CEMACOR08T:Physical Chemistry - III

Dipole Moment and Polarisability

The spatial distribution of bonding electrons between the two nulei of a diatomic molecule depends on the nature of the two involved atoms. For homonuclear diatomic molecules such as H_2, N_2 etc. the distribution of electron cloud is symmetrical around the two nuclei of the molecule. In heteronuclear diatomic molecules like HCl, HBr etc. the charge distribution is not symmetrical, the bonding electron is more near to the more electronegative atom. As a result the molecule acquires separation of charges at the two ends. The distribution of charges in a molecule can be described by a physical parameter, known as the dipole moment. For diatomic molecule it is defined as the product of the charge Q at either end of the molecule and distance between two charges. i.e.

$$\mathbf{P} = Q\, r$$

Dipole moment is a vector quantity, hence represented by bold symbol. In general for polyatomic molecule dipole moment can be expressed as,

$$\mathbf{P} = \sum_i Q_i\, r_i$$

Units of dipole moment:

CGS-esu units: esu cm

SI units: C m

Most molecules possess dipole moment of the order of 10^{-18} esu cm. In order to express dipole moment of the molecules in simpler numbers, 10^{-18} esu cm unit of dipole moment is named as Debye units and is represented by the symbol D. It is obvious that

$$4.8 \text{ D} = 1.602 \times 10^{-29} \text{ C m} = 3.3356 \times 10^{-30} \text{ C m}$$

Question:

If one electronic charge is separated from an equal positive charge by a distance of 0.1 nm, calculate its dipole moment in CGS and SI units.

Induced dipole moment

The electronic distribution of a molecule is distorted in the presence of a static electric field and thus an induced dipole moment is generated. All the molecules having symmetric or non symmetric charge distribution are polarizable in the presence of an electrostatic field and thus carry induced dipole moment. In general, the induced dipole moment in a molecule is directly proportional to the strength of the electrostatic field. i.e,

$$P_{ind} \text{ is proportional to E}$$

$$P_{ind} = \alpha E$$

Where α is the constant of proportionality and is a measure of easiness with which a molecule can be polarized, and is known as the polarisability of the molecule. By definition α is equal to the induced dipole moment generated by a unit strength of an electrostatic field.

Different kinds of polarization

The molecule in the presence of an electrostatic field is polarized in three different ways as follows.

(i)   Electronic polarization:
        In this, the electronic cloud of the molecule is distorted towards the positive end of the electrical field. The corresponding polarizability is represented as α_e
(ii)   Atomic polarization:
        In this, the nuclei (atoms) are distorted towards the negative end of the field. The corresponding polarizability is represented as α_a
(iii)   Orientation polarization:
        This is operative only when the molecule carries a permanent dipole moment. The electric field tends to orient the molecular dipoles along the field direction. The corresponding polarizability is represented as α_o

The total polarizability α of the molecule is an algebraic sum of the above three polarizabilities. i.e.,

$$\alpha = \alpha_e + \alpha_a + \alpha_o$$

The electronic and atomic polarizations taken together is referred to as distortion polarization. Thus distortion polarizability α_d is given as

$$\alpha_d = \alpha_e + \alpha_a$$

Units of polarizability

Since $\alpha = p_{ind}/E$, we have,

CGS-esu units: esu cm/esu cm^{-2} = cm^3

Thus α has units of volume.

SI units: C m/ N C^{-1} = C^2 m N^{-1}

In the SI system, $\alpha/4\pi\varepsilon_0$ has the units of volume as shown below.

$$\alpha/4\pi\varepsilon_0 = C^2 \text{ m N}^{-1}/ C^2 \text{ N}^{-1} \text{ m}^{-2} = m^3$$

Question:

Show that polarizability has the dimension of volume.

Efffect of a Dielectric on the electrical field of a parallel plate condenser

Let σ be the charge density on the parallel plates of a condenser.

Electric field E_0 without dielectric = $4\pi\sigma$ (1a)

Electric field with dielectric = $4\pi\sigma/D$ (1b)

Where D is the dielectric constant of the medium.

SI units:

Electric field E_0 without dielectric = σ/ε_0

Electric field with dieeleectric = σ/ε

 Where ε_0 and ε are the permittivities of vacuum and medium, respectively. Since D is greater than one or ε is greater than ε_0 for most of the dielectric, we have

$E < E_0$

That is , the presence of a dielectric in a parallel plate condenser decreases its electrical field. This decrease is explained as follows.

The charge density σ on the plates polarizes the molecules of the dielectric a d thereby generates induced dipole moment in the molecules. These induced dipoles, in turn, are

oriented in the field; positive ends of dipoles point towards the negatively charged plate and negative ends towards the positively charged plates.

This arrangement of molecules adjacent to the plates decreases the net charges on the plates. If σ_{ind} is the induced charge per unit area on each plate, we have

Net charge per unit area on each plate = $\sigma - \sigma_{ind}$

The term σ_{ind} is known as polarization. The factor σ_{ind} will also be equal to the induced dipole moment per unit volume of the dielectric. This may be understood as follows;

σ_{ind} = induced positive or negative charge per unit area of the plate

σ_{ind} = Induced charge/ Unit of area

σ_{ind} = (Induced charge)(Unit of length)/ (Unit of area)(Unit of length)

σ_{ind} = Induced dipole moment / Unit of volume

The electric field E may be written as:

CGS-esu units: $\qquad E = 4\pi(\sigma - \sigma_{ind})$ $\qquad\qquad\qquad\qquad$ (2a)

SI unit $\qquad\qquad E = (\sigma - \sigma_{ind})/ \varepsilon_0$ $\qquad\qquad\qquad\qquad$ (2b)

Substituting (1a) and (1b) in equation (2a) and (2b), we find that

CGS-esu units: $\qquad E = E_0 - 4\pi\ \sigma_{ind}$

SI units: $\qquad\qquad E = E_0 - (\sigma_{ind}/ \varepsilon_0)$

By rearrangement we get,

CGS-esu units: $\qquad E = 4\pi\ \sigma_{ind} /(D-1)$ $\qquad\qquad\qquad\qquad$ (3a)

SI units: $\qquad\qquad E = (\sigma_{ind}/ \varepsilon_0)/[(\varepsilon/ \varepsilon_0) - 1]$ $\qquad\qquad\qquad$ (3b)

Where $D = (\varepsilon/ \varepsilon_0) = (E_0/E)$ = Dielectric constant of the medium.

Equation (3a) and (3b) relates the electric field with the distortion polarization and relative permittivity or the dielectric constant of the medium.

Question

The electric field gets reduced in the presence of a dielectric medium – Justify or criticize.

Arrive at expression of modified electric field in terms of dielectric constant of the medium.

Clausius Mosotti Equation

CGS-esu units:

$$\frac{D-1}{D+2}\frac{M}{\rho} = \frac{4}{3}\pi N_A \alpha_d \qquad (4a)$$

SI units:

$$\frac{\frac{\varepsilon}{\varepsilon_O}-1}{\frac{\varepsilon}{\varepsilon_0}+2}\frac{M}{\rho} = \frac{1}{3\varepsilon_0}\pi N_A \alpha_d \qquad \textbf{(4b)}$$

Equation (4a) and (4b) are known as the Clausius Mosotti equation. The left hand side oh the equation is known as molar polarization and is represented as P_m. P_m is independent of temperature as the right hand side of the equation is independent of temperature.

Clausius Mosotti equation is applicable only for non polar molecules which do not possess permanent dipole moment like CO_2, H_2, CH_4 etc. For molecules having permanent dipole moment Clausius Mosotti equation fails.

[*Derivation of Clausius Mosotti equation is not included in WBSU syllabus*]

Question

Write down Clausius Mosotti equation and explain terms. For which type of molecule does the equation is good to calculate molar polarization?

Debye Equation

Debye modified Clausius Mosotti equation to explain the behavior of polar molecule. According to him, the effect of an applied electrostatic field, besides producing distortion polarization, is to align molecular dipoles in the field direction. This polarization is known as the orientation polarization. The only factor which opposes the orientation polarizatioj is the thermal energy of molecules. Larger the thermal energy, greater will be randomness and hence lesser will be the orientation polarization. Since thermal energy of gaseous system depends on temperature, it follow that the value of orientation polarization depends on the temperature of the system.

In general orientation polarizability depends on the following two factors.

(a) Directly proportional to the average value of component of permanent dipole moment **P** of the molecule in the applied field direction.

(b) Inversely proportional to the temperature of the system.

Detailed calculations have shown that the orientation polarizability is given by

$$\alpha_o = \frac{p^2}{3kT}$$

Since total polarizability is the sum of distortion and orientation polarizabilities, we have

$$\alpha_{total} = \alpha_d + \alpha_o$$

For polar molecules, the Clausius-Mosotti equation modifies to

CGS-esu units:

$$\frac{D-1}{D+2}\frac{M}{\rho} = \frac{4}{3}\pi N_A \alpha_{total} \qquad\qquad (5a)$$

SI units:

$$\frac{\frac{\varepsilon}{\varepsilon_0}-1}{\frac{\varepsilon}{\varepsilon_0}+2}\frac{M}{\rho} = \frac{1}{3\varepsilon_0}\pi N_A \alpha_{total} \qquad\qquad (5b)$$

Equation (5a) and (5b) are known as Debye equation.

CGS-esu units:

$$\frac{D-1}{D+2}\frac{M}{\rho} = P_m = \frac{4}{3}\pi N_A\left\{\alpha_d + \frac{p^2}{3kT}\right\} \qquad\qquad (6a)$$

SI units:

$$\frac{\frac{\varepsilon}{\varepsilon_0}-1}{\frac{\varepsilon}{\varepsilon_0}+2}\frac{M}{\rho} = P_m = \frac{4}{3}\pi N_A\left\{\alpha_d + \frac{p^2}{3kT}\right\} \qquad\qquad (6b)$$

Equations (6a) and (6b) are known as Debye equation.

[*Derivation is not included in WBSU syllabus*.]

According to (6a) or (6b), P_m varies linearly with inverse of temperature. The slope and intercept of linear plots are $(4/9)\pi N_A p^2/k$ or $(1/9)N_A p^2/k\varepsilon_o$, and $(4/3)\pi N_A \alpha_d$ or $(1/3)N_A \alpha_d/\varepsilon_o$, respectively. From slope and intercept, p and α_d of the molecule may be determined.

P_m

$p \neq 0$

$p = 0$

$1/T \longrightarrow$
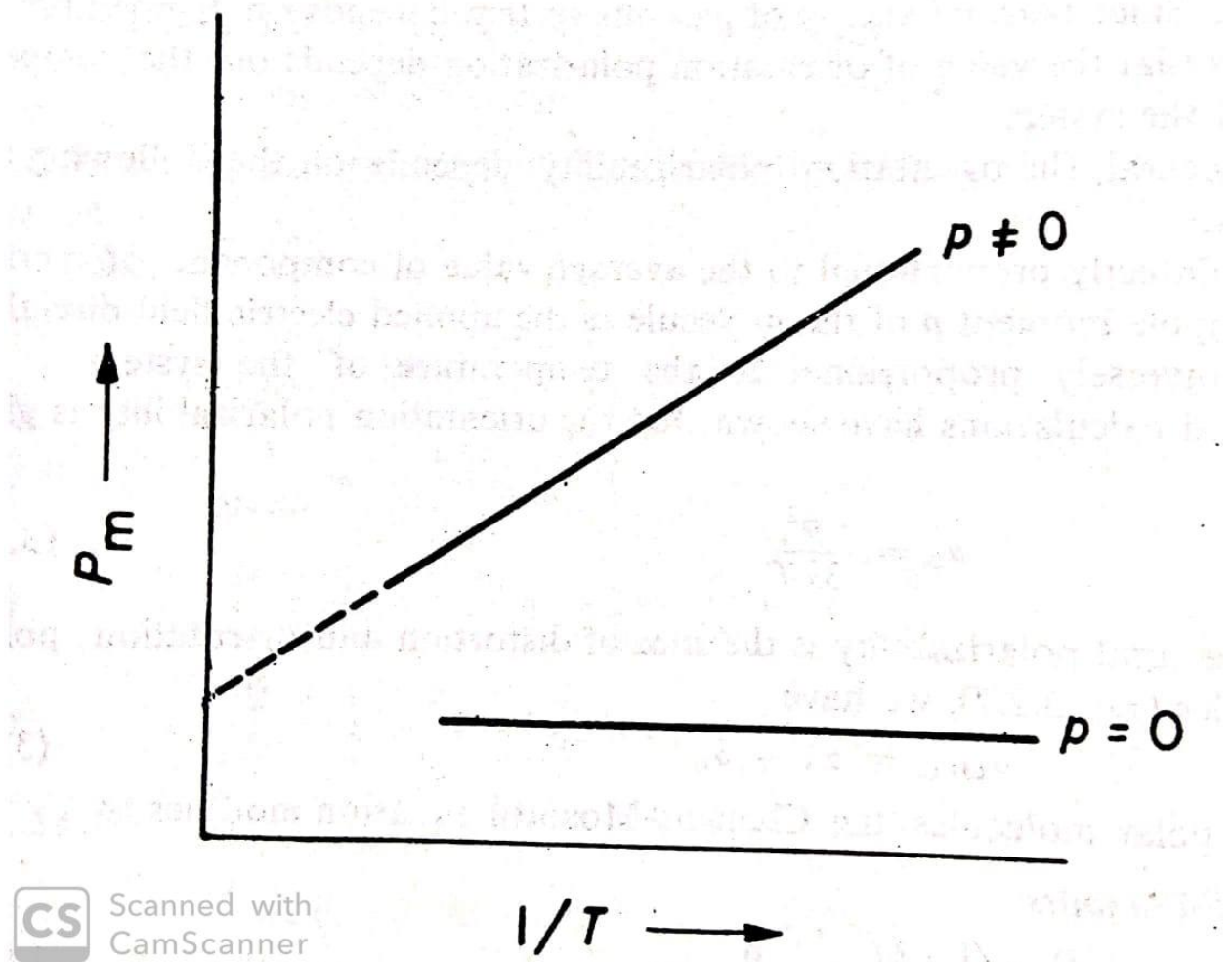
The graph above illustrates the linear plots for the two gaseous systems. For nonpolar molecules, since p =0 , the plot of P_m versus 1/T would yield a straight line parallel to 1/T asix.

Question:

Write down Debye equation for molar polarization. In which context it is better than Clausius Mosotti equation? Explain how molar polarization can be obtained for both polar and non polar molecules from graphical representation of the equation.