Electrical and Magnetic Properties of Atoms and Molecules:

Basic Ideas of Electrostatics:

Electrostatics is the branch of physics that deals with the phenomena and properties of stationary or slow moving electric charges with no acceleration. It is the study of forces between charges, as described by Coulomb's Law. It is the study of electric fields in static equilibrium.. Many practical applications of electrostatics exist, including photocopier, laser printers, inkjet printers and electrostatic air filters.

Electric Properties of Molecules:

When a molecule is placed in an electric field, the field distorts the electronic structure of the molecule. It changes the equilibrium positions of the nuclei giving rise to the separation of the centres of positive and negative charges. The electric field induces a dipole moment in the molecule. The induced dipole moment is (μ_{ind}) is directly proportional to the strength of the applied electrostatic field.

i.e. $\mu_{ind} \propto E$

$\Rightarrow \mu_{ind} = \alpha E$

where α is proportionality constant. α is called polarizability of the molecule. α is equal to the induced dipole moment generated by unit electric field strength.

Dipolemoment:

In heteronuclear diatomic molecule, the more electronegative atom withdraws the shared pair of electrons more towards itself and acquires negative charge. The other atom ~~share~~

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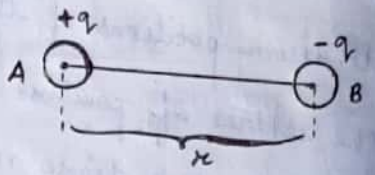
acquires the same amount of positive charge. Such a molecule is called polar molecule. Such molecules having positive and negative charges separated by some distance (equal to their bond length) form dipole and thus possess dipole moment.

The dipole moment of a polar diatomic molecule is the product of the charge on each end of the molecule and the average distance between the centres of their nuclei, ie. the bond length.

Let us consider a heteroatomic molecule AB. Let $+q$ be the charge on the end A and $-q$ on the end B of the molecule. Let r is the average distance between the centres of their nuclei. Then, dipole moment of the molecule, AB is given by:



$$\mu = q \times r.$$

$+q$ or $-q$ is the charge and is of the order of 10^{-10} esu.

r = distance between the charges and is of the order of 10^{-8} cm.

Thus, dipole moment, μ has a value of the order of 10^{-10} esu $\times$ 10^{-8} cm or 10^{-18} esu cm. This quantity is called debye (D).

Note: 1 debye $= 3.336 \times 10^{-30}$ C.m

C = Coulombs.

$\therefore \mu = 1.602 \times 10^{-19}$ C $\times 10^{-10}$ m.

$= 1.602 \times 10^{-29}$ C.m $= 4.8$ D.

$\left\{ \because q = 1.602 \times 10^{-19} \text{ C}, \quad r = 10^{-10} \text{ m.} \right.$

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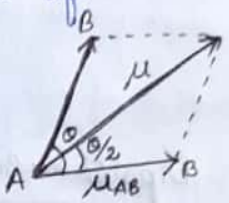
Dipole moment in molecules having more than one polar bond:

The dipole moment of molecules with more than one polar bond is equal to the resultant of dipole moments of all the individual bonds. It also depends upon the orientations in space of the bonds in a molecule.

Let us consider a molecule AB_2 in which two A–B bonds are at an angle of θ and μ_{AB} is the value of each bond moment, then the dipole moment of the molecule will be:



$$\mu = 2\mu_{AB}\cos\frac{\theta}{2}$$

Now consider a more general molecule ABC with two bonds AB and AC having bond moments μ_1 and μ_2 and inclined at an angle of θ, the net dipole moment of the molecule will be:

$$\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}$$

e.g. ① Dipole moment of CO_2:

CO_2 is a linear molecule in which the two C=O bonds are oriented at an angle of 180° w.r.t. each other. The dipole moment of each C=O bond is 2.3 D but due to linear geometry of CO_2, the dipole moment of two C=O bonds cancel each other and net dipole moment is zero.

$$\overset{\delta-}{O} \leftarrow\!\!+ \overset{\delta+}{C} +\!\!\rightarrow \overset{\delta-}{O}$$

Hence CO_2 is a non-polar ~~molecule~~ molecule.

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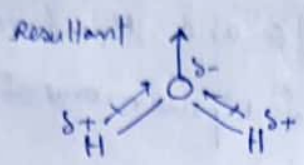
② Dipole moment of H_2O:

Water is a polar molecule having dipole moment 1.84 D. It is because, water has bent structure in which two O-H bonds are oriented at angle of 104.5° and do not cancel the dipole moments of each other. Hence, water has a net dipole moment.



Dipole moments and molecular structure:

① Calculation of percentage ionic character in a molecule:

Let us consider the bond H–X where X is a halogen atom. If the bond is purely covalent, its dipole moment would be negligibly small, which is given by the product of the charge (δ) separated due to polarization and the internuclear distance. The magnitude of δ will depend upon the extent of the ionic character developed in the bond. Thus,

$$\% \text{ ionic character} = \frac{\text{Actual dipole moment of the bond}}{\text{dipole moment of pure ionic bond}} \times 100$$

② In predicting the shapes of molecules:

A diatomic molecule is polar if the bond formed between the atoms is polar. In such a molecule, the dipole moment of the bond gives the dipole moment of the molecule. e.g. The dipole moment of HCl molecule is the

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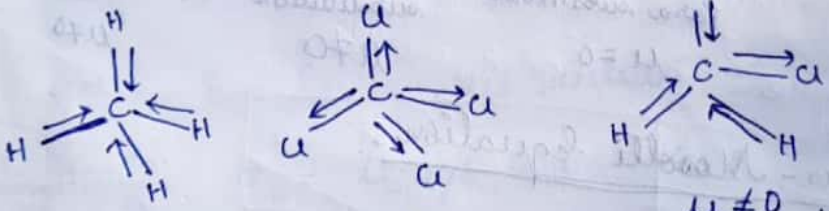
same as the dipole moment of HCl bond and is known to be 1.03 D. However, in the case of molecules containing more than two atoms, the dipole moment not only depends upon the individual dipole moments of the bonds but also on the spatial arrangement of various bonds in the molecule. In such cases, the dipole moment of the molecule is the vector sum of the dipole moments of the various bonds. The polar or non-polar nature of molecule will depend upon the spatial arrangement of atoms in the molecule. The bonds may be polar yet the molecule may be non-polar.

e.g. CH_4 and CCl_4 molecules have symmetrical tetrahedral structures and their resultant dipole moments are zero. But CH_3Cl inspite of having tetrahedral structure, has a non-zero dipole moment. It is because, its structure is not symmetrical and the dipole moments of C-Cl and H-C bonds are not equal.



$\mu = 0$ $\mu = 0$ $\mu \neq 0$.

③ In distinguishing between the cis and trans isomer:

Dipole moments are helpful in distinguishing between the cis and trans isomers. eg. The cis isomer of 1,2-dichloroethene has a dipole moment whereas the trans isomer does not. The zero dipole moment of the trans isomer is due to the fact that the vector sum of the bond moments of the two C-Cl bonds cancel out:

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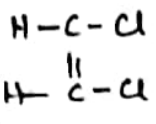
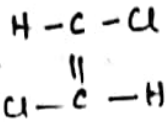


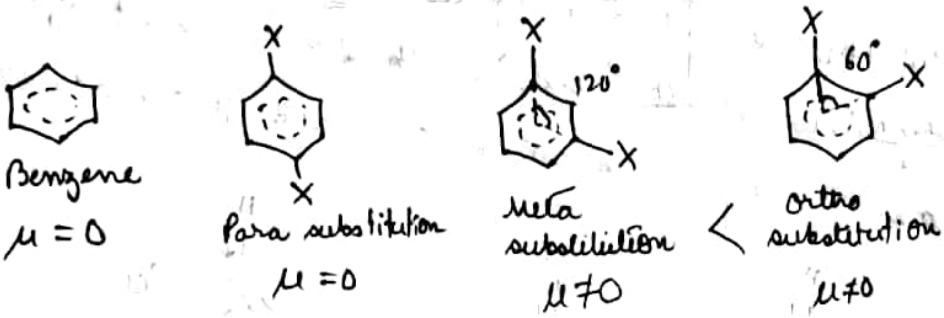
cis form
($\mu = 1.86$ D)



trans form
($\mu = 0$).

④ In distinguishing the ortho, meta and para isomers:

In benzene is a regular hexagon, its dipole moment is zero. But, in case of benzene ring, being substituted at ortho, meta and para positions, the resulting distributed molecule have zero dipole moment in case of para substitution. Whereas for ortho and meta substitution the dipole moment is not zero. The ortho ~~and~~ substituted isomer will have higher dipole moment than meta isomer.



Clausius - Mosotti equation:

Let us consider that several molecules of a substance in the solid, liquid or gaseous state are introduced into the space between the plates of a condenser which is charged by applying a constant electrostatic field. The substance is called a dielectric and is assumed

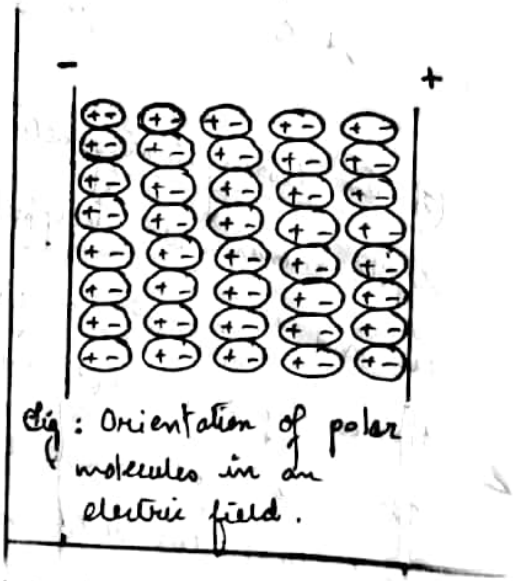


Fig: Orientation of polar molecules in an electric field.

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to be an insulator. The charges on the condenser plates are partially compensated by the induced charges on the boundary of the dielectric. The electric field strength in the dielectric is, therefore, reduced to a value E from its value E_0 in vacuum such that,

$$E_0 = E + 4\pi P \longrightarrow (i)$$

where, P is called dielectric polarization and is the induced dipole moment per unit volume of the dielectric.

$$\therefore P = N\mu_{ind} \longrightarrow (ii)$$

where N is the no. of molecules per unit volume of the dielectric.

$$\text{Eqn } (i) \Rightarrow \frac{E_0}{E} = 1 + \frac{4\pi P}{E} \longrightarrow (iii)$$

$$\Rightarrow \frac{E_0}{E} = 1 + 4\pi\left(\frac{N\mu_{ind}}{E}\right).$$

$$\Rightarrow \varepsilon_r = 1 + 4\pi N\alpha_d \longrightarrow (iv)$$

where, $\varepsilon_r = \frac{E_0}{E}$ is called dielectric constant or relative permitivity. $\alpha_d = \mu_{ind}/E$, where α_d is called distortion polarizability.

Again, $\varepsilon_r = \frac{C}{C_0} \longrightarrow (v)$

where C and C_0 are the capacitances of the condenser with the medium and the vacuum respectively.

If one mole of a substance of molar volume V_m, density ρ and molar mass M is used as a dielectric, then,

$$N = \frac{N_A}{V_m} = \frac{N_A \rho}{M} \longrightarrow (vi)$$

where N_A is Avogadro's no.

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$\therefore$ eqn (iv) $\Rightarrow$ $\boxed{(\varepsilon_r - 1)\frac{M}{\rho} = 4\pi N_A \alpha_d}$ ⟶ (vii)

$\because \alpha_d$ is a constant.

$\therefore (\varepsilon_r - 1)$ is independent of ρ.

Eqn (vii) holds for gases at very low pressures, when the interaction of the dipole moments between the neighbouring molecules is negligible.

However, at high pressures and for condensed phases (solids or liquids), this relation doesn't hold since interactions between induced moments have to be taken into consideration.

Clausius and Mosotti, taking into consideration these interactions for condensed phases, introduced the following relation:

$$\boxed{P_m = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} V_m = \left(\frac{4\pi}{3}\right) N_A \alpha_d} \longrightarrow \text{(viii)}$$

where the quantity P_m is called molar polarization.

Eqn (viii) is called Clausius - Mosotti equation.

In S.I system, the eqn is written as,

$$\boxed{P_m = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} V_m = \left(\frac{N_A}{3\varepsilon_0}\right) \alpha_d}$$

The Clausius - Mosotti eqn is not obeyed by polar molecules such as HCl, H_2O, NH_3, etc. which possess a permanent dipole moment.

~~Mos~~

Variation of Polarization with Temperature:

Debye Equation:

In 1912, Debye considered the behaviour of polar molecules placed between the plates of a condenser.

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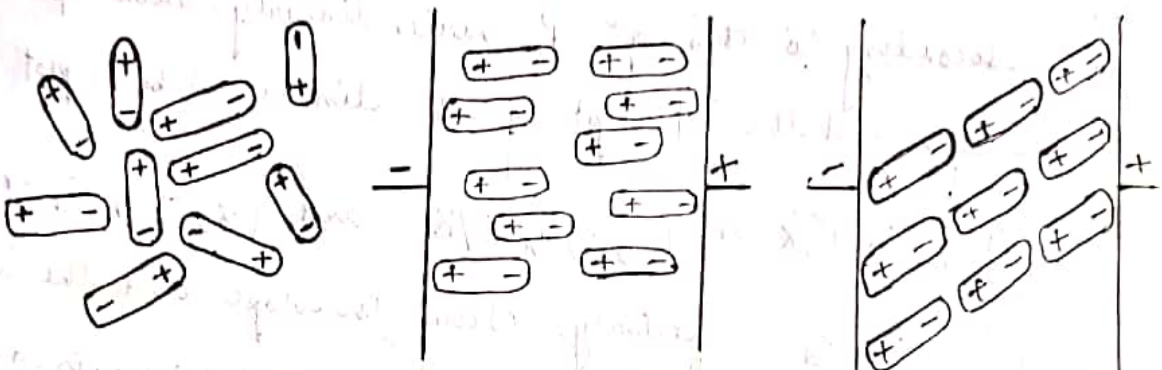
The permanent dipoles, ordinarily are oriented in a random manner. However, when placed in an electric field, the molecules rotate and orient themselves in the direction of the field, as shown in the figure.



(a) Electric dipoles in the absence of electric field.

(b) Tendency of electric dipoles to rotate in an electric field.

(c) Actual alignment of electric dipoles in an electric field.

In case of molecules with permanent dipoles (e.g. HCl, H_2O, CH_3Cl), the molar polarization according to debye is,

$$P_m = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \times \frac{M}{\rho}$$

$$\Rightarrow P_m = P_i + P_o \quad \longrightarrow (i).$$

Again, Molar orientation polarization is given by.

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

where μ is permanent dipole moment of the molecule and k is the Boltzmann constant.

∴ The Induced molar polarization,

$$P_i = \frac{4}{3}\pi N_A \alpha_d. \quad \longrightarrow (iii)$$

$$\therefore \text{Eqn } (i) \Rightarrow P_m = \frac{4}{3}\pi N_A \alpha_d + \frac{4}{3}\pi N_A \left(\frac{\mu^2}{3kT}\right).$$

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$$\Rightarrow P_m = \frac{4}{3}\pi N_A \left(\alpha_d + \frac{\mu^2}{3kT}\right). \longrightarrow (iv)$$

In S.I. units, $$P_m = \left(\frac{N_A}{3\varepsilon_0}\right)\left(\alpha_d + \frac{\mu^2}{3kT}\right) \longrightarrow (v)$$

Eqn (iv) or (v) is called Debye equation.

According to this eqn, P_m varies linearly with $\frac{1}{T}$. The slope and the intercept of the linear Debye plot are $\left(\frac{4}{3}\right)\pi N_A \mu^2/k$ or $\left(\frac{1}{9\varepsilon_0}\right)N_A \mu^2/K$ and $\left(\frac{4}{3}\right)\pi N_A \alpha_d$ or $\left(\frac{1}{3\varepsilon_0}\right)N_A \alpha_d$ respectively. From the slope and the intercept, μ and α_d of the molecule can be determined.

The plot of P_m vs $\frac{1}{T}$ is shown in the following figure. For a polar molecule ($\mu \neq 0$) a linear plot is obtained and for non-polar molecules ($\mu = 0$), a straight line is obtained parallel to $\frac{1}{T}$ axis.

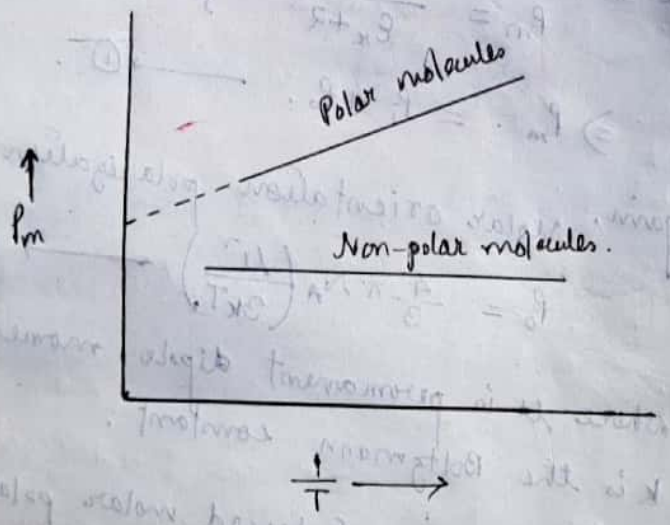

Fig: Plot of P_m v/s $\frac{1}{T}$ for gaseous polar and non-polar molecules.

Units: $\alpha = \frac{\text{Unit dipole}}{E} = \frac{C\,m}{V\,m^{-1}} = \frac{C\,m}{J\,C^{-1}\,m^{-1}} = J^{-1}C^2m^2$

Polarizability volume, $\alpha' = \frac{\alpha_d}{4\pi\varepsilon_0} = \frac{J^{-1}C^2m^2}{J^{-1}C^2m^{-1}} = m^3$.

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Measurement of Dipole Moment by Refraction Method:

Dependence of polarizability on Frequency (Lorentz-Lorenz eqn):

In presence of an oscillating electric field, both the Clausius-Mossotti equation and Debye equation are not applicable because when the frequency is very high, the permanent dipole moment of the molecules can't orient themselves rapidly to align with the ever changing field direction.

The example of a rapidly changing field is the electromagnetic radiation which has a rapidly changing electric and magnetic field. In presence of such a light wave, the electric field polarizes the medium through which it passes, pulling the electrons back and forth rapidly.

Maxwell in his electromagnetic theory of light showed that at optical frequencies, the dielectric constant and the refractive index of the medium are related as,

$$\varepsilon_R \approx n_R^2 \longrightarrow (1).$$

where, n_R is the refractive index of the medium.

Relation (1) is called Maxwell Relation and holds only when the permanent dipole moment of a molecule doesn't contribute to ε_R and hence to P_m.

On incorporating Maxwell relation in Clausius-Mossotti equation, we get,

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$$P_m = R_m = \left(\frac{n_R^2 - 1}{n_R^2 + 2}\right) V_m = \frac{N_A \alpha_d}{3\varepsilon_0} \longrightarrow (11)$$

Equation (11) is called the Lorentz-Lorenz equation.
R_m is called molar refraction.

From this equation, the refractive index of the medium, distortion polarizability and polarizability volume are given by the following equations.

$$n_R = \left(\frac{V_m + 2R_m}{V_m - R_m}\right)^{\frac{1}{2}} \longrightarrow (111)$$

$$\alpha_d = 3\varepsilon_0 R_m / N_A \longrightarrow (iv)$$

$$\alpha' = \alpha / 4\pi\varepsilon_0 = \frac{3R_m}{4\pi N_A} \longrightarrow (v)$$

Magnetic properties of Molecules:

The magnetic properties of the materials are due to the electrons present in it. Each electron in an atom is associated with a magnetic moment that originates from two sources:

(a) Magnetic moment due to orbital motion of electron around the nucleus.

(b) Magnetic moment due to electron spin along the spin axis.

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Magnetic Permeability:

The force F acting between two magnetic dipoles of pole strengths m_1 and m_2 separated by a distance r, is given by,

$$F = \frac{m_1 m_2}{\mu r^2}$$

where μ is a constant characteristic of the medium and is called magnetic permeability of the medium. Magnetic permeability measures the tendency of the magnetic lines of force to pass through the medium, compared with their tendency to pass through vacuum for which $\mu = 1$.

Diamagnetic and paramagnetic substances:

If magnetic permeability of a substance is less than unity ($\mu < 1$), then the magnetic lines of force prefers to pass through the vacuum than through the substance. In other words, the magnetic lines of force are repelled away from the substance. Such substances are said to be diamagnetic. e.g. Cu, Graphite, Bi, Sb, etc.

If magnetic permeability of a substance is greater than unity ($\mu > 1$), the magnetic lines of force have greater tendency to pass through the substance rather than through the vacuum. In other words, the magnetic lines of force are attracted towards the substance. Such substances are said to be paramagnetic, e.g. Al, Pt, etc.

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The behaviour of diamagnetic and paramagnetic substances in magnetic field is shown below:—

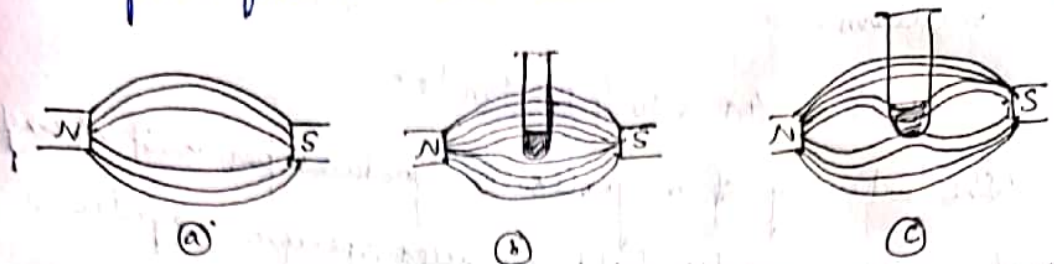

Fig: Magnetic lines of force showing the effect of diamagnetic and paramagnetic substance on the magnetic field.
(a) Vacuum (b) Diamagnetic (c) Paramagnetic.

Magnetic Susceptibility:

The magnetic properties of matter are discussed in terms of the magnetic field intensity vector, H and the magnetic induction (or magnetic flux density) B. When a substance is placed in a magnetic field, the magnetization M, i.e. the magnetic moment per unit volume, is related to B and H by the relation,

$$B = \mu_0 (H + M). \longrightarrow (i)$$

where μ_0 is the permeability of vacuum.

Also, $B = \mu H$. $\longrightarrow (ii)$

$\therefore$ Eqn (i) and (ii) $\Rightarrow$ $B = \mu_0 H + \mu_0 M$.

$$\Rightarrow M = \frac{B - \mu_0 H}{\mu_0}$$

$$\Rightarrow M = \frac{\mu H - \mu_0 H}{\mu_0}$$

$$\Rightarrow M = H\left(\frac{\mu}{\mu_0} - 1\right).$$

$$\Rightarrow M = H(\mu_r - 1) \longrightarrow (iii).$$

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where, $\mu_R = \frac{\mu}{\mu_0}$ is the relative permeability of the medium.

$$\mu_0 = 4\pi \times 10^{-7}\ J\,C^{-2}\,m^{-1}\,s^2.$$

The intensity of magnetisation produced per unit strength of applied magnetic field is called specific magnetic susceptibility.

Magnetic susceptibility is denoted by χ.

$$\chi = \frac{M}{H} = \mu_R - 1.$$

The magnetic susceptibility is a dimensionless quantity.

The molar magnetic susceptibility is defined as,

$$\chi_m = V_m \cdot \chi.$$

where V_m is the molar volume.

Magnetic susceptibility is related to magnetic permeability as,

$$\chi = (\mu - 1)/4\pi\rho$$

where ρ is the density in $g\,cm^{-3}$.

Note:
Diamagnetic : $\chi < 0$
Paramagnetic : $1 > \chi > 0$
Ferromagnetic : $\chi >> 1$

Measurement of Magnetic Susceptibility by Gouy's method

The magnetic susceptibility of a substance is measured by means of the Gouy balance designed by the French physicist L.G. Gouy. The substance is taken in a vertical tube which is suspended vertically by means of a wire

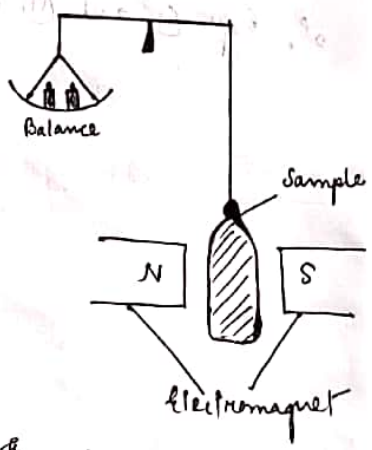

Fig : Gouy's method for measurement of magnetic susceptibilities.

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from one arm of the balance such that its lower part which contains the substance lies in the middle of the two poles of an electromagnetic. Weights are added to the pan to balance the weight of the cylinder.

When the current is switched on, the cylinder is attracted downward towards the electromagnetic field if the substance under test is paramagnetic and pushed upward away from the field if the substance is diamagnetic. In the first case, weights are added to the pan while in the second case, weights are removed to restore the cylinder to its original position.

Let $\Delta\omega$ be the change in weight of the substance. This is related to magnetic susceptibility of the compound by the following equation,

$$\Delta\omega = \frac{1}{2}\left(\rho\chi - \rho_a\chi_a\right) A H^2$$

where ρ_a and χ_a are respectively, the density and magnetic susceptibility of air, A is cross sectional area of the cylinder and H is the strength of the magnetic field produced by the electromagnet.

$\therefore$ ρ_a, χ_a, A and H are known, χ can be calculated.

Also, molar magnetic susceptibility (χ_M) can also be used to determine χ as,

$$\chi_M = \frac{M}{\rho}\chi$$

Applications of Magnetic Susceptibility:

(1) In confirming the structure of a given molecule.

(2) For calculation of the no. of unpaired electrons in a molecule or ion:

No. of unpaired e⁻s can be calculated by,

$$\chi_m = \alpha_m + \frac{N_n \mu^2}{3kT}$$

$$\Rightarrow \chi_m = \alpha_m + \frac{N_n}{3kT}[n(n+2)].$$

{n = no. of unpaired e⁻s.}

(3) For determination of structure of coordination compounds.

e.g. In $[NiCl_4]^-$ and $[Ni(CN)_4]^{2-}$ although each has the same coordination number i.e. 4, but their magnetic susceptibility values suggest that the former has 2 unpaired e⁻s while the later has no unpaired e⁻s.

Thus, $[NiCl_4]^-$ is paramagnetic and has tetrahedral structure.

$[Ni(CN)_4]^{2-}$ is diamagnetic and has square planar structure.

(4) In establishing the formulas of certain compounds.

e.g. The formula of hydrophosphoric acid is $H_4P_2O_6$ and not H_2PO_3.

(5) In explaining the existence of odd electron molecules:

The presence of an unpaired electron in NO and ClO_2 molecule has been confirmed on the basis of magnitudes of

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paramagnetic susceptibility of these molecules. They are formed as odd-electron molecules.

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