**electrical & magnetic properties of atoms & molecules**

**Syllabus:** Basic ideas of electrostatics, Electrostatics of dielectric media, Clausius-Mosottii equation,Lorentz-Lorenz Equation, Dipole moment and molecular polarizabilities and theirmeasurements. Diamagnetism, paramagnetism, magnetic susceptibility and its measurement,molecular interpretation

**Introduction:**

When a substance (atom or molecule) is placed in an external **electric** or **magnetic** field, there might be occurred some certain change in the **structural** features of the substance. This chapter deals with the structural information that can be derived when a substance is placed in an electrostatic or magnetic field.

The basic electrical property of a molecule is its **dipole** **moment**, which helps in understanding the relative location of the various bonds in the molecule.

The study of a substance in a magnetic field helps in knowing whether the substance is **paramagnetic** or **diamagnetic**, which are directly linked to the presence (paramagnetic) or absence (diamagnetic) of unpaired electrons in the substance. Thus, the study of magnetic property helps in understanding the **electronic** **configurations** of atoms or molecules.

**Electric Dipole moment**:

The electric dipole moment deals with the **spatial** **distribution** of the bonding **electrons** between the covalently bonded atoms and the **nature** of the two atoms involved.

For **homonuclear** diatomic molecules such as the distribution of electronic cloud is symmetrical around the two nuclei of the molecule, *i.e*. covalently bonded electron pair is shared equally between the bonded atoms in the molecule. Thus, is , symmetrical distribution of electronic charge density.

But, in the case of **heteronuclear** diatomic molecules such as , *etc*. because of the electronegativity difference between the bonded atoms, the electron pair is not shared equally between the bonded atoms, *i.e*. the charge distribution is not symmetrical and, the bonding electron pair are more neared to the more electronegative atom. Thus, is more likely to exist as , *i.e*. unsymmetrical distribution of electronic charge density as .

Because of the unsymmetrical distribution of electronic charge density in heteronuclear diatomic molecules such as , *etc*., the molecule acquires a partial separation of charges at the two ends, called the **dipoles**, the more electronegative atom serves as the end and the lesser electronegative atom serves as the end. Thus, may be written as .

The distribution of charges in a molecule (heteronuclear) can be described by a physical parameter, known as the dipole moment, represented by the symbol ‘’. For diatomic molecules, the dipole moment is **defined** as the ***product of the charge ‘’ at either end of the molecule and the distance ‘’ between the two charges*** (*i.e*. internuclear distance). Mathematically, dipole moment is defined as —

The dipole moment is a vector quantity, *i.e*., it has both magnitude as well as direction. It can be represented by an arrow that indicated the direction from to end of the molecule. The length of the arrow is directly proportional to the magnitude of the dipole moment as shown in the figure (a) given below.



**Dipole moment as Vector Addition**:

The definition of dipole moment given by the equation () *viz*. can be expressed as the vector addition, *i.e*.

Here is the charge of the species and is the vector length of this charge from any arbitrary distance point. ***For example***, the dipole moment of the molecule shown in the figure (a) & (b) is —

The above vector addition can be conveniently done by making use of the expression —

Here are the - and - components of dipole moment. From figure (b), we have —

The definition of dipole moment given by equation () may be extended to any assembly of charges (as explained by the following problem given below). For **polyatomic molecules**, equation () may be written as —

Here is the charge density at a position defined by the vector and is the volume element.

**Problem** (1): For the assembly of charges shown in the figure, evaluate the expression of the dipole moment. Given: The angle between the dashed lines is .



**Solution**: Let us have the origin at charge as in the above figure,

Thus, we have —

Now, —

Now, —

**Units of Dipole moment**:

Since, dipole moment,

Hence, we will have, —

**-** : The units of are

**-** : The units of are

If one electronic charge is separated from an equal charge by a distance of , its dipole moment would be —

**-** :

**-** :

It has been observed that most of the molecules possess dipole moment of the order of . In order to express the dipole moment of molecules in simpler numbers,  **unit of dipole moment is named as the Debye units** and is represented by the symbol ‘’. Thus, it is obvious that —

**Induced Dipole Moment**:

When a molecule is placed in an external static electric field, its electronic distribution is distorted, and thus an **induced dipole moment** is generated and the molecule is **polarized** temporarily because, as soon as the applied electric field is removed the molecule retained its original electronic distribution. All molecules having **symmetrical** or **non**-**symmetrical** charge distribution are **polarisable** in the presence of an electrostatic field and thus, carry induced dipole moment. It has been observed that —

The **extent of polarization** or **induced dipole moment** in a molecule is **directly** ***proportional*** to the **strength** of **electrostatic** **field** applied, *i.e*. —

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

**Different types of Polarization**:

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

() **Electronic Polarization**: In the electronic polarization, the electronic cloud of the molecule is distorted towards the end of the electric field. The corresponding polarizability id represented as .

(**)** **Atomic Polarization**: In the atomic polarization, the nuclei (atoms) are distorted towards the end of the electric field. The corresponding polarizability id represented as .

() **Orientation Polarization**: The orientation polarization 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 id represented as .

The total polarizability ‘’ of the molecule is an algebraic sum of all the polarizabilities

The electronic and atomic polarization taken together is referred to as **distortion polarization** (). Thus, distortion polarization, is given by —

**Units of Polarizability**:

Since, polarizability, , hence, we have —

**- Units**: The units are —

**Units**: Here, we have —

In SI system, has the units of volume as shown below —

**Effect of a Dielectric on the Electric Field of a Parallel Plate Condenser**: [To Page 14]

**[Important**: Before this, it will be better to know some basic and fundamental principles of **Electrostatics** & **Magnetic** **Fields** —

**A few Definitions regarding the Electrostatic Field**:

A few definitions in both the units, viz. **Gaussian** (- ) and , needed for the study of a **substance** in the **electrostatic** **field** are described below —

**Coulomb’s Law**:

In **- units**, the **force** of **attraction** or **repulsion** between two electrostatic point charges placed at a distance is defined as —

Here is the **dielectric constant** of the medium. For **air** or more precisely for a **vacuum**, . If have the same sign (), is a quantity meaning the force between the two charges is **repulsive**; if have the **opposite signs**, is a quantity implying that the force between the two charges is **attractive**.

In **- systems**, equation () is taken as the **basis** for **defining** a unit of electrostatic charge (). The two unit charges (known as **stat coulomb**, ) placed at a distance of will attract or repel each other with a force of . Thus —

In **- system**, the unit of **charge** is **not** taken as **fundamental quantity**. It is the unit of **current** that is taken as the fundamental quantity. In this system, a unit of current is the **ampere**, which is **defined** as the current which when flowing through the two infinitely long parallel wires  **apart** causes an electromagnetic force of per metre of its length to act on each wire. Since, the electric **current** () is **defined** as the rate of flow of charge through a conductor, we have —

The **unit of charge** is the **coulomb** (), which is **defined** as the amount of **charge** when of current flows for . Thus, —

In terms of **charges in coulombs**, **Coulomb’s law** is written as —

Here, is the proportionality constant and is written as —

Here, ‘’ is the permittivity of the space. For free (empty) space, we write it as . The experimental value of

**Relationship between Stat Coulomb & Coulomb**:

Let us consider two charges separated by in a vacuum, hence from equation (), we have —

Since, —

Now, substituting the above value of and in equation (1), we get

**Relationship between** :

From the above discussions, it is evident that —

In **- units** —

In **- units** —

Thus, the **dielectric** **constant** () is equal to the **relative** **permittivity** ().

**Intensity of Electric Field**:

Around each charge, an electric field exists because of which another charge placed at a certain distance experiences a force of attraction or repulsion. The ***intensity of electric field*** or ***electric field strength*** at a point is **defined** as the **force** experienced by a **unit charge** at that point. **Mathematically**, we can write —

The electric field strength of a charge at a distance ‘’ will be given by —

In **- units** —

In **- units** —

Since, is a vector quantity, the electric field (intensity) is also a vector quantity. At a point in space, the electrical field can be represented by an arrow; the length of the arrow is directly proportional to the magnitude of and it points towards the charge if is and away from it if Q is .

The ***total electrical field strength*** all around the charge at a distance is given by —

Thus, in **- units** —

In **- units** —

Thus, the **dielectric constant**, in **-**  units or the **relative permittivity** () in  **units** of a substance can be **defined** in terms of **electrical** **field** as —

**Electrical Potential**:

Instead of describing interactions at a point in terms of electrical field, it is more **convenient** to use the electrical potential. The **electrical potential is defined** as the ***amount of reversible electrical work done in bringing a unit charge from infinity to the point under study***.

Mathematically, electrical potential may be evaluated as follows —

In **- units** —

In **- units** —

The **change** of potential with distance can be derived by differentiating Eq. (8), such that —

In **- units** —

In **- units** —

From equation (), it follows that —

Thus, the electrical field intensity is the  ***gradient of potential with distance***.

**Units of** : From the expressions , we have —

Therefore, it can conclude that —

**- Units** —

The unit of electrical potential in **- system** is stat volt (). Thus, —

The following identity for the units of may be established —

**- Units** —

The unit of electrical potential in **- system** is volt (). Thus, —

The following identity for the units of may be established —

**The Relationship between** :

Since, we have —

Again, we have —

**Capacitance of the parallel Plate Condenser**:

A condenser or capacitor is made up of two parallel plates as shown in the figure given below. Let ‘’ be the distance between two parallel plates and let ‘’ be the area of cross section of each of the two plates. Let, a potential difference of be generated by connecting the parallel condenser to a battery. Let and be the charges generated on the plates.



Thus, —

Charge density, on each plate

***The following facts can be derived for the condenser*** —

***CGS*- units**: Electrical field, generated by the charges in between the plates —

Potential difference, between the two plates —

Capacitance of the condenser

In a vacuum or free space, we will have —

***SI*- units**: Electrical field —

Potential difference, between the two plates —

Capacitance of the condenser,

Capacitance in a vacuum or free space, we will have —

From equations () and (), we find that —

The unit of capacitance is farad. Since, , therefore, we have —

**The Magnetic Field**:

There exists a magnetic field around a magnet due to which another magnet placed at a certain distance experiences force of attraction or repulsion. The **intensity** of **magnetic** **field** at a point can be **defined** by writing an expression for the force between two magnetic poles in a way analogous to the electrical field (Eq. ). However, because of the clumsy nature, magnetic field is best defined (explained) in terms of its interaction with moving charge.

The **magnetic** **force** on a moving charged particle is known as the ***Lorentz force***. If a particle with charge moves with velocity through a magnetic field acting perpendicular to the direction of velocity, the **Lorentz force** is given by —

In **Gaussian system**, is expressed in (or stat coulomb), (**speed of light**) in , and in . The unit of in this system is ***gauss*** (). From equation , we have —

In **SI units**, is expressed in , in , and in . The unit of is ***tesla*** (), also called , where stands for ***Weber***. From equation , we have —

The magnetic field is a **vector** **quantity** and is known as **magnetic** **induction** or magnetic **flux** **density**. The direction of can be determined with the help of **right-hand rule**: If thumb, index finger and middle finger point towards the -, - and - axes in a right handed coordinate system, then they represent the direction of of a charge, respectively.

**Relationship between *tesla* and *gauss* units**:

Considering a charge of flowing perpendicular to the magnetic field of with a velocity of . The force acting on the charge is —

Since, , therefore, we have —

In ***Gaussian system***, the equivalence of can be worked out as follows —

Hence,

Therefore,

**Magnetic Field produced by an Electric Current**:

Experimentally, it has been seen that the magnetic field at distance from a very long () straight wire in a vacuum carrying a current is directly proportional to and inversely proportional to , such that —

Here, is the proportionality constant. In the two units mentioned above, the constant is as described below —

In ***Gaussian system***,

In ***SI units***,

Here, is the permeability of the vacuum. The has the following dimensions —

In ***Gaussian system***:

Thus, has no units and is assigned a value of .

In ***SI units***:

The unit of is also known as , and will be equal to .

**Force between two Electric Currents**:

Because of the associated magnetic fields, the two electric currents in two parallel rectangular conductors of length separated by a distance in a vacuum will exert force on each other which is given by the following expressions —

In ***Gaussian system***:

Since, , therefore, the above equation reduces to —

In ***SI units***:

Since, , therefore, the above equation reduces to —

Equation is the **basis** of **defining** a unit of current (**ampere**) in SI units. The **ampere** is **defined** as that current which when flowing through two long, straight parallel wires exactly apart will exert a force on each other of exactly of the wire. From equation , we can find that will have the value of —

**The Magnetic Field Strength**:

We know that the magnetic field is a **vector** **quantity** and is also known as the **magnetic** **induction** or magnetic **flux** **density**. However, the magnetic **field strength** () is a **different vector**. In a vacuum, the two () are interrelated, and the relationship between then are as follows —

In ***Gaussian system***:

The unit of is the ***oersted*** (), which has the **same** dimension as ***gauss***.

In ***SI units***:

Here, is the permeability of the vacuum. The units of may be worked out as follows:

**Relationship between *Oersted* &** :

Let a magnetic field strength be . In Gaussian units, the magnetic induction will be equal to . Now, with this magnetic induction,  **in - units** will be equal to —

**]**

**Effect of a Dielectric on the Electric Field of a Parallel Plate Condenser**:

Let ‘’ be the **charge** **density** on the parallel plates of a condenser. Since, we know that —

In **- units**, **electric field** () **without** **dielectric**

[See as above as in Equation () of page for ]

And, **electric field** () **with** **dielectric**

Here, ‘’ is the dielectric constant of the medium

But, in **- units**, **electric field** () **without** **dielectric**

And, **electric field** () **with** **dielectric**

Here, are the permittivities of vacuum and medium respectively.

Since, is greater than is greater than for most of dielectric, hence, we have —

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

The charge density () on the plates polarizes the molecules of the dielectric and thereby generates induced dipole moment in the molecules. These induced dipoles, in turn, are oriented in the field; ends of dipoles point towards the charged plate and vice-versa as shown in the figure given below.



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

***Net charge per unit area on each plate***

The term “” is known as the ***polarization***. The factor will also be equal to the induced **dipole moment per unit volume** of the dielectric. This can be explained as follows —

Induced charge per unit area of the plate. Thus, —

Multiplying and dividing by a unit of length, we have —

Using equation (), we may write the electric field in the presence of dielectric as —

**- Units**:

**- Units**:

Substituting equation () in equation (), we get —

**- Units**:

**- Units**:

Dividing equation () by and then using [see top of page 8), we get —

**- Units**:

**- Units**:

Equation () relates the electric field with distortion polarization and the relative permittivity or the dielectric constant of the dielectric in the condenser. //

**Clausius-Mosottii Equation**:

The Clausius-Mosottii equation relates the **distortion polarizability** [see Equation (), page ] of the molecule () with the dielectric constant () of the substance.

**Derivation of Clausius-Mosottii Equation**:

Let be the number of molecules per unit volume of the dielectric material and let be the induced dipole moment on each of the molecule. Since, the polarization represents induced dipole moment per unit volume of the dielectric, therefore, we have —

If is the distortion polarizability of the molecule, then —

Substituting equation () in equation (), we have —

If is the molar volume of the dielectric, then we will have —

Here, ‘ ’ is the density of the medium, is the Avogadro’s number and is the molar mass of the substance. Again, the relation between is —

Substituting equations () and () in equation (), we have —

In **- units** —

In **- units**, the above equation is —

Since, is a **molecular property**, it is expected to be **independent** of the density of the medium. Thus, from equation (), it may be concluded that the quantity or is independent of the density of the medium. However, it is found to be so only when the molecules do **not** possess any **permanent dipole moment** and for which the pressure is low so that the interaction between neighbouring induced dipoles is negligible because of relatively larger distance between them. Equation () **does not hold good** at () **high pressure** and () for the condensed phases because of the considerable interaction between the neighbouring induced dipoles. If this interaction is taken into account, the expression of electrical field as given by —

Modifies to —

**In - units**:

**In - units**:

Where or is the factor which takes into account the interaction terms. Equation () in the present case becomes —

Substituting the value of from equation () and from relations —

[See equation () page 15]

In the equation (), we will have —

**In - units**:

**In - units**:

Equation ( is known as the ***Clausius-Mosottii equations***. The left hand side of this equation is known as the ***molar polarization*** and is represented by . Thus, —

From the above equation, it is evident that the molar polarization, is **independent** of temperature, as the right hand side of the equation is independent of temperature term.

**Clausius-Mosottii equation** is found to be **applicable** only for **non-polar molecules** which do **not** possess **permanent dipole moment**. Examples include For molecules such as , *etc*., which have permanent dipole moment, the Clausius-Mosottii equation fails very badly. Moreover, the molar polarization of such molecules as determined by using equation () varies with temperature.

**Debye Equation**:

**Debye equation** **deals** with the explanation for the **non-applicability** of **Clausius-Mosottii** equation for the polar molecules such as , *etc*., which have permanent dipole moment.

**According to** **Debye**, 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 polarization is the **thermal** **energy** of the 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 follows that the value of ***orientation polarization depends on the temperature*** of the system.

In general, the ***orientation polarizability*** depends on the following **two** factors —

1. Directly proportional to the average value of permanent dipole moment () of the molecule in the applied electric field direction, and
2. Inversely proportional to the temperature of the system.

Detailed calculations have been shown that the orientation polarizability is given by —

Since, total polarizability () is the sum of distortion () and orientation polarizabilities (), that is —

For polar molecules, the Clausius-Mosottii equation modifies to —

In **-**  units:

In **-** units:

Equation (3) is known as ***Debye equation***. Using equations () and (), equation () becomes —

In **-**  units:

In **-** units:

From equation (), it is evident that the **molar polarization**, **varies** **linearly** with **inverse** of **temperature**. The slope and intercept of linear plots are and respectively. From the slope and intercept, and of the molecule may be determined.

Figure given below illustrates the linear plots for the two gaseous systems. For non-polar molecules, since , the plot of versus would yield a straight line parallel to axis.



**Problem** (): For at and pressure, the dielectric constant (or relative permittivity) is . This molecule has a permanent dipole moment of . Assuming that behaves as an ideal gas, calculate per () total, () orientation, () induced polarizations, and () distortion polarizability.

**Solution**: Given that —

Dielectric constant (or relative permittivity),

Dipole moment, and

Molar volume, at and pressure ()

Now, () the **total (molar) polarization** —

**In - units** —

() **Orientation polarization** —

() **Induced polarization** —

() **Distortion polarization** —

**In - units** —

() **Orientation polarization** —

() **Induced polarization** —

() **Distortion polarization** —

**Problem** (): At , the dipole moment of is reported to be and the atomic and electronic polarization total about . Calculate the dielectric constant or permittivity of at and if is a perfect gas.

**Solution**: For , given that —

Dipole moment,

Distortion polarization,

Molar volume, at and pressure ()

**In - units** —

Substituting the given data in Debye equation *viz*. —

**In - units** —

Substituting the given data in Debye equation *viz*. —

**Experimental Method to Determine (measurement)** :

For gaseous substances, the value of polarizability () and dipole moment ( can be determined from the slope and intercept of linear plot of molar polarization () versus of Debye equation. From **Debye equation**, *viz*. —

In **-**  units:

In **-** units:

Where each terms involved have possess their usual meaning, and we have —

In **-**  units:

Therefore, —

In **- units**:

Therefore, —

The above method of determining is applicable only for gaseous systems. For condensed systems, the Debye equation cannot be applied as such because of stronger interactions amongst the closely packed polar molecules. However, Debye equation can be applied for dilute solutions of a polar substance in non-polar solvent because of the strong solute-solute and solute-solvent interactions. The solute-solute interactions can be eliminated by extrapolating the plot of versus (mole fraction of the solute in solution) to zero.

**Lorentz-Lorenz Equation**:

The **molar polarization** of polar molecules were well described by **Debye** equation —

Now, it has been shown that the **molar** polarization includes only the **electronic** polarization when the substance under study is subjected to alternating **electric** **field** of frequency about . Under these conditions, the above equation () may be written as —

Equation () cannot be utilized as such to calculate the electronic polarization as the data of dielectric constant are measured by employing alternating current of low frequency of the order of . However, this difficulty is removed by using Maxwell relation —

Here ‘’ is the refractive of the dielectric. Equation () requires that both dielectric constant and refractive index be measured at the same frequency or even at different frequencies. This is possible because, orientation polarizability is absent in polar molecules and distortion polarizability (nuclei) is negligible compared to electronic distortion polarizability.

In other words, the measurement of at different frequencies includes only electronic polarization. Thus, equation () will be applicable provided both are measured at the same frequency. Since such measurements are not feasible, hence equation () does not hold good for polar molecules. The dielectric constant measurement includes all the three polarizabilities, *viz*., orientation, electronic and nuclei, whereas the refractive index includes only the electronic polarizability. The major contribution to the total polarizability is from the orientation polarizability.

Consequently, the value of dielectric constant differs very much from that of refractive index. In support of this, considering the examples of benzene and water —

For **benzene** (non-polar): and ,

For **water** (polar): and ,

Thus, the **electronic polarization** of a molecule (polar or non-polar) may be determined by replacing by in equation (), such that —

Equation () is known as the ***Lorentz-Lorenz equation***. The quantity —

* is known as the ***molar refraction*** and is represented by the symbol .

**Important**: Both the molar polarization and molar refraction are additive quantities, i.e., the molar values of the quantities for a molecule can be obtained by adding the appropriate atomic values.

**Problem** (): The refractive index of gaseous molecule at and is and its dielectric constant is . () Calculate its dipole moment, and () How are the atoms arranged in the molecule?

**Solution**: Since, for the given molecule —

Dielectric constant () Square of the Refractive index ()

Therefore, the molecule is **non-polar** (*i.e*. **dipole moment is zero**). Thus, the arrangement of the atoms in the molecule is (linear).

**Problem** (): Calculate the value of the molar refraction for , given the same for the following compounds.

Also calculate the values of atomic refractions of .

**Solution**: Since, the molar refraction of a molecule can be obtained by the addition of appropriate atomic refractions, hence we have —

Adding equations () and () and then subtracting equation (), we get —

The atomic refractions for the molecule can be calculated as —

Subtracting equation () from equation (), we get —

Again, subtracting equation () from equation (), we get —

Now, from equation (), we get —

Again, from equation (), we get —

Finally, from equation (), we get —

**Problem** (): The index of refraction of gaseous paraffin is found to be when the gas is at . Given the atomic refractions as for , respectively, determine the formula for the hydrocarbon.

**Solution**: The refraction of the molecule is given by —

Here,

This will also be given by —

Substituting the values, we get —

Hence, the compound is //

**Combined form (union of) Debye and the Lorentz-Lorenz Equation**:

It is possible to determine the dipole moment of polar molecules by taking measurements at one temperature as compared to the Debye method whose measurements at various temperatures are required. This is possible by the union of Debye and Lorentz-Lorenz equations. This can be done as follows —

Units:

From equations and , we find that —

Since is much smaller than , we may write equation as —

In Units:

From equations and , we find that —

Since is much smaller than , we may write equation as —

The terms and appearing in equations and can be determined from dielectric constant and refractive index of the substance, respectively and are the combined form of the Debye & Lorentz-Lorenz equations. For polar molecules in non-polar solvents, is used in place of . The value of can be calculated from refractive index and density of the pure polar substance. //

**Ionic Character of Diatomic Molecules**:

The dipole moment value of a diatomic molecule provides an insight into the sharing of valence electrons between the two atoms. If the electrons are **equally** shared, the centre of charge **coincides** with the centre of charge and hence, the dipole moment of the molecule is **zero**. If the sharing is **unequal**, the molecule has a **net dipole** moment.

If it is assumed that the bonding electrons lie in the bond between the two atoms, the ionic character of the bond may be determined from the dipole moment of the molecule. ***For example*** —

Considering molecule, it can be shown that its dipole moment is and its bond length is . If the two bonding electrons were completely held by - atom, we would have a situation of ionic bond where the carrying **uninegative** and **unipositive** charges, respectively. Since, the bond length is , the dipole moment of such a completely ionic structure () would be —

In **- units**:

In **- units**:

On the other hand, if the bonding electrons are equally shared by - atoms, the molecule would have carried ionic character. The actual value of dipole moment is , suggesting that is neither ionic nor , but in between.

The amount of ionic character can be calculated using the relation —

Thus, for , we have —

**Bond Moments**:

We know that the bond connecting - atoms of different electronegativity constitutes an electric dipole. Evidently, in polyatomic molecules, each bond is associated with its own dipole moment value and net dipole moment of the molecule is the vector sum of these **bond moments**. Considering water molecule as an example, we find that it has two bond moments inclined at an angle of (as shown in the **figure** given below).



Let be the bond moment of bond. Form the figure, it is obvious that —

For water, , and dipole moment is . Therefore, we have —

While employing the expression of the type given by equation (), it has been assumed that the contribution of nonbonding electrons (if any) towards the total dipole moment is included within the bond moments of the molecule.

For the molecules having **centre of symmetry** (), dipole moment is **zero**. For such molecules, though the individual bonds may have bond moments, but the arrangement of the bonds is such that the resultant dipole moment is aero. For example, in , the two bonds constitute a linear structure. Each bond carries bond moment, but the vector addition (resultant) of the two bond moments is zero, as .

For **symmetrical top** molecules (), dipole moment is **zero**. Here, each bond has a bond moment, but the vector addition of bonds in is zero.

Finally, considering molecules of type , for such molecules net dipole moment is not zero. In such molecules, the bond moment of bond is (by Meyer) and the - atom being the end of the dipole. With this information, it is possible to evaluate the bond moment of bond from the dipole moment of molecule.

Considering as an example, as shown in the figure given below, from the figure it is evident that the vector addition of bond moments will give a bond moment which acts in the same direction of bond moment. Therefore, —

Since, the experimental value of , therefore, —



**Problem** (): The bond angle in is and its dipole moment is . Find the bond moment. Estimate the ionic character of the bond in . The bond distance is .



**Solution**: From the figure, we have —

For hydrogen sulphide, , and dipole moment is . Therefore, we have —

**Per cent ionic character**:

**Group Moments**:

In evaluating the dipole moment of polyatomic molecules, instead of using **bond moments**, it is better to use the term group moments. ***For example***, in chlorobenzene, if it is assumed that all linkages in benzene have zero bond moments, the observed dipole moment of of chlorobenzene may be assumed to arise from the linkage. Thus, the group moment of - atom is . The **sign of group moment** indicates the direction in which the group moment acts;  **sign** implies that the group moment acts away from the benzene ring whereas  **sign** implies that it acts towards the benzene ring. Similarly, the value of group moments of a few commonly used groups are shown below —

**Group**:

**Group moment** (D):

**Dipole moment of substituted benzene**: The dipole moment of any substituted benzene can be derived from the following expression of vector addition of group moments.

As an ***example***, let us consider that the arrangement of two bond moments inclined at an angle with respect to each other. The addition of these two may be done by adding separately the two - and - components of so as to give , respectively, and then by employing the expression —

We get the resultant moment of the two moments. If are the respective angles of with - axis, then we have —

Hence, —

**Problem** (): Show that the dipole moments of - disubstituted benzene () and - disubstituted benzene () are and , respectively, where is the dipole moment of monosubstituted benzene ().

**Solution**: For - disubstituted benzene (), the angle between the two vectors is . Substituting this value in the expression —

Again, for - disubstituted benzene (), the angle between the two vectors is . Substituting this value in the expression —

**Problem** (): The dipole moments of chlorobenzene is . Calculate the corresponding values for - and - dichloro substituted benzenes. Compare these values with the experimental values of , respectively.

**Solution**: From problem (), we have —

For, monosubstituted benzene (here, chlorobenzene),

Comparing these calculated values with the experimental values, we find that the agreement is excellent for - dichlorobenzene whereas for - dichlorobenzene, the agreement is not satisfactory. This may be due to either or both the following reasons —

1. The angle between bond vectors may be larger than because of mutual repulsion of the relatively - atoms.
2. The magnitude of bond moments may be modified by their proximity.

**Problem** (): The dipole moments of nitrobenzene, toluene and chlorobenzene are , respectively. Calculate the dipole moments of the following compounds —

1. -, -, - Dinitrobenzenes
2. -, -, - Dimethylbenzenes
3. -, -, - Dichlorobenzenes
4. -, -, - Nitrotoluenes
5. -, -, - Chlorotoluenes
6. - - Chloronitrobenzenes

**Solution**: It can be shown that [problem ()], for two similar substituents at —

Here ‘’ is the dipole moment for monosubstituted benzene. In the present case, the value of for nitrobenzene, toluene and chlorobenzene a nitrobenzene, toluene and chlorobenzene are , respectively re , respectively.

Therefore, the dipole moment —

() **-, -, - Dinitrobenzenes**:

- Dinitrobenzene:

- Dinitrobenzene:

- Dinitrobenzene:

() **-, -, - Dimethylbenzenes**:

- Dimethylbenzene:

- Dimethylbenzene:

- Dimethylbenzene:

() **-, -, - Dichlorobenzenes**:

- Dichlorobenzene:

- Dichlorobenzene:

- Dichlorobenzene:

() **-, -, - Nitrotoluenes**: Nitrotoluenes can be represented as —



Thus, , therefore, in —

**- Nitrotoluene**: Angle between the substituents, , and hence from —

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***Alternatively***, for **- nitrotoluene**, the dipole moment may be calculated directly by simple algebraic addition of the two dipole moments as the two vectors point in the same direction. Thus,

() **-, -, - Chlorotoluenes**: Nitrotoluenes can be represented as —



Thus, here , therefore, in —

**- Chlorotoluene**: Angle between the substituents, , and hence from —

**- Chlorotoluene**: Angle between the substituents, , and hence from —

**- Chlorotoluene**: Angle between the substituents, , and hence from —

() **- - Chloronitrobenzenes**: These compounds can be represented as —



Thus, , therefore, in —

**- Chloronitrobenzene**: Angle between the substituents, , and hence from —

**- Chloronitrobenzene**: In **- chloronitrobenzene** the two vectors is in the opposite direction, hence the magnitude of the dipole moment is —

**Applications of Dipole Moments**:

The main application of dipole moment values is in the field of molecular structure. ***For example*** —

If a molecule has a ***centre of symmetry***, its dipole moment is ***zero***. In general, if the various **identical** groups are **symmetrically** placed around the centre of symmetry, the molecule has a **zero** dipole moment. A few examples given below illustrating the structural application of dipole moment values —

**Shapes of Molecules and Dipole Moment values**:

The dipole measurements have been used to determine the shapes of simple molecules. ***For example*** —

[] ***The triatomic molecule***: The dipole moment values for simple triatomic molecules like have zero dipole moments. On the other hand, for the triatomic molecules like have non-zero dipole moments. Thus, it may be concluded that the former molecules are linear molecules with centre of symmetry, and the latter are nonlinear molecules. Hence, the structures are —



[] ***Polyatomic molecules of type*** : The dipole moment of molecules of type () have been found to possess **zero moment**. Thus, their structures are either **tetrahedral** (symmetrical top) or **square** **planar**. Some of molecules of type () and () have also zero moment. Thus, these molecules must have symmetrical structures. Their structures are —



[] ***The Geometrical Isomers***: The dipole moment values can be used to distinguish between - (-) and - (-) forms of a molecule. The - (-) geometrical isomers always have definite - values, whereas for - (-) geometrical isomers .



[] ***Dipole Moments for - Substituted Benzene Molecules***: The dipole moment values have been extensively used to show whether the linkage in - substituted benzenes are coplanar with the benzene ring or not. ***For example***, for - dichlorobenzene, , whereas for - dihydroxybenzene (**hydroquinone**), . These values lead to the conclusion that the bonds are coplanar whereas bonds might not be so.

**Magnetic Field in a Substance**:

In a vacuum, the ***magnetic flux density***  is related to the ***magnetic field intensity***  by the relation (see top of page 14) —

Within a substance is, in general, not given by the above relation. It may be greater or less than and is given by —

Here is the magnetic moment per unit volume and is known as the **magnetization**. It is a measure of the capacity of a substance to develop magnetization when placed in a magnetic field. In **- units** it has the unit of .

The magnetization of a substance is directly proportional to the applied field and is thus given by —

Here, is a dimensionless quantity known as the ***magnetic susceptibility***.

Depending upon the **sign** of ***magnetic susceptibility***, following two types of substances are of interest —

1. **Paramagnetic Substance**: For such substance, is and has a value of the order of . The magnetization of the substance has a value and thus .
2. **Diamagnetic Substance**: For such substance, is and has a value of the order of . The magnetization of the substance is and thus .

Experimentally, the more useful quantity is the product of magnetic susceptibility and molar volume, defined as —

Since, has no units, the unit of is that of volume, i.e. in **Gaussian** system or in - system.

**Molecular interpretation of Diamagnetism and Paramagnetism**:

We know that there are - types of magnetic materials based on the sign of intensity of magnetization *viz*. **diamagnetic** and **paramagnetic** materials. These two types of materials can be well explained on the basis of molecular interpretation *i.e*. the motion of the electrons present in the materials.

**Diamagnetism**:

The **diamagnetism** in atoms, ions or molecules is due to the ***orbital motion of electrons***. A simple interpretation of diamagnetism is obtained if we imagine the motion of electrons in orbital to constitute a **current flowing** in a **coil of wire**.

According to ***Lenz’s law***, when such a coil of wire is placed in a magnetic field, the field induces the current so as to produce an induced magnetic field acting in the opposite direction of the applied magnetic field. Thus, when a substance is placed in a magnetic field, orbital motions of electrons are polarized and thus an induced magnetic field acting in the opposite direction of the external magnetic field produced.

In the case of electric current in a wire, the induced field quickly dies out owing to the atomic resistance. Inside the atom, there is no resistance to the electronic current and thus induced magnetic field persists as long as the external magnetic field is maintained.

Diamagnetism is **exhibited** by **all** types of **substances**, whether the substance is diamagnetic or paramagnetic. If the substance is paramagnetic, the underlying diamagnetism is entirely concealed by the large value of magnetic moment of the substance.

Since, the orbital motion of electrons is **independent** of the **thermal** **energy**, it follows that **diamagnetism** is **independent** of the **temperature** of the substance. Besides this, the substance has the **same** value of magnetic **susceptibility** whether it is present in the gaseous or liquid state.

If  **is the induced diamagnetic susceptibility** per atom (or **magnetizability**), the magnetic ***susceptibility per mole*** of the substance is given by —

As in the electrical case, describes the tendency of the applied field to induce an opposing field in an otherwise homogenous medium.

***P Pascal*** observed that the diamagnetic susceptibilities are approximately additive and thus, the diamagnetic susceptibilities of a substance can be obtained by adding the appropriate atomic and bond contributions.

**Paramagnetism**:

The phenomenon of paramagnetism is due to the presence of **unpaired** electron(s) in the atom or molecule. Since, electrons are charged particles; therefore the orbital motion of an electron and the spinning of electron around its own axis produce tiny magnets. An external magnetic field tends to align these tiny magnets parallel to itself, and thus produces a net magnetization on the microscopic level. The magnetic moments of tiny magnets are given by —

Here ‘ ’ are the azimuthal and spin quantum numbers, respectively and is the basic unit of magnetic moment called ***Bohr Magneton*** and is given by the expression —

The value of , ***Bohr Magneton*** is evaluated as —

Since

Therefore, we have —

Since

Therefore, we have —

If an atom has more than one unpaired electron, the magnetic moment due to the spins of electron is given by —

In the case of **molecules or ions**, the only contribution which is important is due to the spinning of electrons. In such cases, **orbital contribution** is found to be **ineffective** because the electrons are **strongly held** by the nuclear configuration of the molecule or ions and thus, are **unable** **to line up** with the external magnetic field. Thus, the orbital contribution towards the **magnetic** **susceptibility** is generally quite small and the majority contribution comes from the spinning of unpaired electrons.

Thus, it can be concluded that the **paramagnetic susceptibility** comes from the spinning of unpaired electrons. If **all** electrons are **paired**, the value of ‘’ is **zero** and consequently is also **zero**. This is due to the fact that the **magnetic moment** generated by the spinning of one electron in one direction (say **- spin**) is completely balanced by the opposite spinning of the other electron in opposite direction (say **- spin**), *i.e*. mutually cancelled.

The **paramagnetic susceptibility** contribution towards the **molar** **magnetic** **susceptibility** can be determined and is given by —

As expected, the value of varies **inversely with temperature**, because the only factor which opposes the perfect alignment of dipoles is the **thermal energy**. Larger the thermal energy (*i.e*. larger temperature), lesser is the alignment. //

**Total Molar Magnetic Susceptibility**:

The total molar magnetic susceptibility is the algebraic sum of molar diamagnetic susceptibility and molar paramagnetic susceptibility, *i.e*. sum of —

Thus, the total magnetic susceptibility is —

For diamagnetic substances, , and hence, —

Thus, diamagnetic susceptibility is independent of temperature.

For paramagnetic substances, both the contributions are present. For such a substance, is usually of the order of and thus, the small diamagnetic contribution () is overwhelmed. Thus, we may write —

**Calculation of the Number of Unpaired Electrons**:

The number of unpaired electrons present in an atom, molecule or ion can be determined by using the following two (equation) relationships —

Equation () represents the magnetic moment () due to the spin of the electrons and

Substituting the value of from equations () into the Eq. (), we have —

The molar magnetic susceptibility () can be determined experimentally (by **Gouy magnetic balance method**). By knowing the value of , the value of can be determined by using equation (). The value of thus obtained can be interpreted in terms of the number of unpaired electrons () or (). //

**Gouy Balance Method to Measure Magnetic Susceptibility**:

In the Gouy balance method, the sample whose magnetic susceptibility is to be determined, is taken in a tube. The tube is suspended from one arm of a balance in such a way that it is partly in the magnetic field of an electromagnet as shown in the figure given below —



When the magnet is turned on the following two alternatives are observed —

1. If the sample is **paramagnetic**, it is **attracted** towards the magnetic field. The attraction is due to alignment of the tiny magnets generated in the magnetic field. The potential energy of the system is lowered because of these alignments.
2. If the sample is **diamagnetic**, it is **repelled** by the field. The system has lower potential energy outside the magnetic field.

Since the sample moves in a non-homogenous field (maximum at the centre and minimum outside the magnetic field), one has to find out the total force experienced by the sample by considering the force experienced by the small segment of the sample and then integrating the resultant expression from . This force is related to the magnetic susceptibility and can be worked out as follows —

Since the magnetic moment per unit volume (**magnetization**) of the sample is given by —

Here, is a dimensionless quantity known as the ***magnetic susceptibility***, is the magnetic field also known as the **magnetic** **induction** or magnetic **flux** **density** and is the permeability of the vacuum.

Considering a small segment of length of the sample tube, and let is its area of cross sectional area. Then, the magnetic moment of the material within the volume is —

The magnetic moment acts in the direction of magnetic field. If the magnetic induction () changes by the value of over the length , the change in **potential energy** of the sample will be given by —

The **force experienced** by the sample is the **rate of change of potential energy** with respect to , *i.e*. —

The total force experienced by the sample when it moves from outside the magnetic field (where it has zero value) to the centre of the field (where it has the maximum value) can be obtained by integration of equation (). Thus, we have —

If buoyancy correction is included, equation () becomes —

Here, ‘’ is the susceptibility of air (in Gaussian system, )

The force ‘’ is measured in terms of the masses that are added or removed from the balance pan in order to keep the position of the sample un-shifted. Thus, —

Thus, by knowing ‘’, the magnetic susceptibility can be calculated by using equation (). In practice, the process is repeated with a reference for the evaluation of . //

**Problem** (): A sample of an organometallic compound was placed in a susceptibility balance. The following data were obtained —

Find the susceptibility of the compound.

**Solution**: Given —

Rearranging the expression —

**The End**

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