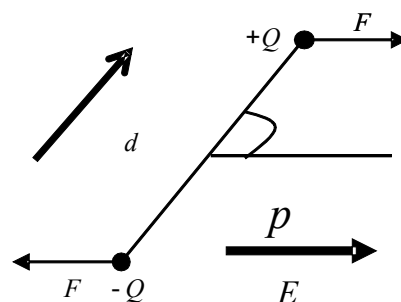
The electric force on the dipole produces a couple and the torque acting to rotate the dipole about its centre is

$$\tau = \frac{d}{2} F \sin\theta + \frac{d}{2} F \sin\theta = Q E d \sin\theta = p E \sin\theta$$

$$\overrightarrow{\tau} = \overrightarrow{p} \times \overrightarrow{E}$$

Set the potential energy $U(\theta)$ of the dipole to zero when $\theta = 90°$. The potential energy of the dipole for an arbitrary angle θ is then given by

$$U(\theta) = \int_{\theta=90°}^{\theta} p E \sin\theta \, d\theta = -p E \cos\theta = -\overrightarrow{p} \cdot \overrightarrow{E}$$

The dipole has the lowest potential energy when dipole is parallel to the electric field and the highest energy when anti-parallel to the field → small angles are preferred over larger ones. And if they were no thermal motion, all dipoles would line along the direction of the external electric field. The greater the temperature, the greater the thermal motion → reduced alignment of the dipoles with the field.
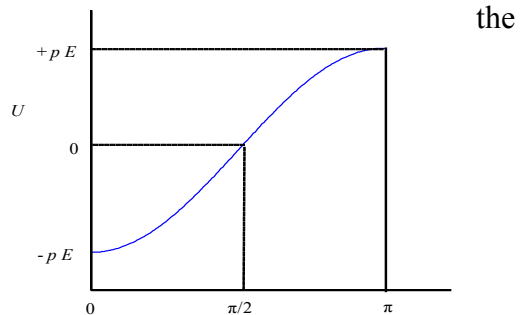
The orientation polarization P_o is given by the Langevin function (1905)

$$P_o = n \, p \left(\coth\left(\frac{p E}{k T}\right) - \frac{1}{\frac{p E}{k T}} \right)$$
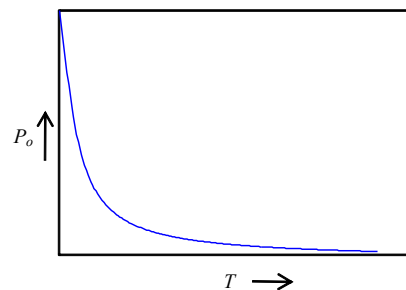
$\frac{p E}{k t}$ 1 $P_o \to 1$

Complete alignment – this does not occur in gases
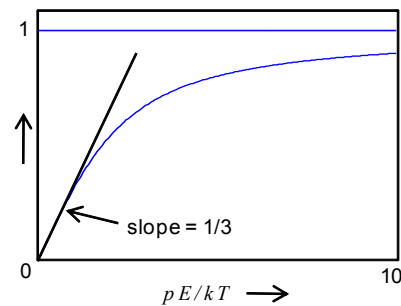
$\frac{p E}{k t}$ 1 $P_o \to n \, p \left(\frac{p E}{3 k T} \right)$

Most practical case:

$$P_o \propto p^2 \qquad P_o \propto \frac{1}{T}$$

The total polarization of a polyatomic gas is given by where $E_{loc} = E$

$$P = P_e + P_i + P_o$$

$$P = n \left(\alpha_e + \alpha_i + \frac{p^2}{3 k T} \right) E$$

Macro view $P = \chi_e \, \varepsilon_0 \, E = (\varepsilon_r - 1) \varepsilon_0 \, E$

ε_r is related to the molecular properties by

$$(\varepsilon_r - 1)\varepsilon_0 = n\left(\alpha_e + \alpha_i + \frac{p^2}{3kT}\right)$$

How well does this prediction agree with experiment?
If dielectric constant ε_r plotted against $1/T$ → straight line

Slope $\quad n\,p^2/3k \quad$ → measurement of p

Intercept $\quad n(\alpha_e + \alpha_i)$ → measurement of $(\alpha_e + \alpha_i)$

Dipole moments of gases in debye units (3.33×10^{-30} C.m)

NO	0.1	CO	0.11	HCl	1.04
HBr	0.79	HI	0.38	NO_2	0.4
CO_2	0	CH_4	0	H_2O	1.84
H_2	0	A	0	NH_3	1.4

Dielectric constant measurements have played an important part in determining molecular structure: CO_2 has zero resultant dipole moment, whereas each CO bond does have a non-zero dipole moment → O=C=O. H_2O molecule must have a triangular structure.

Dipole Moment

A molecule is composed of positively charged nuclei and negatively charged electrons. The arrangement of these charged particles is different for different molecules. There are two possibilities :

1. Centre of gravity of positive nuclei coincides with that of negatively charged electrons, the resulting molecule is called *nonpolar molecule*. e.g., H_2, Cl_2, N_2, C_6H_6, etc.

2. The centre of gravity of positive nuclei does not coincide with that of electrons, the resulting molecule is called *polar molecule*. For example, HCl, CH_3Cl, NH_3, H_2O, etc. Since the molecule, as a whole is neutral, we have equal positive ($+ q$) and negative ($- q$) charges separated by a certain distance (l) in a polar molecule. Thus a polar molecule behaves like a small magnet and becomes *dipolar* and hence is called an *electric dipole* or simply a *dipole* (two poles). Sidgwick proposed that a dipole may be shown by an arrow with a crossed tail. The arrow is placed parallel to the line of the positive and negative charges and should be from *positive end to negative end* (as a convention) of the dipole. Hence HCl molecule may be represented as
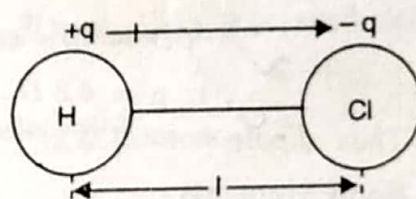
Fig. 8.1. Representation of dipole, where l is the bond length.

The polar molecules have permanent dipoles and nonpolar molecules do not have permanent dipoles.

1. DIPOLE MOMENT OR ELECTRIC MOMENT

I. Definition

The degree of polarity of a molecule can be expressed in terms of dipole moment. *It is the product of the magnitude of the charge (positive or negative) and distance between them, i.e., bond length.* If q is the charge at each end of dipole and l is the distance between the positive and negative centres (*i.e.*, bond length), the dipole moment (μ) is given by

$$\mu = q \times l$$

In a nonpolar molecule, the distance l is zero because centres of gravity of positive and negative charges coincide, hence dipole moment is zero.

The dipole moment is a *vector quantity* and is represented by an arrow showing direction from positive to negative end of the dipole. The
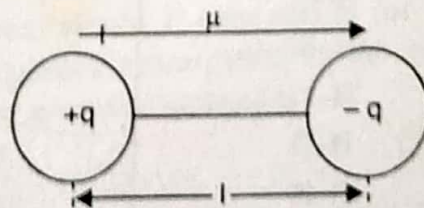
Fig. 8.2. Representation of dipole moment.

633

length of arrow represents the magnitude of dipole moment. *Dipole moments being vectorial quantities, may be added vectorially.*

The dipole moment arises due to difference in the electronegativities of two atoms held together by a chemical bond. If there are two or more bonds in a molecule, the net dipole moment will be the vector addition of dipole moments of chemical bonds. *Each chemical bond possesses a definite dipole moment. The magnitude of bond dipole moment in a polar molecule depends on the difference in the electronegativities. The greater the difference in electronegativities, the greater is the dipole moment.* Hence, *greater the value of dipole moment, greater is the degree of polarity of polar covalent bond between the two atoms.* Hence we have the following relation :

$$\text{Percentage ionic character} = 16 (x_A - x_B) + 3.5 (x_A - x_B)^2$$

where x_A and x_B = Electronegativities of atoms A and B forming bond A–B.

II. Units of dipole moment

We know that

$$\text{Dipole moment} = \text{Electronic charge} \times \text{Distance}$$

The charge is expressed in electrostatic unit (e.s.u.) and distance in angstrom unit $(10^{-8} \text{cm} = 1 \text{ Å})$. If an electron (charge of electron $= 4.8 \times 10^{-10}$ esu) is assumed to be placed at a distance 1 Å (10^{-8}cm) from an equally positive charge, then for such a system, the dipole moment is given by

$$\mu = 4.8 \times 10^{-10} \text{ esu} \times 10^{-8} \text{ cm}$$

or

$$\mu = 4.8 \times 10^{-18} \text{ esu-cm}$$

But the quantity 10^{-18} esu-cm is called one debye unit denoted by D. Hence

$$1 D = 10^{-18} \text{esu-cm}$$

$$\therefore \qquad \mu = 4.8 \, D$$

Thus *dipole moment is generally expressed in debye units.*

III. Bond Moments

The polyatomic molecules contain number of bonds between the atoms. Each bond has a definite dipole moment and hence makes a definite contribution to the overall dipole moment of the molecule. This dipole moment of a chemical bond is called *bond moment*. It does not depend on the nature of molecule.

The dipole moment of a molecule is really vectorial sum of the individual bond moments present in it. No direct method is known to obtain the magnitude of a bond moment. On the empirical basis, Eucken and Meyer prepared a table of moments of different bonds (Table 8.1). The bond is directed towards the more electronegative of the two atoms linked.

Table 8.1. Bond Moments (D).

Bond	Bond Moment	Bond	Bond Moment
H–F	1.9	H–C	0.4
H–Cl	1.1	C–C	0.0
H–Br	0.8	C–F	1.4
H–I	0.4	C–Cl	1.5
H–O	1.5	C–Br	1.4
H–N	1.3	C–I	1.2
C–O	0.7	C=O	2.3

Dipole Moment

2. POLARIZATION OF MOLECULES IN ELECTRIC FIELD: INDUCED POLARIZATION

A molecule as a whole is neutral, but is composed of positively charged nuclei and negatively charged electrons. When a molecule is put under the influence of an electric field, the positive nuclei will be attracted towards negative plate and electrons towards positive plate. This results in a change in the molecule, causing positive charges at one end and negative charges at the other i.e., formation of electrical dipoles takes place. Such distortion is called *distortion polarization or electrical distortion (polarization)* of the molecule. Hence *electrical polarization is defined as the creation of electrical dipoles in a neutral molecule, under the influence of an electric field.*

The molecule, even though nonpolar in nature, acquires a dipole moment, when kept in an electric field.

The electrical polarization of molecule is temporary and disappears as soon as the electric field is removed. This type of electrical polarization is called *induced polarization* and the dipole formed is called *induced dipole*. The dipole moment of this induced dipole is called *induced dipole moment or induced moment* denoted by μ_i. Induced moment is directly proportional to the strength of applied electric field and is given by $\mu_i = \alpha \cdot \chi$

where
α = A constant called distortion polarizability
χ = Strength of applied electric field

If $\chi = 1$, then $\mu_i = \alpha$, hence μ_i is the measure of dipole moment induced by unit field.

Induced polarization is of two types :

(i) **Atomic polarization.** When the nuclei are distorted with respect to each other, it is called atomic polarization, denoted by P_a

(ii) **Electric (electron) polarization.** When the electrons are distorted, it is called *electrical polarization,* denoted by P_e.

Induced polarization = Atomic polarization + Electric polarization
$$P_i = P_a + P_e$$

or

According to Clausius and Mosotti–relation

$$\frac{4}{3}\pi N\alpha = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho}$$

where
M = Molecular weight of substance
ρ = Density of substance
N = Avogadro's number
α = Distortion polarizability
D = Dielectric constant of medium

The left hand side of the above equation is called *molar polarization* of substance and is denoted by P. Hence

$$P = \frac{4}{3}\pi N\alpha = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho}$$

In nonpolar molecules, the polarization is all induced. Hence P also stands for induced polarization (P_i) in case of nonpolar molecules only. Induced polarization is the electrical distortion caused in one mole of substance by unit field. For nonpolar molecules

$$P_i = P = \frac{4}{3}\pi N\alpha = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho}$$

In this equation N and α are independent of temperature, hence P_i will also be independent

of temperature. Since D is a dimensionless number, polarization will be expressed in the unit of volume. It is important to note that the substances which do not have permanent dipole moment (*i.e.*, nonpolar substances) the molar polarization is independent of temperature. But the substances which have permanent dipole moment (*i.e.*, polar or partial polar molecules) their molar polarization changes with temperature.
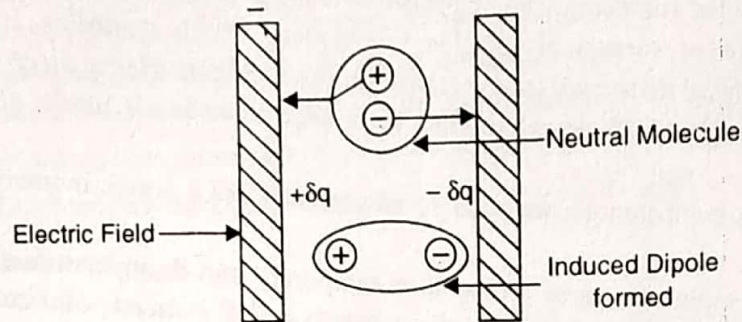

Fig. 8.3. Polarization of molecule in the presence of electric field *i.e.*, showing the formation of induced dipole from neutral molecule.

3. POLARIZATION OF POLAR MOLECULES IN ELECTRIC FIELD

The induced polarization (P_i) is common to all substances (polar and nonpolar both). Polar molecules, in absence of electric field, are oriented in all directions (as they have dipoles) due to thermal effects. But when such molecules are put in an electric field, two effects will arise :

(*i*) *Induced polarization* (P_i). Usual distortion of positive and negative charges will take place giving rise to *induced polarization*.
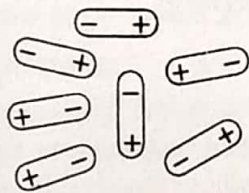
Fig. 8.4. Polar molecules are randomly oriented in all directions, in absence of electric field.
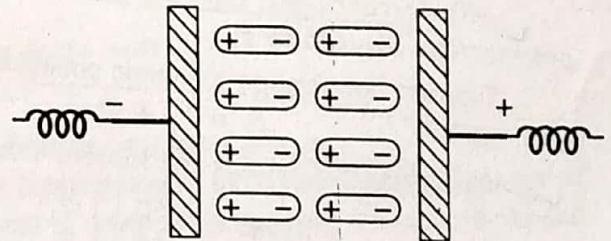
Fig. 8.5. If the polar molecules are stationary, they would orient at $180°$ to the direction of electric field (*i.e.*, perpendicular to the electric plates).
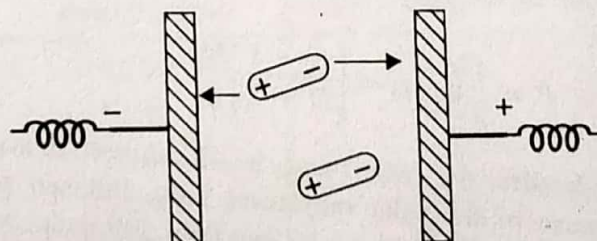
Fig. 8.6. Due to thermal agitation, molecules occupy mean position between the direction of electric field and original positions of molecules, it is orientation polarization.

(ii) *Orientation polarization* (P_o). Since the molecules are polar, the electric field tries to orient them in the direction of electric field.

But the molecules themselves are constantly moving in all possible directions, this is called *thermal agitation*. This thermal agitation opposes such orientation of molecules. Under such condition, the molecules would occupy some mean position between the direction of field and their original position. *This kind of effect of the electric field on the molecules is called orientation polarization.*

Thus for a polar molecule, the molar polarization is given by

Molar polarization = (Induced polarization) + (Orientation polarization)

or
$$P = P_i + P_o$$

But from dielectric constant measurements,

$$P = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho} \qquad \ldots (2)$$

We know
$$P_i = \frac{4}{3}\pi N \alpha \qquad \ldots (3)$$

$\therefore$
$$P = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho} = \frac{4}{3}\pi N \alpha + P_o \qquad \ldots (4)$$

But Debye has shown that

$$P_o = \frac{4}{3}\pi N \left(\frac{\mu^2}{3kT}\right) \qquad \ldots (5)$$

where μ = Dipole moment

k = Boltzmann constant = R/N

T = Temperature in Å

Thus from the equation (5) the following conclusions are drawn :

(a) P_o is inversely proportional to temperature

(b) For nonpolar molecule μ = 0. Therefore, P_o = 0. That is, there is no orientation polarization.

From equations (4) and (5), we get

$$P = \frac{4}{3}\pi N \alpha + \frac{4}{3}\pi N \left(\frac{\mu^2}{3kT}\right) = A + B/T \qquad \ldots (6)$$

In equation (6) the first term on R.H. Side is constant (because N and α are constant) and μ is also constant in the second term. Hence equation (6) may be expressed as

$$P = A + B/T \qquad \ldots (7)$$

where
$$A = \frac{4}{3}\pi N \alpha$$

$$B = \frac{4}{3}\pi N \left(\frac{\mu^2}{3kT}\right)$$

Equation (7) represent a straight line *i.e.*, plot of P against $1/T$ will be a straight line, as shown in Fig. 8.7.

$$\text{Intercept} = A = \frac{4}{3}\pi N \alpha \qquad \ldots (8)$$

For non polar molecule $P = P_i$

,,   ,,   ,, $P = P_i + P_o = A + B/T$

and $\qquad$ slope $= \tan\theta = \dfrac{4}{3}\pi N\left(\dfrac{\mu^2}{3kT}\right)$ $\qquad$ ... (9)

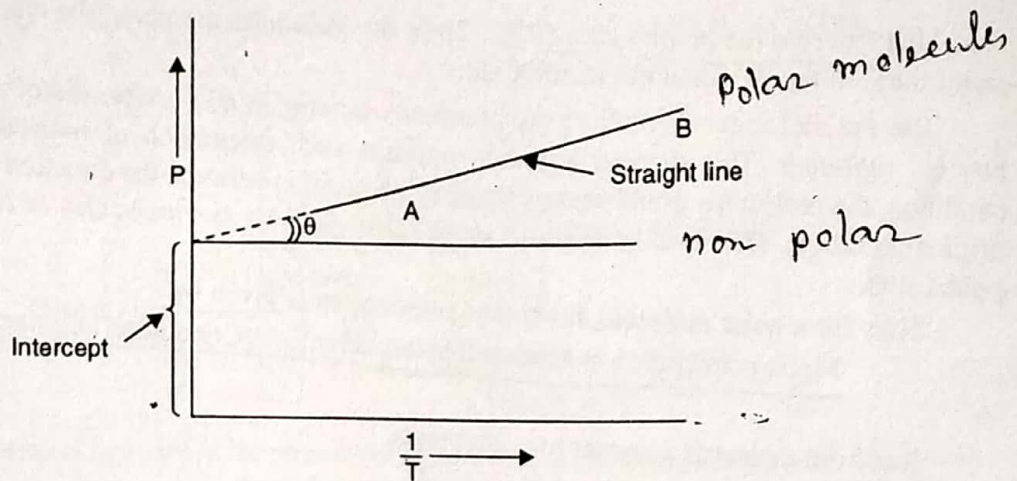Thus from equation (8) α can be calculated and from equation (9) μ is calculated.

Fig. 8.7.

4. MEASUREMENT OF DIPOLE MOMENT

The following are some important methods normally used to determine the dipole moment.

(i) Temperature Method. We know that

$$P = A + B/T$$

where $\qquad$ $P = \underline{\text{Total molar polarization}}$

If total molar polarization P_1 and P_2 be determined at two temperatures T_1 and T_2, then

$$P_1 = A + B/T_1$$

and $\qquad$ $P_2 = A + B/T_2$

$\therefore \qquad P_1 - P_2 = B\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right) = B\left(\dfrac{T_2 - T_1}{T_1 T_2}\right)$

or $\qquad B = (P_1 - P_2)\left(\dfrac{T_1 T_2}{T_2 - T_1}\right)$ $\qquad$ ... (1)

Now $\qquad B = \dfrac{4\pi N\mu^2}{9k} = \dfrac{4}{3}\pi N\left(\dfrac{\mu^2}{3k}\right)$

$\therefore \qquad \mu = \sqrt{\dfrac{9kB}{4\pi N}}$

Putting the standard values of π, N and k, the equation becomes

$$\mu = 0.0128 \times 10^{-18}\sqrt{B}\ \text{ esu-cm}$$

or $\qquad \mu = 0.0128 \times \sqrt{B}\ \text{debye}$ $\qquad$ ... (2)

Putting the value of B from equation (1) in equation (2), μ is calculated.

(ii) Ebert's Method. The polar molecules in a gas state, when kept in electric field, show both induced and orientation polarizations, but the same polar molecules, in solid state, show only induced polarization. Hence for a given polar substance, total molar polarization is :

In gas state : $\qquad P_{gas} = P_i + P_o$ $\qquad$ ... (1)

In solid state : $\qquad P_{solid} = P_i$ $\qquad$ ... (2)

Dipole Moment

Hence from equations (1) and (2) ... (3)

$$P_{gas} - P_{solid} = P_o$$

But, $$P_o = \frac{4\pi N}{3}\left(\frac{\mu^2}{3kT}\right)$$

$$P_{gas} - P_{solid} = \frac{4\pi N}{3}\left(\frac{\mu^2}{3kT}\right)$$

... (4)

or $$\mu = \sqrt{\frac{9kT}{4\pi N}(P_{gas} - P_{solid})}$$

Thus μ is calculated with the help of equation (4).

(iii) **Refraction Method.** The method involves the measurement of dielectric constant of vapours in terms of refractive index (n).

We know that

$$P = P_i + P_o$$

or $$P = P_i + \frac{4\pi N}{3}\left(\frac{\mu^2}{3kT}\right)$$

$\therefore$ $$\mu = \sqrt{\frac{9kT}{4\pi N}(P - P_i)}$$

Hence to calculate μ, we must know P and P_i.

We know that $$P = \left[\frac{D-1}{D+2}\right]\frac{M}{\rho}$$

Maxwell showed that for the same electromagnetic wave, the refractive index (n) of the medium is related to its dielectric constant (D) by the expression

$$D = n^2$$

Hence, the total molar polarization (P) expressed by

$$P = \frac{D-1}{D+2}\cdot\frac{M}{\rho}$$

seems replaceable by the molar refraction (R_M)

$$R_M = \frac{n^2-1}{n^2+2}\cdot\frac{M}{\rho}$$

Thus, we have

$$P = \frac{D-1}{D+2}\cdot\frac{M}{\rho} = \frac{n^2-1}{n^2+2}\cdot\frac{M}{\rho}$$

But this is not strictly so.

The refractive index (n) is measured with visible radiation of lower wavelength (higher frequency), say D-line of sodium whereas dielectric constant is measured with long wavelength. The n changes somewhat with wavelength. The correction for refractive index (n) for lower frequency (higher wavelength) is obtained with empirical Cauchy formula

$$n = n_\infty + \frac{a}{\lambda^2}$$

where $n =$ Refractive index at wavelength λ

$n_\infty =$ Refractive index at very high wavelength

a = A constant whose value may be as obtained from two measurements of n at known wavelengths (λ) in the visible region

We shall therefore replace D by n_∞^2.

More important is the fact that *in refraction only the electrons are affected by the radiation.* Even when corrected for long wavelengths, the refractive index gives the effect of the long waves on the electrons only. The nuclei remain unaffected. As such the total molar polarization expressed by

$$\frac{n_\infty^2 - 1}{n_\infty^2 + 2} \cdot \frac{M}{\rho}$$

gives only the electron polarization (P_e) and not the molar polarization (P),

$$P_e = \frac{n_\infty^2 - 1}{n_\infty^2 + 2} \cdot \frac{M}{\rho}$$

$$\therefore \quad P = \frac{D - 1}{D + 2} \cdot \frac{M}{\rho} = P_a + P_e + P_o$$

or

$$P = \frac{D - 1}{D + 2} \cdot \frac{M}{\rho} = P_a + \frac{n_\infty^2 - 1}{n_\infty^2 + 2} \cdot \frac{M}{\rho} + \frac{4\pi N}{9kT} \cdot \mu^2$$

This indeed gives us a method for determination of atomic polarization (P_a). μ may be obtained by any method described previously and then if D and n_∞^2 be separately measured, their substitution will enable us to evaluate P_a. For relatively large organic molecules, it has been found that P_a is quite small compared to P_e. Usually

$$P_a = 5\% \text{ of } P_e = 0.05 \times P_e$$

On this assumption we may write the above equation as

$$P = \frac{D - 1}{D + 2} \cdot \frac{M}{\rho} = 0.05 \, P_e + P_e + P_o$$

or

$$\frac{D - 1}{D + 2} \cdot \frac{M}{\rho} = 1.05 \left(\frac{n_\infty^2 - 1}{n_\infty^2 + 2} \right) \frac{M}{\rho} + \frac{4\pi N}{9kT} \cdot \mu^2$$

In such cases, measurement of dielectric constant and of refractive index would give the value of the dipole moment.

(iv) Measurement of Dipole Moment of Substance which are not Easily Obtained in Gaseous State, Solutions in Nonpolar Solvents are Used. In such cases the total molar polarization of a solution (P_{12}) in a nonpolar solvent like benzene, carbon tetrachloride, etc., follows the additivity rule and may be expressed as

$$P_{12} = \frac{D - 1}{D + 2} \cdot \frac{(x_1 M_1 + x_2 M_2)}{\rho}$$

where x_1 = Mole fraction of solvent

x_2 = Mole fraction of solute

Suffix 1 is used for solvent and suffix 2 for solute. Then

$$P_{12} = x_1 P_1 + x_2 P_2$$

where P_1 and P_2 = Molar polarizations of solvent and solute respectively

or

$$\frac{D - 1}{D + 2} \cdot \frac{(x_1 M_1 + x_2 M_2)}{\rho} = x_1 \cdot \left[\frac{D_1 - 1}{D_1 + 2} \cdot \frac{M_1}{\rho_1} \right] + \left[\frac{D_2 - 1}{D_2 + 2} \cdot \frac{M_2}{\rho_2} \right] x_2$$

where ρ = Density of mixture

ρ_1 and ρ_2 = Densities of solvent and solute respectively.

The value of P_1 is first separately determined from dielectric-constant measurement of pure solvent. Subsequently, from the determination of dielectric constant of the solution at known values of x_1 and x_2, the value of P_2 can be obtained. In this way P_2 is measured at different temperatures and the same is plotted against $\frac{1}{T}$, from the slope of which, as usual, the dipole moment μ is evaluated. Some corrections are however necessary sometimes to eliminate the solvent effects, if any.

Table 8.2. Dipole Moments of Some Substance (Debye).

Substance	μ	Substance	μ	Substance	μ
$H_2, O_2, N_2, Cl_2, Br_2$	0.00	SO_2	1.63	Allyl chloride	2.03
$I_2, CO_2, CS_2, SnCl_4$	0.00	PH_3	0.55	CH_3OH	1.70
SnI_4	0.00	PCl_3	0.78	CH_3NH_2	1.24
HCl	1.07	CO	0.13	CH_3COOH,	1.74
HBr	0.79	CH_4, C_2H_6	0.00	C_6H_5Cl	1.73
HI	0.38	C_2H_4, C_2H_2, CCl_4	0.00	p-dichlorobenzene	0.00
H_2O	1.82	CBr_4, C_6H_6	0.00	m-dichlorobenzene	1.72
H_2O_2	2.10	Naphthalene	0.00	o-dichlorobenzene	2.50
NH_3	1.49	Diphenyl	0.00	Nitrobenzene	4.23
N_2H_4	1.84	Cyclohexane	0.00	p-nitrochlorobenzene	2.83
N_2O	0.17	CH_3Cl	1.86	m-nitrochlorobenzene	3.73
H_2S	1.10	CH_3Br	1.80	o-nitrochlorobenzene	4.64
HCN	2.90	CH_3I	1.35	Aniline	1.56

5. DETERMINATION OF MOLECULAR RADIUS BY POLARIZATION

The induced polarization (P_i) may be used to find out molecular radius.

$$P_i = \frac{4}{3}\pi N \alpha$$

Putting the standard values of π and N, we get

$$P_i = 2.54 \times 10^{24}\,\alpha \qquad \qquad \text{... (1)}$$

For gases or vapours refractive index is very close to unity, hence we may write

$$P_i = \frac{D_0 - 1}{D_0 + 2} \cdot \frac{M}{\rho}$$

$$= \frac{D_0 - 1}{(1 + 2)} \cdot \frac{M}{\rho}$$

$$P_i = \frac{D_0 - 1}{3} \cdot \frac{M}{\rho} = \frac{D_0 - 1}{3} \cdot V_m \qquad (V_m = \text{Molar volume})$$

At NTP $P_i = \frac{D_0 - 1}{3} \times 22400 \text{ cc} \qquad \qquad \text{... (2)}$

$(\text{At NTP, } V_m = 22400 \text{ cc})$

From equations (1) and (2)

$$2.54 \times 10^{24} \, \alpha = \frac{D_0 - 1}{3} \times 22400$$

$$\therefore \qquad \alpha = 2.94 \times 10^{-21}(D_0 - 1) \qquad \qquad \dots (3)$$

Again if a conducting sphere of radius r be placed in an electric field of intensity χ, the induced electric moment (induced dipole moment) would be

$$\mu_i = r^3 \cdot \chi$$

Since

$$\mu_i = \alpha \cdot \chi$$

Hence

$$\alpha \cdot \chi = r^3 \chi$$

$$\therefore \qquad \alpha = r^3 \qquad \qquad \dots (4)$$

From equations (3) and (4), we get

$$r^3 = 2.94 \times 10^{-21} (D_0 - 1)$$

$$\therefore \qquad r = [2.94 \times 10^{-21} (D_0 - 1)]^{1/3} \text{ cm}$$

$$= [2.94 (D_0 - 1)]^{1/3} \times 10^{-7} \text{ cm}$$

It is thus easy to obtain radius of a spherical molecule from polarizability or dielectric constant. The result will however be approximate in view of liberal assumptions made. Thus, for hydrogen molecule from dielectric constant relation, the radius comes to be 0.92 Å, while from viscosity measurements it is 1.09 Å.

6. APPLICATIONS OF DIPOLE MOMENT

The following are the main application of dipole moment :

(i) **Determination of Molecular Structure.** Dipole moment gives the following valuable informations regarding molecular structure of the compounds :

(a) Percentage of ionic character in the bond.

(b) Geometry of molecules, especially the bond angles and symmetry of the molecules.

(a) **Calculation of Percentage of Ionic Character in the Bond.** Chemical bonding between two atoms is necessarily associated with an electrical moment arising out of the difference in the electronegativity of the two atoms. This means that every bond carries with it an electrical moment called the *bond moment* or *bond dipole*. The dipole moment of a molecule is vectorial sum of individual bond moments present in the molecule. The bond dipole moment gives information regarding the extent to which bond is permanently polarized, *i.e., the extent of ionic character in the bond.* How the bonding electrons are located and shared between the two atoms can be somewhat assessed from the calculations of dipole moment. This can be illustrated by taking following examples :

1. HCl has dipole moment 1.07 D and bond length 1.275 Å. If we suppose that HCl is completely ionized *i.e.,* the pair of bonding electrons is completely held by chlorine atom, then H will carry a charge of + 1 electron unit and Cl atom will have a charge of − 1 electron unit.

Now 1 electron unit charge $= 4.8 \times 10^{-10}$ esu

Distance between positive and negative charge centres $= 1.275$ Å

$$= 1.275 \times 10^{-8} \text{ cm}$$

Expected (calculated) dipole moment $= (4.8 \times 10^{-10}) (1.275 \times 10^{-8})$ esu-cm

$$= 6.05 \times 10^{-8} \text{ esu-cm}$$

$$= 6.05 \text{ debye}$$

But, observed dipole moment $= 1.07$ debye

Per cent ionic character of the bond $= \dfrac{100 \times \text{Observed dipole moment}}{\text{Calculated dipole moment}}$

Per cent ionic character $= \dfrac{100 \times 1.07}{6.05} = 17.7$

Thus the bond in HCl has 17.7 per cent ionic character.

2. In NaCl molecule, bond length is 2.36 Å and its dipole moment is 8.5 debye. Hence

Expected (calculated) dipole moment $= 4.8 \times 10^{-10} \times 2.36 \times 10^{-8}$

$= 11.3 \times 10^{-18}$ esu-cm $= 11.3$ debye

Observed dipole moment $== 8.5$ debye

Per cent ionic character $= \dfrac{100 \times 8.5}{11.3} = 75$

Thus bond in NaCl has 75 per cent ionic character.

(b) **Calculation of Bond Angle.** *The angle subtended by the two axes of overlaps or the bond is referred to as Bond Angle.* The bond dipole moment enables us to determine the bond angle. If m_1 and m_2 be the bond moments and α be the angle between their directions, then

$$\mu = \sqrt{m_1^2 + m_2^2 + 2 m_1 m_2 \cos \alpha}$$

The calculation of bond angle is illustrated by taking following examples :

1. In water molecules (H_2O) there are two identical O–H bonds each of bond moment of 1.5 debye. The net dipole moment of water molecule is 1.84 debye. Hence

$$1.84 = \sqrt{(1.5)^2 + (1.5)^2 + 2 \times 1.5 \times 1.5 \cos \alpha}$$

$$\therefore \quad \alpha = 104.5°$$

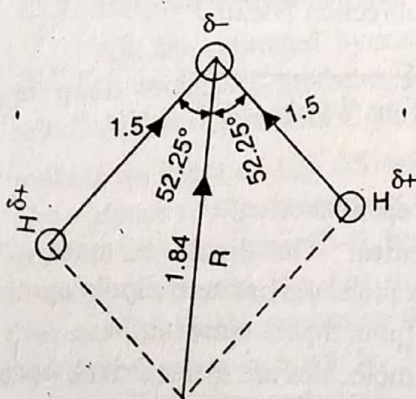Hence two O–H bonds are directed at an angle of $104.5°$ with respect to each other.

Fig. 8.8. Dipole moment of water molecule.

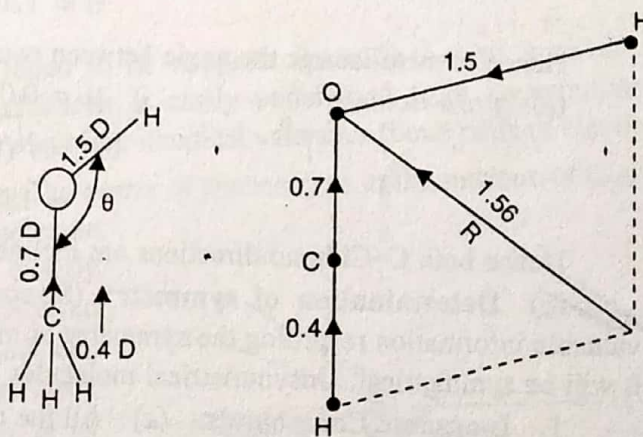**Fig. 8.9.**

2. In methyl alcohol, the bond moments are —

$$m_{OH} = 1.5 \, D$$

$$m_{C-O} = 0.7 \, D$$

$$m_{CH_3} = m_{CH} = 0.4 \, D$$

Resultant Dipole moment of $CH_3OH = 1.56 \, D$

$$\therefore \quad \mu = \sqrt{m_1^2 + m_2^2 + 2 m_1 m_2 \cos \theta}$$

$$1.56 = \sqrt{(0.7+0.4)^2 + (1.5)^2 + 2(0.7+0.4) \times 1.5 \cos \theta}$$

$$\therefore \quad \theta = 110°$$

3. Benzene, which is nonpolar ($\mu = 0$) acquires dipole moment when some of its hydrogens are substituted. Let us take dichlorobenzene. It has three isomers.

The bond angle between two C–Cl bonds in each case can be calculated with the help of bond moments.
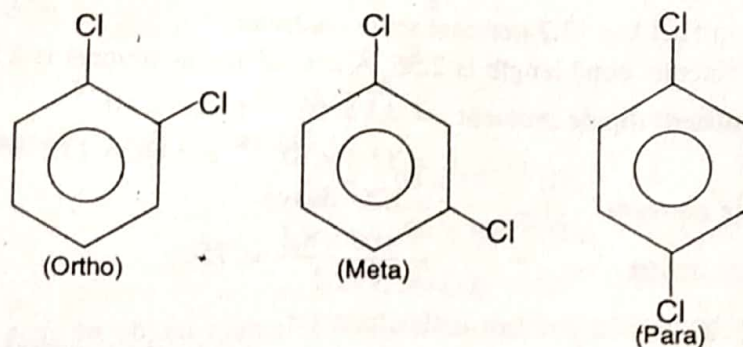

(Ortho) (Meta) Cl (Para)

Fig. 8.10.

(a) *Ortho-isomer* $\mu = 2.6\ D$

$$m_{C-Cl} = 1.5\ D$$

$$\therefore \quad \mu = \sqrt{m_1^2 + m_2^2 + 2m_1 m_2 \cos \theta}$$

$$2.6 = \sqrt{(1.5)^2 + (1.5)^2 + 2 \times (1.5)^2 \cos \theta}$$

$$\therefore \quad \theta = 60°$$

Hence two C–Cl bond directions are inclined at angle of 60° to each other in ortho-isomer.

(b) *Meta-isomer* $\mu = 1.5\ D$

$$1.5 = \sqrt{(1.5)^2 + (1.5)^2 + 2(1.5)^2 \cos \theta}$$

$$\therefore \quad \theta = 120°$$

Hence in meta-isomer the angle between two C–Cl bond direction is 120°.

(c) *Para-isomer* $\mu = 0.0\ D$

$$0.0 = \sqrt{(1.5)^2 + (1.5)^2 + 2(1.5)^2 \cos \theta}$$

$$= 180°$$

Hence both C–Cl bond directions are inclined at 180° to each other.

(c) **Determination of symmetry (Shape) of Molecules.** The dipole moment gives valuable information regarding the symmetry of molecules. If a molecule has zero dipole moment, it will be symmetrical. Unsymmetrical molecules possess a definite dipole moment.

1. **Inorganic Compounds.** (a) All the monoatomic molecules are symmetrical, because their dipole moment is zero.

(b) Homonuclear diatomic molecules have zero dipole moment, hence they are symmetrical linear molecules. The heteronuclear diatomic molecules are also linear, though they do have dipole moment.

(c) Triatomic molecules like CO_2, CS_2, $HgCl_2$ have zero dipole moment and hence they are linear

$$O=C=O; \quad S=C=S; \quad Cl-Hg-Cl$$

(symmetrical linear triatomic molecules)
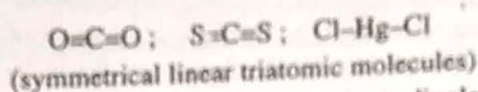
But, if the triatomic molecule has polarity (*i.e.*, possesses dipole moment) it cannot be linear. They will have triangular bent arrangement. For example H_2O, H_2S, SO_2 etc., have V-shaped structure.
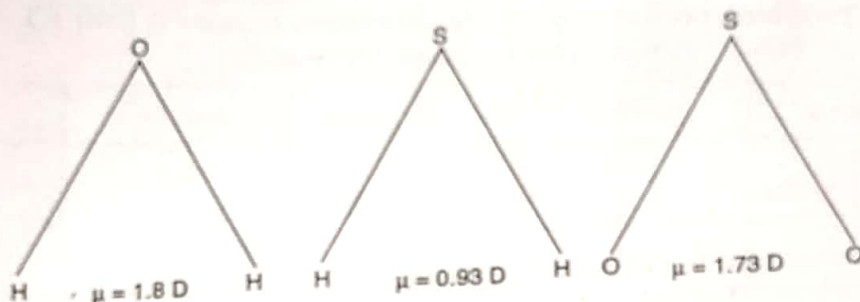

Fig. 8.11.

(*d*) Boron trichloride is non-polar ($\mu = 0$), which suggests that it has planar configuration with three chlorine atoms at the corners of an equilateral triangle and boron at the centre. But PCl_3, NH_3 molecules have dipole moments. In these molecules, the three halogens or hydrogens are in one plane and symmetrically placed in relation to phosphorus (or nitrogen) which is at the apex of a regular pyramid.

2. **Organic Compounds.** All the symmetrical molecules have zero dipole moment. For example in benzene the six hydrogen atoms lie in the same plane, hence molecule is symmetrical. This is also confirmed by dipole moment study, as benzene has zero dipole moment.

In CCl_4 molecules, each C–Cl bond has dipole moment of 1.6 *D*. All the four bonds are arranged in tetrahedral manner, and the vector sum of four bond moments comes to be zero. Hence CCl_4 molecule is symmetrical.

All the saturated hydrocarbons are found to be nonpolar ($\mu = 0$). Let us consider the simplest molecule, methane. Its nonpolar character is easily understood from its symmetrical tetrahedral structure with C-atom at the centre and four identical valencies (bond pairs of electrons) making an angle of 109° 28' with each other. The *centre of symmetry* is at the nucleus of C-atom. The absence of dipole moment in methane molecule implies that any one C–H bond moment exactly counter balances the net moment contributed (vectorially) by the remaining three C–H bonds *i.e.*, the methyl group as a whole. The CH_3-group has a regular pyramidal configuration with C-atom at its apex and three hydrogens at the base (Fig. 8.12). The resultant moment of three C–H bonds will be directed along a line from the centre of the base towards the apex and opposite to the fourth C–H bond moment direction.
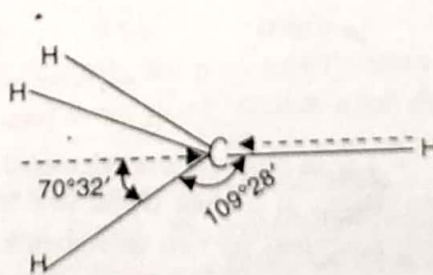

Fig. 8.12.

Using symbol *m* for bond moments, the resultant moment of the CH_3-group is given by

$$m_{CH_3} = 3 \cdot m_{C-H} \cos(180° - 109° 28') = 3\, m_{C-H} \times \frac{1}{3} = m_{C-H}$$

That is, the moment of CH_3-group is the same as that of C–H bond *i.e.*, 0.4 *D*. It is obvious

that for identical reasons the moment of C_2H_5-group or other alkyl group will also be equal to C–H bond moment.

Not only alkyl groups, other groups or radicals such as $-NH_2$, $-NO_2$, $-OH$, etc., have definite moments, called **Group Moments**. These group moments will naturally depend upon the nature of linkages present in those groups. When one or more of such radicals are present in a molecule, these contribute towards the dipole moment of the same.

It leads to the conclusion that if a hydrogen atom in different saturated hydrocarbons be replaced by –OH to produce homologous alcohols, all of the latter should have the same dipole moment. Similarly all alkyl amines, or alkyl chlorides could be expected where identical dipole moment. This is borne out from experimental observations as shown in Table 8.3.

<div align="center">Table 8.3. Dipole Moments (D).</div>

Alkyl group	Alcohols	Amines	Chlorides	Nitriles
ethyl	1.70	1.3	2.04	3.57
propyl	1.66 ·	1.4	2.04	3.57
butyl	1.65	1.3	2.04	3.57

The magnitude of *group moments* varies slightly in aromatic compounds from those in aliphatic ones. In 1929 Williams computed the following group moments for aromatic compounds :

$-NO_2$	$-CHO$	$-OH$	$-Cl$	$-Br$	$-COOH$	$-CH_3$	$-NH_2$	H
-3.9	-2.8	-1.7	-1.5	-1.5	-0.9	$+0.4$	$+1.5$	0.00

[**Note.** Negative sign indicates the group moment directed away from the aromatic ring.]

Benzene, which is nonpolar ($\mu = 0$), acquires dipole moment when one of its hydrogen is substituted. Thus, we have,

μ= 0.00 D   1.7 D   1.40 D   3.9 D   1.5 D   0.4 D
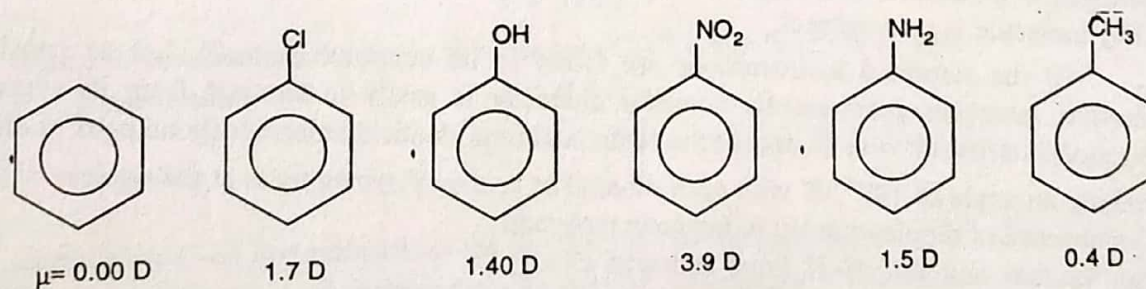
Let us consider the calculated and measured dipole moments of many disubstituted benzene derivatives. If μ_1 and μ_2 be two bond moments or group moments and θ be the angle between their directions for two substituents of benzene, then calculated value of μ is given by

$$\mu_{cal} = \left[\mu_1^2 + \mu_2^2 + 2\,\mu_1\,\mu_2 \cos\theta \right]^{1/2}$$

It is easily seen that $\theta = 60°$ for ortho, $120°$ for meta and $180°$ for para derivatives. The values for some of these compounds are tabulated here (Table 8.4).

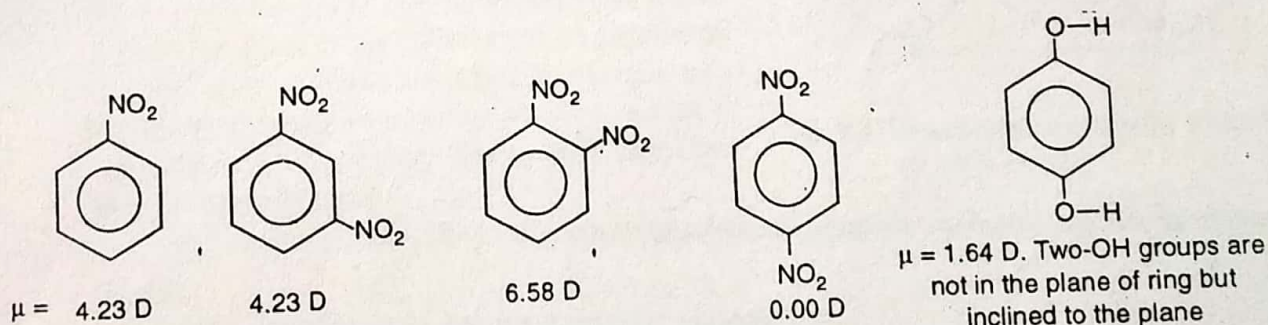## Table 8.4. Dipole moments of $C_6H_4X_1X_2$ Compounds.

X_1	X_2	ortho		meta		para	
		μ_{cal}	μ_{obs}	μ_{cal}	μ_{obs}	μ_{cal}	μ_{obs}
CH_3	Cl	1.39	1.35	1.79	1.78	1.95	1.90
CH_3	NO_2	3.76	3.66	4.16	4.17	4.30	4.40
Cl	NO_2	5.26	4.60	3.68	3.69	2.52	2.70
NH_2	NO_2	3.64	4.26	4.74	4.85	5.17	5.21
Cl	CN	4.88	4.75	3.40	3.40	2.40	2.50

The concordance of the experimental values with the calculated ones is inescapable. In disubstituted ortho compounds, some deviation is often noticed specially when the substituents have strong bond moments. This is due to inductive and mesomeric effects of two groups in close proximity.

In the special case when $X_1 = X_2$, i.e., two substituents are identical, we have

For ortho-isomer $\quad \mu = \sqrt{3}\,m_1$

For meta-isomer $\quad \mu = m_1$ } $(m_1 = $ bond or group moment)

For para-isomer $\quad \mu = 0$

For example,

$\mu = $ 4.23 D $\qquad$ 4.23 D $\qquad$ 6.58 D $\qquad$ NO$_2$ 0.00 D $\qquad$ $\mu = 1.64$ D. Two-OH groups are not in the plane of ring but inclined to the plane

Further the observation that p-dihydroxy benzene, p-$C_6H_4(OH)_2$, has $\mu = 1.64\,D$ shows that two –OH groups are not in the plane of the ring but inclined to the plane, so that a net dipole moment has resulted

$\mu = 1.64\,D$. Two – OH groups are not in the plane of ring but inclined to the plane

(ii) **Explanation for the Behaviour of Solutions and Gases.** The knowledge of dipole moments is quite helpful in the interpretation of behaviour of solutions and gases, which is often different from their ideal states.

(iii) **Explanation of Solubilities.** Dipole moment study is quite valuable in explaining the solubilities of substances.

(iv) **Influence of Solvent.** The dipole moment is helpful in explaining the influence of solvents on the reaction rates. Also the dipole moment suggests that polar substance can dissolve better in polar solvents and most ionic substance can dissolve in water.

(v) **Distinction between Cis- and Trans-isomers.** The cis-isomer has higher dipole moment than the trans-isomer.