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(Deemed to be University Established Under Section 3 of UGC Act 1956) Coimbatore – 641 021.

#### SYLLABUS DEPARTMENT OF CHEMISTRY B.Sc CHEMISTRY

### Semester - VI 15CHU602 PHYSICAL METHODS & CHEMICAL STRUCTURES 5H- 5C Instruction Hours/week:L: 5 T:0 P:0 Marks: Internal:40 External: 60 Total:100

#### Scope

The course allows one to get a fundamental idea about the physical methods used to identify structures. The course helps the students in improving their diverse skills in various areas such as laboratory skills, numerical and computing skills, ability to approach to the problems both analytically and logically, time management skills, etc. The principles in this course are used in almost every field such as medicines, food products, and electronics and even in construction industry.

#### Methodology

Black board teaching and Group discussion.

#### **Programme Outcome**

- 1. To enable and impart the knowledge of physical methods used to identify structures.
- 2. To understand the Electrical properties of molecules such as polarization, magnetic Properties and Dipole moment.
- 3. To understand how to characterize a compound, identify functional groups and Interpret a spectrum.
- 4. To get the knowledge about the principles of various chromatography methods.

#### Programme Learning Outcome

- > The students know the various physical methods used to identify structures.
- $\succ$  The students understood how to characterize a compound, identify functional groups and interpret a spectrum.
- > To learn the separation of mixture of compounds using chromatography methods.

#### UNIT-I

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

Magnetic properties of molecules: Meaning of the terms magnetic susceptibility, magnetic moment, diamagnetism, paramagnetism and ferromagnetism. Determination of magnetic susceptibility by Gouy's method. Application of magnetic measurements.

#### UNIT-III

Spectroscopy: Absorption spectra- Fundamental concepts of electromagnetic spectrum- The various regions of the spectrum and the relative energies of the radiation in each region-Type of changes induced by the interaction of the radiation with matter. Theory of rotation spectra – Diatomic molecule as rigid rotor and non rigid rotor - Intensities of spectral lines.

Theories of IR spectra – simple harmonic oscillator, model anharmonic oscillator, model of diatomic molecules information on molecular constitution from IR spectra; Application of IR spectra.

#### UNIT-IV

Theory of Raman spectra – Comparison of IR and Raman spectra - Theory of UV and visible spectra–Franck-Condon principle-Application of UV spectra to simple molecules.

NMR spectra – Basic principles – Chemical shift – Application of NMR spectra to simple molecules. High resolution Raman spectra (details not expected). Examples-Ethanol and o, m & p-xylenes.

#### UNIT-V

Chromatography – classification- Principles of Column, Paper and Thin Layer chromatography.

#### **TEXT BOOKS:**

- 1. Puri Sharma and Pathania, 2003. Physical Chemistry, Vishal Publishing Co., Jalandar.
- 2. Y.R.Sharma, 2004.Elementary Organic Spectroscopy,1<sup>st</sup>Edition,S.Chand& Company Ltd, New Delhi.

#### **REFERENCES:**

- 1. Gopalan, V., P.S.Subramanan and K.Rangarajan, 2003. Elements of Analytical Chemistry, S.Chand and Sons, New Delhi.
- 2. GurdeepR.Chatwal,ShamK.Anand 2004.Instrumental methods of chemical analysis,1<sup>st</sup> Edition Mrs.Meenapandey for Himalaya publishing House, Mumbai.
- 3. B.K.Sharma, 1999. Instrumental methods of chemical analysis,15<sup>th</sup> Revised and Enlarged Edition Global Publishing House,Meerut.
- 4. Skoog, .D.A., and D.M.West, 2004. Fundamentals of Analytical Chemistry, 8<sup>th</sup> Edition, Thomson book store, Singapore.
- **5.** Galen W.Ewing., 1988. Instrumental Methods of Chemical Analysis. III Edition, McGraw Hill International Editions, Singapore.
- 6. Skoog, D.A., 2004. Instrumental Methods of Analysis, Thomson book store, Singapore.
- 7. Robbert M. Siverstein and Francis X. Webster, 2013, Spectroscopic identification of organic compounds, 6<sup>th</sup> edn, Wiley India, New Delhi.



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#### KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University Established Under Section 3 of UGC Act 1956) Coimbatore – 641 021.

#### LECTURE PLAN DEPARTMENT OF CHEMISTRY

STAFF NAME: Dr.M.MAKESWARI AND Mrs.R.SHARMILA DEVISUBJECT NAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESSUB.CODE:15CHU602SEMESTERVICLASS: III B.Sc (CHEMISTRY)

S.No	Lecture Duration Period	Topics to be Covered	Support Material/Page Nos
		UNIT-I	
1	1	Electrical properties of molecules	T1 :813,
2	1	Molar polarization	T1 :814
3	1	Orientation polarization	T1 :814
4	1	Distortion polarization	T1 :814
5	1	Polar and non-polar molecules	T1 :815
6	1	Determination of dipole moment	T1: 816
7	1	Determination of dipole moment of polar gases	T1: 816
8	1	Determination of dipole moment of polar liquids	T1: 817
9	1	Determination of dipole moment of polar solids	T1: 818
10	1	Application of dipole moment in the study of simple molecules	T1: 819
11	1	Application of dipole moment in the study of simple molecules	T1: 820
12	1	Revision and discussion of possible questions	
13	1	Revision and discussion of possible questions	
	Total No of	Hours Planned For Unit 1=13	
		UNIT-II	

1

1	1	Magnetic properties of molecules	T1: 820
2	1	Magnetic properties of molecules- Introduction	T1: 820
3	1	Meaning of terms magnetic susceptibility,	T1: 821
4	1	Meaning of terms magnetic moment	T1: 823
5	1	Meaning of terms diamagnetism,	T1: 821
6	1	para-magnetism	T1: 820
7	1	Ferro-magnetism	T1: 820
8	1	Determination of magnetic susceptiblity	T1: 821
9	1	Determination of magnetic susceptibility by Gouy's method	T1: 821-823
10	1	Application of Magnetic measurements	T1: 822
11	1	Application of magnetic properties in solving problems in simple ions	T1: 822
12	1	Application of magnetic properties in solving problems in complex ions	T1: 823
13	1	Revision and discussion of possible questions	
14	1	Revision and discussion of possible questions	
	Total No o	of Hours Planned For Unit II=14	
		UNIT-III	
1	1	Absorption spectra-Introduction	T1: 737, R1:2.29
2	1	Fundamental concepts of electro magnetic spectrum	T1: 735-736, R1:2.29-2.30
3	1	The various regions of the spectrum	T1: 737, R1: 2.30
4	1	The relative energies of the radiation in each region	T1: 738, R1:2.31-2.33
5	1	Types of changes induced by the interaction of the radiation with matter	T1: 738, R1: 2.34-2.35
6	1	Types of changes induced by the interaction of the radiation with matter	T1: 739, R1: 2.34-2.35
7	1	Theory of rotation spectra	T1: 740
8	1	Diatomic molecule as rigid rotor	T1: 742, R1: 2.36-2.37

9	1	Diatomic molecule as non rigid rotor	T1: 742 R1: 2 37-2 38
10	1	Intensities of spectral lines and application	T1: 742
11	1	Theories of IR spectra	T1: 744, R1: 2 31
12	1	Simple harmonic oscillator,	T1: 745
13	1	Model anharmonic oscillator	T1: 745-746
14	1	Model of diatomic molecules information on molecular constitution from IR spectra	T1: 746
15	1	Application of IR spectra	T1: 749-750
16	1	Revision and discussion of possible questions	
17	1	Revision and discussion of possible questions	
	Total No o	f Hours Planned For Unit III=17	
		UNIT-IV	
1	1	Theory of Raman spectra-	T1: 750, R1:2.83-2.85
2	1	Comparison of IR and Raman spectra	R1: 2.85-2.86
3	1	Theory of UV- Visible spectra	R1: 2.149
4	1	Franck-condon principle	T1: 757-759
5	1	Application of UV spectra to simple molecules	R1:2.172 - 2.176
6	1	Application of UV spectra to simple molecules	R1:2.177-
7	1	NMR spectra- Introduction	T1: 762
8	1	NMR spectra- Basic principle	T1: 765
9	1	Chemical shift	T1: 765-767
10	1	NMR spectra of simple molecules	R1: 2.220
11	1	High resolution Raman spectra	R1: 2.98
12	1	Examples-Ethanol and o, m & p-xylenes.	R1: 2.99
13	1	Revision and discussion of possible questions	
14	1	Revision and discussion of possible questions	
	Total No o	f Hours Planned For Unit IV=14	

		UNIT-V	
1	1	Chromatography – Introduction and definition	<b>R1:</b> 2.566 - 2.567
2	1	Classifications of Chromatography	<b>R1:</b> 2.567
3	1	Theoretical principles of chromatographic techniques	<b>R1:</b> 2.568
4	1	Column Chromatography- Introduction	<b>R1:</b> 2.646
5	1	Column Chromatography-Principle	<b>R1:</b> 2.646
6	1	Column Chromatography-Experimental details	<b>R1:</b> 2.647
7	1	Column Chromatography-Applications	<b>R1:</b> 2.654
8	1	Paper Chromatography- Introduction	<b>R1:</b> 2.588
9	1	Paper Chromatography-Principle	<b>R1:</b> 2.588
10	1	Paper Chromatography-Experimental details	<b>R1:</b> 2.592
11	1	Paper Chromatography-Applications	<b>R1:</b> 2.597
12	1	Thin layer Chromatography- Introduction	<b>R1:</b> 2.599
13	1	Thin layer Chromatography-Experimental details	<b>R1:</b> 2.600
14	1	Thin layer Chromatography-Applications	<b>R1:</b> 2.606
15	1	Revision and discussion of possible questions	
16	1	End semester question paper discussion	
17		End semester question paper discussion	
Ť	Т	otal No of Hours Planned for unit V=17	
Total Plann ed Hours	75		

#### **TEXT BOOK**

**T1 :** Puri B.R. Sharma L.R, Patania M.S., "physical chemistry", 43<sup>rd</sup> Edition. Vishal Publishing Co., Jalandar.

#### REFERENCES

**R1:** Gurdeep R.Chatwal,Sham K.Anand 2004.Instrumental methods of chemical analysis,1<sup>st</sup> Edition Himalaya publishing House, Mumbai.



#### CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

BATCH-2015-2018

#### <u>UNIT-I</u>

#### **SYLLABUS**

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

#### **ELECTRICAL PROPERTIES OF MOLECULES**

#### **Dipole-moment**

The electric dipole moment ( $\mu$ ) of a molecule is directed from the center of negative charge (-q) to the center of positive charge (+q) distance r away. The units are usually given in Debye (= 3.336 x 10-30 C m).

 $\mu = qr$ 

In liquid water, molecules possess a distribution of dipole moments (range  $\sim$ 1.9 - 3.1 D) due to the variety of hydrogen bonded environments.

If two charges q1 and q2 are separated by distance r, the (Coulomb) potential energy is V (joule)

$$V = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$$

where  $\varepsilon_0$  is the <u>permittivity of a vacuum</u> (= 8.854 x 10-12 C2 J-1 m-1; the ability of a material to store electrostatic energy).

In a medium it is lower, where  $\varepsilon$  is the medium's permittivity.

$$V = \frac{q_1 q_2}{4\pi\epsilon r}$$

The dielectric constant  $(\mathcal{E}_r)$  of the medium (also known as the relative permittivity) is defined as

Prepared by Dr.M.Makeswari & Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 1/20

#### CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

BATCH-2015-2018

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$$

and clearly approaches unity in the dilute gas state. In liquid water, it is proportional to the mean-square fluctuation in the total dipole moment. In liquid water, the <u>dielectric constant is</u> <u>high</u> and there is a linear correlation between it and the number of <u>hydrogen bonds</u>.

#### **Polarization and polarizability**

The polarization (P) of a substance is its electric dipole moment density . The charge density vector (D) is the sum of the effect of the applied field and the polarization.

$$D = \epsilon_{0E} + P$$

$$D = \varepsilon_E$$

 $\mathbf{P} = (\mathbf{\varepsilon}_r - 1)\mathbf{\varepsilon}_{0\mathrm{E}}$ 

#### **Molar Polarization**

The relative permittivity (dielectric constant) (ɛr) is related to the molar polarization of the medium (Pm) using the Debye equation

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

where  $\rho$  is the mass density (kg m-3), M is the molar mass (kg). At high relative permittivity (dielectric constant), such as water, the left hand side of the above equation approximates to unity and the molar polarization (calculated from equation(1) below = 181.5x10-6 m3 at 25 °C) should approximate to the molar volume (18.0685x10-6 m3 at 25 °C) but it clearly does not in the case of water. The molar polarization of the medium (Pm) is defined as

$$P_{\rm m} = \frac{N_{\rm A}}{3\epsilon_0} (\alpha + \frac{\mu^2}{3kT})$$
(1)

Prepared by Dr.M.Makeswari & Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 2/20

#### CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

#### BATCH-2015-2018

where  $\alpha$  is the polarizability of the molecules, which is the proportionality constant between the induced dipole moment  $\mu^*$  and the field strength E ( $\mu^* = \alpha E$ ), NA is the <u>Avogadro</u> <u>number</u>, Mk is the <u>Boltzmann constant</u> (=R/NA), T is the absolute temperature and  $\mu$  is permanent dipole moment. Unfortunately, in line with many other <u>anomalies of water</u>, this equation is not a good predictor for the behavior of water, which shows a minimum molar polarization at about 15 °C. The term in ( $\varepsilon_r + 2$ ) comes from the relationship between the local field (E') and the applied field (E).

 $E' = (E/3)(\epsilon r + 2)$ 

The polarizability ( $\alpha$ ) may be given as the polarizability volume ( $\alpha$ ') where

$$\alpha' = \frac{\alpha}{4\pi\varepsilon_0}$$

#### Clausius-Mossotti Equation (molar polarisation)

The second term in <u>equation (1)</u> is due to the contribution from the permanent dipole moment, which is negligible when the medium is non-polar or when the frequency of the applied field is sufficiently high that the molecules do not have time to change orientation. In this case the Clausius-Mossotti equation holds (but again not for water):

$$\frac{\varepsilon_{\rm r} - 1}{\varepsilon_{\rm r} + 2} = \frac{\rho N_{\rm A} \alpha}{3M\varepsilon_{\rm 0}}$$

The refractive index ( $\eta r$ ) in the visible and ultraviolet is the ratio of the <u>speed of light</u> in a vacuum (c) to that in the medium (c');  $\eta r = c/c'$ . It is also related to the relative permittivity ( $\epsilon r$ ), the absorption coefficient ( $\alpha$ ) and wavelength ( $\lambda$ ).

$$\eta_r^2 = \varepsilon_r + \left(\frac{\lambda\alpha}{4\pi}\right)^2$$

This reduces to  $\varepsilon_{\infty} = \eta r^2$  where  $\varepsilon_{\infty}$  is the relative permittivity at visible frequencies (4x1014 - 8x1014 Hz,  $\eta r \sim 1.34$ ) and  $\varepsilon_s = \eta r^2$  where  $\varepsilon_s$  is the relative permittivity at low frequencies (static region; < 109 Hz,  $\eta r \sim 9$ ). It also follows that, as the temperature is raised,  $\varepsilon_r$  tends towards  $\eta r^2$ 

#### **Orientation Polarization**

Prepared by Dr.M.Makeswari & Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 3/20

#### CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

BATCH-2015-2018

In the case of **orientation polarization** we have a material with *built-in dipoles* that are *independent of each other*, i.e. they can *rotate freely* - in sharp contrast to <u>ionic polarization</u>.

The prime example is *liquid water*, where every water molecule is a little dipole that can have any orientation with respect to the other molecules. Moreover, the orientation changes *all the time* because the *molecules moves*! Orientation polarization for dielectric dipoles thus is pretty much limited to liquids - but we will encounter it in a major way again for *magnetic dipoles*.

A two-dimensional "piece of water" may - very graphically - look somewhat like the picture below that captures *one particular moment in time*. It is like a snapshot with a very, very short exposure time. A few nanoseconds later the same piece of water may look totally different in detail, but pretty much the same in general.

In a three-dimensional piece of water the blue and red circles would not have to be in the same plane; but that is easy to imagine and difficut to draw.



Shown is a bunch of water molecules that form natural dipoles because the negatively charged oxygen atom and the two positively charged  $\mathbf{H}$  - atoms have different centers of charge. Each molecule carries a dipole moment which can be drawn as a vector of constant length. If we only draw a vector denoting the dipole moment, we get - in two dimensions - a picture like this:



Again, remember that both pictures are "*snap shots*" that only appear unblurred for very small exposure times, say picoseconds, because the dipoles wiggle, rotate, and move around rather fast, and that in *three* dimensions the vectors would also point out of the drawing plane.

The total dipole moment is the *vector sum* of the individual dipole moments.

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#### CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

BATCH-2015-2018



For dipoles oriented *at random*, at any given moment this looks like the picture below if we draw all vectors from a common origin: The sum of all dipole moments will be zero, if the dipoles are randomly oriented.

We can see this most easily if we have all dipoles start at the same origin. The picture, of course, is two-dimensional and crossly simplified. There would be a lot more (like  $10^{20}$ ) dipoles for any appreciable amount of water - you really will average them to zero pretty well.

If we now introduce a field  $\underline{E}$ , the dipoles would have a tendency to turn into the field because that would lower their energy.

If you have problems with this statement, just imagine the electrostatic interaction, which will always try to move the positive pole of the dipole towards the negative pole of the field, and vice versa for the negative pole - the dipole would align itself exactly along a field line of the external field for minimum energy.

Naively, we would then expect a *perfect orientation into the field* and a *concomitantly* large polarization because that would lead to the *minimum of the dipole energy*.

Well, water does have a pretty large **DK** of **81**, so there is obviously *some* orientation into the field, but it is easy (not really) to show (in an exercise) that this **DK** is several orders of magnitude too small for *fully* oriented dipole moments at some normal field strengths.

#### **Dipolar polarization**

Dipolar polarization is a polarization that is either inherent to <u>polar molecules</u> (orientation polarization), or can be induced in any molecule in which the asymmetric distortion of the nuclei is possible (distortion polarization). Orientation polarization results from a permanent dipole, e.g., that arising from the 104.45° angle between the asymmetric bonds between oxygen and hydrogen atoms in the water molecule, which retains polarization in the absence of an external electric field. The assembly of these dipoles forms a macroscopic polarization.

#### CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

#### BATCH-2015-2018

When an external electric field is applied, the distance between charges within each permanent dipole, which is related to chemical bonding, remains constant in orientation polarization; however, the direction of polarization itself rotates. This rotation occurs on a timescale that depends on the torque and surrounding local viscosity of the molecules. Because the rotation is not instantaneous, dipolar polarizations lose the response to electric fields at the highest frequencies. A molecule rotates about 1 radian per picosecond in a fluid, thus this loss occurs at about 10<sup>11</sup> Hz (in the microwave region). The delay of the response to the change of the electric field causes friction and heat.

When an external electric field is applied at infrared frequencies or less, the molecules are bent and stretched by the field and the molecular dipole moment changes. The molecular vibration frequency is roughly the inverse of the time it takes for the molecules to bend, and this **distortion polarization** disappears above the infrared.

#### **Polarisation**

The charges in a dielectric material won't experience bulk motion in the presence of an external electric field, but they will rearrange themselves in a more subtle manner. This process is known as polarisation and a dielectric material so stressed is said to be polarized. There are two principal methods by which a dielectric can be polarized: stretching and rotation. There are essentially *four basic kinds of polarization mechanisms*:

#### Interface polarization.

Surfaces, grain boundaries, interphase boundaries (including the surface of precipitates) may be *charged*, i.e. they contain dipoles which may become oriented to some degree in an external field and thus contribute to the polarization of the material.

#### **Electronic polarization**,

also called atom or **atomic polarization**. An electrical field will always displace the center of charge of the electrons with respect to the nucleus and thus induce a dipole moment as discussed before. The paradigmatic materials for the simple case of *atoms with a spherical symmetry* are the noble gases in all aggregate forms.

#### Ionic polarization.

In this case a (solid) material must have some ionic character. It then automatically has internal dipoles, but these built-in dipoles exactly cancel each other and are unable to rotate. The

#### CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

BATCH-2015-2018

external field then *induces net dipoles* by slightly displacing the ions from their rest position. The paradigmatic materials are all simple ionic crystals like **NaCl**.

#### Orientation polarization.

Here the (usually liquid or gaseous) material must have *natural dipoles* which can rotate freely. In thermal equilibrium, the dipoles will be randomly oriented and thus carry no net polarization. The external field aligns these dipoles to some extent and thus induces a polarization of the material. The paradigmatic material is water, i.e.  $H_2O$  in its liquid form.

#### <u>Dipoles</u>

A dipole is a pair of equal and opposite charges. Although overall the pair of charges is electrically neutral, a dipole does give rise to an electrostatic field because the charges are spatially separated. The magnitude of the dipole moment formed from two charges +q and -qseparated by a distance r is defined as

 $\mu = q r$ 

Polar neutral molecules have a permanent dipole moment because of the uneven distribution of charge. The magnitude of the dipole moment for most molecules is of the order of  $10^{-30}$  C m and it is therefore often more convenient to express molecular dipole moments in units of Debyes, symbol D, where  $1 D = 3.33564 \times 10^{-30}$  C m. Conventionally, the direction of a dipole moment is taken as running from negative to positive. This can be rather confusing since some text books use the alternative Debye-Lewis notation in which the dipole appears to run from positive to negative.



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# KARPAGAM ACADEMY OF HIGHER EDUCATION CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES) BATC

BATCH-2015-2018

#### Conventional and Lewis dipole moments for HF

Under certain circumstances nonpolar neutral molecules may possess a transient dipole moment. An external electric field may distort the otherwise symmetrical distribution of charge within the molecule to induce a dipole moment. The magnitude of the induced dipole moment will depend upon both the polarisability of the molecule  $\alpha$  and the strength of the external electric field

 $\mu = \alpha E$ 

Polarisability is an anisotropic, tensor property that depends upon the direction within the molecule. In general, molecules are more polarisable along bonds than perpendicular to bonds. Furthermore, molecules with  $\pi$  bonds are more polarisable than those with only  $\sigma$  bonds.

Random fluctuations in the instantaneous positions of the electrons within a molecule may also result in a transient dipole moment in a nonpolar molecule.

The shape of a molecule and the polarity of its bonds together determine the charge distribution in the molecule. A molecule is said to be **polar** if its centers of negative and positive charge do not coincide. One end of a polar molecule has a slight negative charge and the other a slight positive charge. A molecule that is not polar is called *nonpolar*.

As an example of a polar molecule, we can consider a diatomic molecule with a polar bond. For example, the HF molecule is polar because of the electronegativity difference between H and F: There is a concentration of negative charge on the more electronegative F atom, leaving the less electronegative H atom as the positive end. We can indicate the polarity of the HF molecule in two ways:

 $\delta + \delta -$ H-F or H-F

As we saw in Section 8.5, the " $\delta$ +" and " $\delta$ -" indicate the partial positive and negative charges on the H and F atoms. In the notation on the right the arrow denotes the shift in electron density toward the fluorine atom. The crossed end of the arrow can be thought of as a plus sign that designates the positive end of the molecule.

Polar molecules align themselves in an electric field (Figure 9.8). They also align themselves with respect to each other and with respect to ions. The negative end of one polar molecule and the positive end of another attract each other. Polar molecules are likewise attracted to ions. The

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#### CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

#### BATCH-2015-2018

negative end of a polar molecule is attracted to a positive ion, and the positive end is attracted to a negative ion. These interactions help to explain the properties of liquids, solids, and solutions.



Polar molecules align themselves in an electric field, with their negative ends pointing toward the positive plate.

Whenever two electrical charges of equal magnitude but opposite sign are separated by a distance, a **dipole** is established. Thus, the HF molecule has a dipole. The size of a dipole is measured by its **dipole moment**, denoted #. If two charges of equal magnitude, Q+ and Q-, are separated by a distance r, the dipole moment is the product of Q and r (Figure 9.9):



When charges Q+ and Q- are separated by a distance r, a dipole is produced. The size of the dipole is given by the dipole moment,  $\clubsuit$ , which is the product of the charge separated and the distance of separation:  $\clubsuit = Qr$ .

We see that the dipole moment will increase as the quantity of charge that is separated increases, and as the distance between the charges increases.

Dipole moments of molecules are usually reported in *debyes* (D), a unit that equals  $3.34 \times 10^{-30}$  coulomb-meters (C-m). For molecules, we usually measure charge in units of the electronic charge *e*, 1.60 x  $10^{-19}$  C, and distance in Å. Suppose that two charges, 1+ and 1- (in units of *e*), are separated by a distance of 1.00 Å. The dipole moment produced is:

#### CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

BATCH-2015-2018

$$\mu = Qr = (1.60 \times 10^{-19} \text{ C})(1.00 \text{ Å}) \left(\frac{10^{-10} \text{ m}}{1 \text{ Å}}\right) \left(\frac{1 \text{ D}}{3.34 \times 10^{-30} \text{ C-m}}\right) = \frac{1}{4.79 \text{ D}}$$

Measurement of the dipole moments of molecules can provide us with valuable information about the charge distributions in molecules, as illustrated in the following Sample Exercise.

#### Exercise

The bond length of the HCl molecule is 1.27 Å. (a) Calculate the dipole moment, in D, that would result if the charges on the H and Cl atoms were 1+ and 1-, respectively. (b) The experimentally measured dipole moment of HCl(g) is 1.08 D. What magnitude of charge, in units of *e*, on the H and Cl atoms would lead to this dipole moment?

**SOLUTION** (a) The charge on each atom is the electronic charge, e: 1.60 x 10<sup>-19</sup> C. The separation is 1.27 Å. By analogy to the calculation in the text above, the dipole moment is

$$\mu = Qr = (1.60 \times 10^{-19} \text{ C})(1.27 \text{ Å}) \left(\frac{10^{-10} \text{ m}}{1 \text{ Å}}\right) \left(\frac{1 \text{ D}}{3.34 \times 10^{-30} \text{ C-m}}\right) = \frac{1000}{6.08 \text{ D}}$$

Notice that the dipole moment is greater than in the earlier example because the distance between the charges has increased from 1.00 Å to 1.27 Å.

(b) In this instance we know the value of  $^{\mu}$ , 1.08 D, and the value of r, 1.27 Å, and we want to calculate the value of Q:

$$Q = \frac{\mu}{r} = \left( \frac{(1.08 \text{ D}) \left( \frac{3.34 \times 10^{-30} \text{ C-m}}{1 \text{ D}} \right)}{(1.27 \text{ Å}) \left( \frac{10^{-10} \text{ m}}{1 \text{ Å}} \right)} \right) = 2.84 \times 10^{-20} \text{ C}$$

We can readily convert this charge to units of *e*:

Charge in 
$$e = (2.84 \times 10^{-20} \text{ C}) \left( \frac{1 e}{1.60 \times 10^{-19} \text{ C}} \right) = 0.178 e$$

Thus, the experimental dipole moment indicates the following charge separation in the HCl molecule:

Prepared by Dr.M.Makeswari & Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 10/20

#### CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

BATCH-2015-2018

0.178 + 0.178 -H—C1

Because the experimental dipole moment is less than that calculated in part (a), the charges on the atoms are less than a full electronic charge. We could have anticipated this because the H - Cl bond is polar covalent rather than ionic.

#### **Practice Exercise**

The dipole moment of chlorine monofluoride, ClF(g), is 0.88 D. The bond length of the molecule is 1.63 Å. (a) Which atom is expected to have a negative charge? (b) What is the charge on that atom, in *e*? *Answers:* (a)F; (b) 0.113-.

Table 9.4 presents the bond lengths and dipole moments of the hydrogen halides. Notice that as we proceed from HF to HI, the electronegativity difference decreases and the bond length increases. The first effect decreases the amount of charge separated and causes the dipole moment to decrease from HF to HI, even though the bond length is increasing. For these molecules the change in the difference in electronegativity is a more important factor on the dipole moment than is the bond length.

Compound	Bònđ Length (Å)	Electronegativity Difference	Dipole Moment (D)			
HF	0.92	1.9	1.82			
HC1	1.27	0.9	1.08			
HBr	1.41	0.7	0.82			
HI	1.61	0.4	0.44			

#### TABLE 9.4 Bond Lengths, Electronegativity Differences, and Dipole Moments of the Hydrogen Halides

#### **Dipole Moments of Polyatomic Molecules**

The polarity of a molecule containing more than two atoms depends on both the polarities of the bonds and the geometry of the molecule. For each polar bond in a molecule we can consider the **bond dipole**; that is, the dipole moment due only to the two atoms bonded together. We must then ask what *overall* dipole moment results from adding up the individual bond dipoles. For example, consider the  $CO_2$  molecule, which is linear. As shown in Figure 9.10(*a*), each C —O bond is polar, and, because the C —O bonds are identical, the bond dipoles are equal in magnitude.

#### CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

BATCH-2015-2018



The overall dipole moment of a molecule is the sum of its bond dipoles. (a) In  $CO_2$  the bond dipoles are equal in magnitude but exactly oppose each other. The overall dipole moment is zero. (b) In  $H_2O$ , the bond dipoles are also equal in magnitude but do not exactly oppose each other. The molecule has a nonzero overall dipole moment.

Does the fact that both C—O bonds are polar mean that the CO<sub>2</sub> molecule is polar? Not necessarily. Bond dipoles and dipole moments are *vector* quantities; that is, they have both a magnitude and a direction. The overall dipole moment of a polyatomic molecule is the sum of its bond dipoles. Both the magnitudes *and* the directions of the bond dipoles must be considered in this sum of vectors. The two bond dipoles in CO<sub>2</sub>, although equal in magnitude, are exactly opposite in direction. Adding them together is the same as adding two numbers that are equal in magnitude but opposite in sign, such as 100 + (-100): The bond dipoles, like the numbers, "cancel" each other. Therefore, the overall dipole moment of CO<sub>2</sub> is zero. Note that the oxygen atoms in CO<sub>2</sub> do carry a partial negative charge and that the carbon atom carries a partial positive charge, as we expect for polar bonds. Even though the individual bonds are polar, the geometry of the molecule dictates that the overall dipole moment be zero.

Now let's consider H<sub>2</sub>O, which is a bent molecule with two polar bonds [Figure 9.10(*b*)]. Again, both the bonds are identical, so the bond dipoles are equal in magnitude. Because the molecule is bent, however, the bond dipoles do not directly oppose each other and therefore do not cancel each other. Hence, the water molecule has an overall dipole moment (# = 1.85 D). The oxygen atom carries a partial negative charge, and the hydrogen atoms each have a partial positive charge.

Figure shows examples of polar and nonpolar molecules, all of which have polar bonds. The molecules in which the central atom is symmetrically surrounded by identical atoms (BF<sub>3</sub> and CCl<sub>4</sub>) are nonpolar. For AB<sub>n</sub>molecules in which all the B atoms are the same, certain symmetrical geometries--linear (AB<sub>2</sub>), trigonal planar (AB<sub>3</sub>), tetrahedral and square planar

#### CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

BATCH-2015-2018

 $(AB_4)$ , trigonal bipyramidal  $(AB_5)$ , and octahedral  $(AB_6)$ --must lead to nonpolar molecules even though the individual bonds might be polar.



#### **Determination Of Dipole Moment From Relative Permittivity And Refractive Index**



In most molecules the centre of negative charge due to the electrons does not coincide with the centre of positive charge due to the nuclei. These molecules possess a permanent electric dipole moment p. If charges -q and +q are separated by a distance r, the dipole moment has magnitude

$$p = q r$$

The dipole is drawn from positive to negative charge, indicating the direction of electron drift. The polarization P of a sample is the average dipole moment per unit volume. In a dielectric

(1)

Prepared by Dr.M.Makeswari & Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 13/20

#### CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

#### BATCH-2015-2018

sample, (or just "dielectric"), induction of electric charge occurs when the substance is placed in an electric field. If the molecules in the dielectric are oriented randomly, P will be zero. However in the presence of an electric field they tend to line up so as to counteract the applied field, as shown in Figure 1. As the dipole moment per unit volume is equal to the charge per unit area, surface charges appear on a block of polarized dielectric.

The relative permittivity  $\varepsilon_r$  of a sample is the ratio of the field strength in vacuum to that in the

material for the same distribution of charge.  $\varepsilon_r$  is equal to  $\varepsilon/\varepsilon_o$ , where  $\varepsilon$  is the permittivity of the

sample, and  $\varepsilon_o$  the permittivity of a vacuum (which is almost equal to that of air).  $\varepsilon_r$  is also equal to the ratio of the capacitance *C* of a cell filled with sample to the capacitance *C*<sub>o</sub> of the cell when evacuated.

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon^o} = \frac{C}{C^o}$$
(2)

Capacitance is increased by the presence of a polarizable medium; typical values of  $\varepsilon_r$  are 1.00 (air), 5.94 (chlorobenzene) and 15.5 (liquid ammonia). Water has the unusually high value of 80, and this high value has important consequences for the rate of reactions between charged species in aqueous solution, since the field around an ion falls away very rapidly with distance if the dielectric constant is high.

Suppose that a unit positive charge in the dielectric medium is situated at the centre of a small empty sphere. The size of this sphere, exaggerated in Figure 1, is large compared to molecular

dimensions but is small in relation to the distance between the plates, so the material beyond it can be treated as a continuum. The local field intensity acting on this unit charge is

$$F = 4\pi\sigma - 4\pi P + \frac{4}{3}\pi P \tag{3}$$

The three components of F are, respectively, the force due to the charges on the plates with charge density  $\sigma$ , the induced charges on the material facing the plates which partly counteract the applied field, and the charges on the surface of the small spherical cavity which enhance the applied field.

From this can be derived the Clausius-Mosotti equation:

Prepared by Dr.M.Makeswari & Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 14/20

#### CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

BATCH-2015-2018

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} \frac{M}{\rho} = P = \frac{4\pi L}{3} \alpha$$

where *M* is the molar mass of the sample,  $\rho$  its density, and L is Avogadro's constant. Because of thermal motion, the molecules do not orientate themselves in a completely ordered fashion, but instead take up a range of positions at an angle  $\theta$  to the electric field. The potential energy U of each molecule is given by

(4)

$$U = -pE\cos\theta$$

According to Boltzmann's law, the number of molecules distributed with the axes of their dipoles pointing in the directions within the solid angle  $d\Omega$  is  $Ae_{-U/kT}d\Omega$ , where A is proportional to the number of molecules. From this we may obtain the average moment per molecule as a series expression. Taking the first non-zero term only, and considering the relation between the mean moment and the polarization, we obtain the Debye equation:

(5)

$$P_{or} = \frac{4\pi L p^2}{kT}$$

(6)

The polarization caused by the alignment of molecules with permanent dipole moments is termed the orientation polarization, *Por*. It is one of three effects which contribute to the total polarization, *P*. A second effect, the electronic polarization *Pel*, arises from displacement of the electron cloud by the field, while the third, distortion polarization *Pd*, arises from the stretching and bending of the nuclear framework caused by the field.



Fig. The change of polarization with frequency.

Prepared by Dr.M.Makeswari & Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 15/20

## CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

BATCH-2015-2018

#### Measurement method of dipole moment

At low frequencies, all three effects are present. As the frequency is increased into the infrared region, molecules no longer have time to orient, and the  $P_{or}$  contribution drops out. In the visible region, the applied frequency is too high for molecular distortion to contribute to the polarization, and only  $P_{el}$  remains.

At X-ray frequencies even the electronic contribution drops out. Consequently, the refractive index of materials for X-rays is almost unity, and direct X-ray microscopy is made impractical because no lenses are available.

At optical frequencies *P*<sub>el</sub> is the only component of the polarization and there is a simple relationship between relative permittivity and refractive index:

$$\varepsilon_r = n^2$$

(7)

(Note that equation (7) applies only when  $P_{el}$  is the sole contributor to the polarization.)  $P_{el}$  may therefore be obtained by substituting this expression into the Clausius-Mosotti relation (4), to give the Lorentz equation:

$$P_{el} = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho}$$

As *P* is the sum of the orientation, electronic and distortion polarization

$$P = P_{or} + P_{el} + P_d$$

it follows from equation (6) that

$$P - P_{el} = P_{or} + P_d = \frac{1}{4\pi\varepsilon^o} \frac{4\pi L p^2}{9kT} + P_d$$
(10)

(8)

(9)

The equations derived so far strictly apply only to gases, since interactions between molecules have been ignored. If this approximation is applied to a dilute solution of polar molecules in a non-polar solvent, then both  $\varepsilon_r$  and  $1/\rho$ , where  $\rho$  is the density of the solution, are almost linear functions of solute concentration. Therefore

$$P = x_1 P_1 + x_2 P_2 = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \frac{x_1 M_1 + x_2 M_2}{\rho}$$
(11)

where x is the mole fraction, and the subscripts 1 and 2 refer to the solvent and solute respectively. Employing the same reasoning used to obtain equation (8), we find that

$$x_1 P_{el,1} + x_2 P_{el,2} = \frac{n^2 - 1}{n^2 + 2} \frac{x_1 M_1 + x_2 M_2}{\rho}$$
(12)

Prepared by Dr.M.Makeswari & Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 16/20

#### CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

BATCH-2015-2018

The concentration of solvent, c1, is related to its mole fraction by

$$c_1 = \frac{x_1 \rho}{x_1 M_1 + x_2 M_2} \tag{13}$$

and there is a corresponding relation for c2. From equations (11), (12) and (13)

$$(P_1 - P_{el,1})c_1 + (P_2 - P_{el,2})c_2 = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \frac{n^2 - 1}{n^2 + 2} = \frac{3(\varepsilon_r - n^2)}{(\varepsilon_r + 2)(n^2 + 2)}$$
(14)

Applying equation (10) to each component in equation (14), and noting that for the solvent there is no dipole moment,

$$\frac{3(\varepsilon_r - n^2)}{(\varepsilon_r + 2)(n^2 + 2)} = \frac{1}{4\pi\varepsilon^{\circ}} \frac{4\pi L p_2^2}{9kT} c_2 + P_{d,1}c_1 + P_{d,2}c_2$$
(15)

The distortion polarization terms are assumed to be small and nearly constant. Thus a plot of the term on the left of equation (15) against  $c_2$  (in mol m-3) will yield a line from whose slope we can obtain the dipole moment.



Fig. Apparatus used for heterodyne beat method

To measure capacitance using the heterodyne beat method. An oscillator provides a fixed frequency of 100 kHz, which is fed to the Y plates of an oscilloscope. A second oscillator, connected to the X plates of the scope, provides a variable frequency which is adjusted until a figure (known as a Lissajous figure - see the link on the web page for this experiment) is traced on the oscilloscope screen. At this point the variable frequency is exactly double the fixed frequency.

Prepared by Dr.M.Makeswari & Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 17/20

### CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)B/

BATCH-2015-2018

The variable frequency is controlled by the total capacitance  $C_{tot}$  of an external circuit, as shown in the figure.  $C_{tot}$  is equal to the sum of the capacitance of the cell,  $C_{cell}$ , that of the precision.

measuring capacitor  $C_{meas}$ , and the residual capacitance  $C_{resid}$  of the leads and of the measuring capacitor at its zero position:

$$C_{tot} = C_{cell} + C_{meas} + C_{resid}$$
(16)

When the Lissajous figure 8 is displayed, we know that  $C_{tot}$  has reached a fixed value. *Cresid* is also constant, so from equations (2) and (16) it follows that

 $C_{cell} + C_{meas} = C^o \varepsilon_r + C_{meas} = \text{constant}$  (17)

where  $C_o$  is the capacitance of the empty cell and  $\varepsilon_r$  is the relative permittivity of the sample. The measuring capacitor is an earthed stepped rod which can be moved axially within a live cylinder by a micrometer screw. Its capacity  $C_{meas}$  is directly proportional to the micrometer reading *R*. If the proportionality constant is *k*', then

 $C^{\circ} \varepsilon_r + k' R = \text{constant}$  (18)

We measure R for air ( $R_0$ ), the pure solvent ( $R_1$ ) and the solution (R). It follows from equation (18) that:

$$\frac{R_o - R}{R_o - R_1} = \frac{\varepsilon_r - \varepsilon_{r,0}}{\varepsilon_{r,1} - \varepsilon_{r,0}}$$
(19)

This equation allows the relative permittivity of the solution  $\mathcal{E}_r$  to be obtained from the capacitance readings *R*, given the relative permittivities of the pure components,  $\varepsilon_{r,0}$  and  $\varepsilon_{r,1}$ .

The sample is a chloronitrobenzene of molar mass 157.5 g mol<sup>-1</sup>. Prepare four solutions as follows: First put on a clean pair of protective gloves. Accurately weigh about 2g sample in a weighing bottle. Tip the contents into a clean, dry 100 cm3 volumetric flask and re-weigh the weighing bottle. Dissolve the solid in about 50 cm<sup>3</sup> cyclohexane. Dissolution is slow in cold cyclohexane but rapid if the temperature is raised a few degrees.

CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

BATCH-2015-2018

#### **POSSIBLE QUESTIONS**

### UNIT I

#### PART-A (One Mark)

#### (Multiple Choice Questions)

1.	The dipole moment of HF is
	a. <b>2.0</b> b. 1.03 c. 0.78 d. 0.38
2.	The high dipole moment of HF among hydrogen halides is due to
	a. High electron affinity of fluorine b. Low electron affinity of fluorine
3.	The isomer which shows zero value for dipole moment
	a. Cis-dichloro ethane b. <b>trans-dichloroethene</b> c. chloroethene
	d. trichloro ethane
4.	The dipole moment is high for
	a. <b>HF</b> b. HCl c. HBr HI
5.	The shape of ammonia molecule is
	a. Linear b. V shaped c. Tetrahedral d. Pyramidal
6.	Which compound will have lower dipole moment
	a. ortho disubstituted compound b. m- disubstituted compound
	c. p- disubstituted compound d. tri substituted compound
7.7	The dipole moment is zero for
	a. <b>Carbon dioxide</b> b. ethyl bromide c. methyl iodide d. chlorobenzene
8.	A pentaatomic molecule having zero dipole moment and having a tetrahedral shape
	a. CCl <sub>4</sub> b. CH <sub>3</sub> Cl c. CH <sub>3</sub> Br d. CH <sub>3</sub> I
9.	The bond length of H-I is 1.60 A. Which of the following is the correct value for

9. The bond length of H-I is 1.60 A. Which of the following is the correct value for its dipole moment, if it were present in the completely ionic form
a. 7.68 D
b. 3.00 D
c. 3.20D
d. 2.77D

Prepared by Dr.M.Makeswari & Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 19/20

d. Pyramidal

#### CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

BATCH-2015-2018

10. The shape of ammonia molecule is

a. Linear b. V shaped c. Tetrahedral

#### PART-B (Eight Mark)

#### **Either or Type Questions**

- 1. What is dipole moment? How dipole moment is used to find the structure of molecules
- 2. Discuss in detail about the orientation molar polarization of molecules
- 3. How dipole moment value is used to calculate the percentage ionic character of a polar covalent bond
- 4. How dipole moment values are measured by dilute solution method. Discuss in detail about the induced polarization of molecules
- 5. Predict the shape of triatomic, tetratomic and pentatomic molecules using dipole moment measurements.
- 6. How dipole moment is measured by refraction method
- 7. How can you establish the planar structure of benzene using dipole moment measurements
- 8. Explain how parachlorobenzene has a zero dipole moment
- 9. Differentiate between Cis and trans isomers using dipole moment measurements
- 10. How dipole moment is determined using vapour temperature method.

CLASS : IIIB.Sc CHEMISTRY COURSENAME :PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 UNIT I - (ELECTRICAL PROPERTIES OF MOLECULES)

BATCH-2015-2018

Prepared by Dr.M.Makeswari & Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 21/20

Subject : Physical methods and Chemical structures	
Subject Code : 15CHU602	
Class : III B.Sc Chemistry	
Batch : 2015-2018 Batch	
Staff Incharge : Dr.M.Makeswari and Mrs.R.Sharmila Dev	i

UNIT-I

#### Multiple Choice Questions(Each Carry One Mark)

Questions	Option 1	Option 2	Option 3	Option 4	Answer
The dipole moment of HF is	2	1.03	0.78	0.38	2
The dipole moment of HCl is	2	1.03	0.78	0.38	1.03
The dipole moment of HBr is	2	1.03	0.78	0.38	0.78
The dipole moment of HI is	2	1.03	0.78	0.38	0.38
The dipole moment is high for	HF	HCl	HBr	HI	HF
The dipole moment is low for	HF	HCl	HBr	HI	HI
The high dipole moment of HF among hydrogen halides is due to	High electron affinity of	Low electron affinity of	High ionisation energy of	Low ionisation energy	High electron affinity
	fluorine	fluorine	fluorine	of fluorine	of fluorine
If the HCl molecule is 100% ionic the dipole moment value is	6.11D	1.03D	4.8 D	9.87D	6.11D
The percentage of ionic character in HCl is	89%	50%	25%	17%	17%
The dipole moment is zero for	Carbon dioxide	ethyl bromide	methyl iodide	chlorobenzene	Carbon dioxide
The dipole moment is zero for	Carbon disulphide	ethyl bromide	methyl iodide	chlorobenzene	Carbon disulphide
The shape of the molecule is linear in	Carbon dioxide	methane	methyl iodide	chlorobenzene	Carbon dioxide
The shape of the molecule is linear in	Carbon disulphide	methane	methyl iodide	chlorobenzene	Carbon disulphide
Carbon di oxide is linear because	One bond moment is equal	The bond moments are	bond moment is equal and	They have sp <sup>3</sup>	One bond moment is
	and opposite to the other	different	act in the same side	hybridisation	equal and opposite to
					the other
The dipole moment value for water molecule is	1.63	2	1.84	2.56	1.84
The dipole moment value for sulphur di oxide molecule is	1.63	2	1.84	2.56	1.63
The shape of water molecule is	Linear	V shaped	Tetrahedral	Pyramidal	V shaped
The dipole moment of a tetra atomic molecule, boron tri-fluoride	1.63	1.84	Zero	0.38	Zero
The shape of the molecule boron trifluoride is planar triangle	1.63	1.84	Zero	0.38	Zero
because the dipole moment is					
The shape of ammonia molecule is	Linear	V shaped	Tetrahedral	Pyrami	Pyramidal
				dal	-
The shape of Phosphorous tri fluoride molecule is	Linear	V shaped	Tetrahedral	Pyrami	Pyramidal
				dal	-
The shape of Phosphorous tri-chloride molecule is	Linear	V shaped	Tetrahedral	Pyrami	Pyramidal
				dal	
The % of covalent character in HCl molecule is	34%	89%	83%	17%	83%
The bond angle between -OH bond in H2O molecule	90°	140°	104.50°	110.13	104.50°
Which one of the following is non polar molecule	CCl <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub> O	HCl	CCl <sub>4</sub>

The C=O is a polar bond. But CO <sub>2</sub> is non polar because	Non-linear molecule	The dipole moment of 2 C=O bond is cancel's each	The dipole moment of 2 C=O bond is not cancel's	Trianglar shape	The dipole moment of 2 C=O bond is cancel's
		other	each other		each other
The CCl <sub>4</sub> molecule have no dipole moment because	The 4 C-Cl bond have zero	The 3 C-Cl bond have zero	The 2 C-Cl bond have	The dipole moment of	The 4 C-Cl bond have
	dipole moment	dipole moment	zero dipole moment	bonds cancels each other	zero dipole moment
The BF <sub>3</sub> molecule have a	linear	planar	pyrimidal	trigonal	planar
For an non polar molecule P <sub>0</sub> is	0	1	5	100	0
The total polarization of polar molecule is	$\mathbf{P}_{i} = \mathbf{P}_{E} + \mathbf{P}_{A} + \mathbf{P}_{o}$	$P_i = P_E + P_o$	$P_i < P_A + P_o$	$P_i \neq P_E + P_A + P_o$	$\mathbf{P}_{i} = \mathbf{P}_{E} + \mathbf{P}_{A} + \mathbf{P}_{o}$
The total polarization of non polar molecules	$\mathbf{P}_{i} = \mathbf{P}_{E} + \mathbf{P}_{A} + \mathbf{P}_{o}$	$\mathbf{P}_{i} = \mathbf{P}_{E} + \mathbf{P}_{A}$	$P_i < P_A + P_o$	$P_i \neq P_E + P_A + P_o$	$\mathbf{P}_{i} = \mathbf{P}_{E} + \mathbf{P}_{A}$
The electrostatic moment induced in a unit volume of any material is known as	Dipole moment	Polarization	Magnetic moment	Bond distance	Polarization
The polarisability of unsymmetrical molecule is called as	Molar polarisation	Orientation polarization	Induced polarization	Deformability	Deformability
Induced polarisation is also called as	Molar polarisation	Orientation polarization	Induced polarization	Deformability	Induced polarization
The Orientation polarization of molecule occurs due to	Permanent dipole moment	Partial dipole moment	Charge of the molecules	Ordinary dipole moment	Permanent dipole moment
P <sub>A</sub> is known as	Molar polarisation	Orientation polarization	Atomic polarisation	Induced polarization	Atomic polarisation
The atomic polarisation also called as	Molar polarisation	Orientation polarization	Nuclear polarisation	Induced polarization	Nuclear polarisation
The orientation and distortion polarisation of polar molecules in	Electric field	polarisation	Magnetic property	Bond angle	Electric field
The % of jonic character in HF is	60%	40%	75%	25%	60%
The dipole moment of low volatility compound measured by using	Dilute solution method	Molecular beam method	Refractive index method	Vapour-Temperature	Molecular beam
				method	method
Which of the following state substance dipole moment is	Liquid substance	Gaseous substance	The compound easily	The substance which	The substance which is
determined by using temperature method			decomposed	is not easily decomposed	not easily decomposed
The Ebert's method is used to determine the dipole moment of	Substance in gases state	Substance in liquid state	Substance in solid state	Substances in gases	Substances in gases and
	only	only	only	and also in liquid state	also in liquid state
The ionic character of between C-F bond is	43%	45%	87%	78%	43%
Which of the following group has 39% of ionic character	С-Н	H-F	0-Н	C-Cl	0-Н
The electro-negativity of the atom is more than it form	Ionic bond	Molecular bond	Covalent bond	Co-ordination bond	Covalent bond
The charge separation between atoms in non-polar molecule is	1	0	>5	<5	0
The dipole moment do not occur between two	Identical atom	Non-identical atom	Unsymmetrical atoms	Non-polar atoms	Identical atom
Mono atomic molecules are being	Non-identical atom	Unsymmetrical atoms	Non-polar atoms	Symmetrical atoms	Symmetrical atoms
The dipole moment is represented by	Ŷ	ω	μ	Δ	μ
Which of the following structure has no dipole moment	Trigonal	bipyrimidal	Planar	Tetragonal	Planar
How many number of resonance structure is present in N <sub>2</sub> O	2	3	5	6	2
molecule					
The trans form of dichloroethylene has	$\mu = 0$	$\mu \neq 0$	$\mu > 0$	$\mu = 100$	$\mu = 0$
Which position of substitution has high dipole moment	O-position	P-positon	Meta position	Meta and P- Position	O-position

The $\mu = 6$ is belongs to	P-dinitro benzene	O-dinitro benzene	m-dinitro benzene	Nitro benzene	O-dinitro benzene
The value of dipole moment of m-dinitro benzene is	0.3	6	6.8	3.8	3.8
The dipole moment of dichloro hexane is	0.3	0	6.8	3.8	0
The dipole moment of $Cl-C_6H_6$ bond in p-chloronitro benzene is	1 D	1.5 D	2 D	2.5 D	1.5 D
The dipole moment of $NO_2$ - $C_6H_6$ bond in p-chloronitro benzene is	0.3 D	3.9 D	9.3 D	3.0 D	3.9 D
The greater in dipole moment, the greater is the	symmetry	polar	charge	asymmetry	asymmetry
The dipole moment $\mu$ is equal to	$\mu = e * d$	$\mu \neq e * d$	$\mu = e$	$\mu = d$	$\mu = e * d$

CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602 UNIT: II (MAGNETIC PROPERTY OF MOLECULES) BATCH-2015-2018

#### <u>UNIT-II</u>

#### **SYLLABUS**

Magnetic properties of molecules: Meaning of the terms magnetic susceptibility, magnetic moment, diamagnetism, paramagnetism and ferromagnetism. Determination of magnetic susceptibility by Gouy's method. Application of magnetic measurements.

#### MAGNETIC PROPERTY OF MOLECULES

#### **Definition**

Magnetic susceptibility is a dimensionless proportionality constant that indicates the degree of magnetization of a material in response to an applied magnetic field. A related term is**magnetizability**, the proportion between magnetic moment and magnetic flux density.<sup>[1]</sup> A closely related parameter is the permeability, which expresses the total magnetization of material and volume.

The volume magnetic susceptibility, represented by the symbol  $\chi_v$  (often simply,  $\chi$  sometimes  $\chi_m$  – magnetic, to distinguish from the electric susceptibility), is defined in the International System of Units — in other systems there may be additional constants — by the following relationship:

#### $M = \chi_v H$

Here,

**M** is the <u>magnetization</u> of the material (the <u>magnetic dipole moment</u> per unit volume), measured in <u>amperes</u> per meter, and

H is the <u>magnetic field strength</u>, also measured in amperes per meter.

Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 1/19

#### KARPAGAM ACADEMY OF HIGHER EDUCATION CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602 UNIT: II (MAGNETIC PROPERTY OF MOLECULES) BATCH-2015-2018

 $\chi_v$  is therefore a <u>dimensionless quantity</u>.

Using <u>SI units</u>, the <u>magnetic induction</u> **B** is related to **H** by the relationship

 $B = \mu_0(H+M) = \mu_0_{(1+\chi_v)}H = \mu H$ 

where  $\mu_0$  is the magnetic constant (see table of physical constants), and  $(1+\chi_v)$  is the relative permeability of the material. Thus the *volume magnetic susceptibility*  $\chi_v$  and the magnetic permeability  $\mu$  are related by the following formula:

 $\mu = \mu_0 \left(1 + \chi_v\right)$ 

Sometimes an auxiliary quantity called *intensity of magnetization* (also referred to as *magnetic polarisation* J) and measured in <u>teslas</u>, is defined as

 $I = \mu_0 M$ 

This allows an alternative description of all magnetization phenomena in terms of the quantities **I** and **B**, as opposed to the commonly used **M** and **H**.

Note that these definitions are according to <u>SI</u> conventions. However, many tables of magnetic susceptibility give <u>CGS</u> values (more specifically <u>emu-cgs</u>, short for electromagnetic units, or <u>Gaussian-cgs</u>; both are the same in this context). These units rely on a different definition of the permeability of free space.

 $B^{cgs} = H^{cgs} + 4\pi M^{cgs} = (1 + 4\pi \chi_v^{cgs}) H^{cgs}$ 

The <u>dimensionless</u> CGS value of volume susceptibility is multiplied by  $4\pi$  to give the dimensionless <u>SI</u> volume susceptibility value:

 $X_v^{SI} = 4\pi \gamma_v^{cgs}$ 

For example, the <u>CGS</u> volume magnetic susceptibility of water at 20 °C is  $-7.19 \times 10^{-7}$  which is  $-9.04 \times 10^{-6}$  using the <u>SI</u> convention.

Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 2/19

#### CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602 UNIT: II (MAGNETIC PROPERTY OF MOLECULES) BATCH-2015-2018

In physics it is common (in older literature) to see CGS mass susceptibility given in emu/g, so to convert to SI volume susceptibility we use the conversion

 $X_v^{SI} = 4\pi \rho^{cgs} \chi_m^{cgs}$ 

where  $\rho^{cgs}$  , is the density given in g/cm³, or

 $X_v^{SI} = (4\pi \ x \ 10^{-3}) \rho^{SI} \chi m^{cgs}$ 

given where  $\rho^{SI}$  is the density in kg/m<sup>3</sup>.

#### Magnetic susceptibility (Measurement)

The primary measurement in magnetochemistry is magnetic susceptibility. This measures the strength of interaction on placing the substance in a magnetic field. The **volume magnetic susceptibility**, represented by the symbol is defined by the relationship

where, is the magnetization of the material (the magnetic dipole moment per unit volume), measured in amperes per meter (SI units), and is the magnetic field strength, also measured in amperes per meter. Susceptibility is a dimensionless quantity. For chemical applications the **molar magnetic susceptibility** ( $\chi_{mol}$ ) is the preferred quantity. It is measured in  $m^3 \cdot mol^{-1}$  (SI) or  $cm^3 \cdot mol^{-1}$  (CGS) and is defined as where  $\rho$  is the density in kg·m<sup>-3</sup> (SI) or  $g \cdot cm^{-3}$  (CGS) and *M* is molar mass in kg·mol<sup>-1</sup> (SI) or g·mol<sup>-1</sup> (CGS).

#### CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602 UNIT: II (MAGNETIC PROPERTY OF MOLECULES) BATCH-2015-2018



Schematic diagram of Gouy balance

A variety of methods are available for the measurement of magnetic susceptibility.

- With the Gouy balance the weight change of the sample is measured with an analytical balance when the sample is placed in a homogeneous magnetic field. The measurements are calibrated against a known standard, such as mercury cobalt thiocyanate, HgCo(NCS)<sub>4</sub>. Calibration removes the need to know the density of the sample. Variable temperature measurements can be made by placing the sample in a cryostat between the pole pieces of the magnet.
- The Evans balance. is a torsion balance which uses a sample in a fixed position and a variable secondary magnet to bring the magnets back to their initial position. It, too, is calibrated against HgCo(NCS)<sub>4</sub>.
- With a Faraday balance the sample is placed in a magnetic field of constant gradient, and weighed on a torsion balance. This method can yield information onmagnetic anisotropy.
- SQUID is a very sensitive magnetometer.
- For substances in solution NMR may be used to measure susceptibility.

#### KARPAGAM ACADEMY OF HIGHER EDUCATION CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602 UNIT: II (MAGNETIC PROPERTY OF MOLECULES) BATCH-2015-2018

#### **Types of magnetic behaviour**

When an isolated atom is placed in a magnetic field there is an interaction because each electron in the atom behaves like a magnet, that is, the electron has a magnetic moment. There are two types of interaction.

- 1. **Diamagnetism**. When placed in a magnetic field the atom becomes magnetically polarized, that is, it develops an induced magnetic moment. The force of the interaction tends to push the atom out of the magnetic field. By convention diamagnetic susceptibility is given a negative sign. Very frequently diamagnetic atoms have no unpaired electrons *ie* each electron is paired with another electron in the same atomic orbital. The moments of the two electrons cancel each other out, so the atom has no net magnetic moment. However, for the ion Eu<sup>3+</sup> which has six unpaired electrons, the orbital angular momentum cancels out the electron angular momentum, and this ion is diamagnetic at zero Kelvin.
- 2. <u>Paramagnetism</u>. At least one electron is not paired with another. The atom has a permanent magnetic moment. When placed into a magnetic field, the atom is attracted into the field. By convention paramagnetic susceptibility is given a positive sign.

When the atom is present in a chemical compound its magnetic behaviour is modified by its chemical environment. Measurement of the magnetic moment can give useful chemical information.

In certain crystalline materials individual magnetic moments may be aligned with each other (magnetic moment has both magnitude and direction). This gives rise to ferromagnetism, antiferromagnetism or ferrimagnetism. These are properties of the crystal as a whole, of little bearing on chemical properties.
CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602 UNIT: II (MAGNETIC PROPERTY OF MOLECULES) BATCH-2015-2018

### **Diamagnetism**

Diamagnetism is a universal property of chemical compounds, because all chemical compounds contain electron pairs. A compound in which there are no unpaired electrons is said to be diamagnetic. The effect is weak because it depends on the magnitude of the induced magnetic moment. It depends on the number of electron pairs and the chemical nature of the atoms to which they belong. This means that the effects are additive, and a table of "diamagnetic contributions", or Pascal's constants, can be put together. With paramagnetic compounds the observed susceptibility can be adjusted by adding to it the so-called diamagnetic correction, which is the diamagnetic susceptibility calculated with the values from the table.

### **Paramagnetism**

#### Mechanism and temperature dependence



Variation of magnetic susceptibility with temperature

A metal ion with a single unpaired electron, such as  $Cu^{2+}$ , in a coordination complex provides the simplest illustration of the mechanism of paramagnetism. The individual metal ions

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are kept far apart by the ligands, so that there is no magnetic interaction between them. The system is said to be magnetically dilute. The magnetic dipoles of the atoms point in random directions. When a magnetic field is applied, first-order Zeeman splitting occurs. Atoms with spins aligned to the field slightly outnumber the atoms with non-aligned spins. In the first-order Zeeman effect the energy difference between the two states is proportional to the applied field strength. Denoting the energy difference as  $\Delta E$ , the Boltzmann distribution gives the ratio of the two populations as, where *k* is the Boltzmann constant and *T* is the temperature in kelvins. In

most cases  $\Delta E$  is much smaller than kT and the exponential can be expanded as  $1 - \Delta E/kT$ . It follows from the presence of 1/T in this expression that the susceptibility is inversely proportional to temperature.<sup>[10]</sup>

This is known as the Curie law and the proportionality constant, C, is known as the Curie

constant, whose value, for molar susceptibility, is calculated as

where *N* is the Avogadro constant, *g* is the Landé g-factor, and  $\mu_B$  is the Bohr magneton. In this treatment it has been assumed that the electronic ground state is not degenerate, that the magnetic susceptibility is due only to electron spin and that only the ground state is thermally populated.

While some substances obey the Curie law, others obey the Curie-Weiss law.

 $T_c$  is the Curie temperature. The Curie-Weiss law will apply only when the temperature is well above the Curie temperature. At temperatures below the Curie temperature the substance may become ferromagnetic. More complicated behaviour is observed with the heavier transition elements.

#### **Effective magnetic moment**

When the Curie law is obeyed, the product of molar susceptibility and temperature is a

constant. The effective magnetic moment,  $\mu_{eff}$  is then defined as

Where C has CGS units  $cm^3 mol^{-1} K$ ,  $\mu_{eff}$  is

Where C has SI units  $m^3 \text{ mol}^{-1}$  K,  $\mu_{eff}$  is

The quantity  $\mu_{eff}$  is effectively dimensionless, but is often stated as in units of <u>Bohr</u> <u>magneton</u> ( $\mu_B$ ).

For substances that obey the Curie law, the effective magnetic moment is independent of temperature. For other substances  $\mu_{eff}$  is temperature dependent, but the dependence is small if the Curie-Weiss law holds and the Curie temperature is low.

#### Temperature independent paramagnetism

Compounds which are expected to be diamagnetic may exhibit this kind of weak paramagnetism. It arises from a second-order Zeeman effect in which additional splitting, proportional to the square of the field strength, occurs. It is difficult to observe as the compound inevitably also interacts with the magnetic field in the diamagnetic sense. Nevertheless, data are available for the permanganateion. It is easier to observe in compounds of the heavier elements, such as uranyl compounds.

#### **Exchange interactions**





Figure 3. X-band EPR spectra for copper complexe [Cu(qibsa)<sub>2</sub>] in the frozen DMF solution. (—) Experimental spectrum and (…) simulated spectrum using the Winepr SimFonia®Program

Copper(II) acetate dihydrate

Exchange interactions occur when the substance is not magnetically dilute and there are interactions between individual magnetic centres. One of the simplest systems to exhibit the result of exchange interactions is crystalline copper(II) acetate,  $Cu_2(OAc)_4(H_2O)_2$ . As the formula indicates, it contains two copper(II) ions. The  $Cu^{2+}$  ions are held together by four acetate ligands, each of which binds to both copper ions. Each  $Cu^{2+}$  ion has a d<sup>9</sup> electronic configuration, and so should have one unpaired electron. If there were a covalent bond between the copper ions, the electrons would pair up and the compound would be diamagnetic. Instead, there is an exchange interaction in which the spins of the unpaired electrons become partially aligned to each other. In fact two states are created, one with spins parallel and the other with spins opposed. The energy difference between the two states is so small their populations vary significantly with temperature. In consequence the magnetic moment varies with temperature in a sigmoidal pattern. The state with spins opposed has lower energy, so the interaction can be classed as antiferromagnetic in this case. It is believed that this is an example of superexchange, mediated by the oxygen and carbon atoms of the acetate ligands.<sup>[15]</sup> Other dimers and clusters exhibit exchange behaviour.

Exchange interactions can act over infinite chains in one dimension, planes in two dimensions or over a whole crystal in three dimensions. These are examples of long-range magnetic ordering. They give rise to ferromagnetism, antiferromagnetism or ferrimagnetism, depending on the nature and relative orientations of the individual spins.

Compounds at temperatures below the Curie temperature exhibit long-range magnetic order in the form of ferromagnetism. Another critical temperature is the Néel temperature, below which anti-ferromagnetism occurs. The hexahydrate of nickel chloride, NiCl<sub>2</sub>·6H<sub>2</sub>O, has a Néel temperature of 8.3 K. The susceptibility is a maximum at this temperature. Below the Néel temperature the susceptibility decreases and the substance becomes antiferromagnetic.

CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602 UNIT: II (MAGNETIC PROPERTY OF MOLECULES) BATCH-2015-2018

### **Complexes of transition metal ion**

The effective magnetic moment for a compound containing a transition metal ion with one or more unpaired electrons depends on the total orbital and spin angular momentum of the

unpaired electrons, and , respectively. "Total" in this context means "vector sum". In the approximation that the electronic states of the metal ions are determined by Russell-Saunders coupling and that spin-orbit coupling is negligible, the magnetic moment is given by

### Spin-only formula

Orbital angular momentum is generated when an electron in an orbital of a degenerate set of orbitals is moved to another orbital in the set by rotation. In complexes of <u>low symmetry</u> certain rotations are not possible.

In that case the orbital angular momentum is said to be "quenched" and is smaller than might be expected (partial quenching), or zero (complete quenching). There is complete quenching in the following cases. Note that an electron in a degenerate pair of  $d_{x^2-y^2}$  or  $d_{z^2}$  orbitals cannot rotate into the other orbital because of symmetry.

CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602 UNIT: II (MAGNETIC PROPERTY OF MOLECULES) BATCH-2015-2018

d <sup>n</sup>	Octahedr	al		Tetrahedral		
		high-spin	low-spin			
dı				e <sup>1</sup>		
d <sup>2</sup>				e <sup>2</sup>		
d <sup>3</sup>	$t_{2g}^{3}$					
d⁴		$t_{2g}^{3}e_{g}^{1}$				
d⁵		$t_{2g}^{3}e_{g}^{2}$				
d⁰			t <sub>2g</sub> <sup>6</sup>	e <sup>3</sup> t <sub>2</sub> <sup>3</sup>		
d <sup>7</sup>			$t_{2g}{}^{6}e_{g}{}^{1}$	$e^{4}t_{2}^{3}$		
d <sup>8</sup>	$t_{2g}{}^{6}e_{g}{}^{2}$					
d <sup>9</sup>	$t_{2g}^{6}e_{g}^{3}$					

legend:  $t_{2g}$ ,  $t_2 = (d_{xy}, d_{xz}, d_{yz})$ .  $e_g$ ,  $e = (d_x^2 d_z^2, d_z^2)$ .

When orbital angular momentum is completely quenched, and the paramagnetism can be attributed to electron spin alone. The total spin angular momentum is simply half the number of unpaired electrons and the spin-only formula results.

where n is the number of unpaired electrons. The spin-only formula is a good first approximation for high-spin complexes of first-row <u>transition metals</u>.

Ion	Number of unpaired electrons	Spin-only moment /µ <sub>B</sub>	observed moment /µ <sub>B</sub>	
Ti <sup>3+</sup>	1	1.73	1.73	
V <sup>4+</sup>	1		1.68–1.78	
Cu <sup>2+</sup>	1		1.70–2.20	
<b>V</b> <sup>3+</sup>	2	2.83	2.75–2.85	
Ni <sup>2+</sup>	2		2.8–3.5	
<b>V</b> <sup>2+</sup>	3	3.87	3.80–3.90	
Cr <sup>3+</sup>	3		3.70–3.90	
Co <sup>2+</sup>	3		4.3–5.0	

# CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602 UNIT: II (MAGNETIC PROPERTY OF MOLECULES) BATCH-2015-2018

Mn <sup>4+</sup>	3		3.80-4.0
Cr <sup>2+</sup>	4	4.90	4.75-4.90
Fe <sup>2+</sup>	4		5.1–5.7
Mn <sup>2+</sup>	5	5.92	5.65-6.10
Fe <sup>3+</sup>	5		5.7–6.0

The small deviations from the spin-only formula may result from the neglect of orbital angular momentum or of spin-orbit coupling. For example, tetrahedral  $d^3$ ,  $d^4$ ,  $d^8$  and  $d^9$  complexes tend to show larger deviations from the spin-only formula than octahedral complexes of the same ion, because "quenching" of the orbital contribution is less effective in the tetrahedral case.

### Low-spin complexes

According to crystal field theory, the *d* orbitals of a transition metal ion in an octahedal complex are split into two groups in a crystal field. If the splitting is large enough to overcome the energy needed to place electrons in the same orbital, with opposite spin, a low-spin complex will result.



Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 13/19

# CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602 UNIT: II (MAGNETIC PROPERTY OF MOLECULES) BATCH-2015-2018

d <sup>4</sup>	4	2	Cr <sup>2+</sup> , Mn <sup>3+</sup>
d <sup>5</sup>	5	1	Mn <sup>2+</sup> , Fe <sup>3+</sup>
d <sup>6</sup>	4	0	Fe <sup>2+</sup> , Co <sup>3+</sup>
d <sup>7</sup>	3	1	Co <sup>2+</sup>

With one unpaired electron  $\mu_{eff}$  values range from 1.8 to 2.5  $\mu_B$  and with two unpaired electrons the range is 3.18 to 3.3  $\mu_B$ . Note that low-spin complexes of Fe<sup>2+</sup>and Co<sup>3+</sup> are diamagnetic. Another group of complexes that are diamagnetic are <u>square-planar</u> complexes of d<sup>8</sup> ions such as Ni<sup>2+</sup> and Rh<sup>+</sup> and Au<sup>3+</sup>.

### Spin cross-over

When the energy difference between the high-spin and low-spin states is comparable to kT (k is the Boltzmann constant and T the temperature) an equilibrium is established between the spin states, involving what have been called "electronic isomers". Tris-dithiocarbamato iron(III),  $Fe(S_2CNR_2)_3$ , is a well-documented example. The effective moment varies from a typical d<sup>5</sup> low-spin value of 2.25  $\mu_Bat$  80 K to more than 4  $\mu_B$  above 300 K.

#### 2nd and 3rd row transition metals

Crystal field splitting is larger for complexes of the heavier transition metals than for the transition metals discussed above. A consequence of this is that low-spin complexes are much more common. Spin-orbit coupling constants,  $\zeta$ , are also larger and cannot be ignored, even in elementary treatments. The magnetic behaviour has been summarized, as below, together with an extensive table of data.

### CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602 UNIT: II (MAGNETIC PROPERTY OF MOLECULES) BATCH-2015-2018

d-count	kT/ζ=0.1 μ <sub>eff</sub>	kT/ζ=0 μ <sub>eff</sub>	Behaviour with large spin-orbit coupling constant, $\zeta_{nd}$
dı	0.63	0	$\mu_{eff}$ varies with $T^{1/2}$
d <sup>2</sup>	1.55	1.22	$\mu_{eff}$ varies with T, approximately
d <sup>3</sup>	3.88	3.88	Independent of temperature
d <sup>4</sup>	2.64	0	$\mu_{eff}$ varies with $T^{1/2}$
d⁵	1.95	1.73	$\mu_{eff}$ varies with T, approximately

### Lanthanides and actinides

Russell-Saunders coupling, LS coupling, applies to the lanthanide ions, crystal field effects can be ignored, but spin-orbit coupling is not negligible. Consequently, spin and orbital

angular momenta have to be combined

and the calculated magnetic moment is given by

Magnetic pro	Magnetic properties of trivalent lanthanide compounds <sup>[25]</sup>													
Lanthanide	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu

# CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602 UNIT: II (MAGNETIC PROPERTY OF MOLECULES) BATCH-2015-2018

Number of unpaired électrons	1	2	3	4	5	6	7	6	5	4	3	2	1	0
calculated moment $/\mu_B$	2.54	3.58	3.62	2.68	0.85	0	7.94	9.72	10.65	10.6	9.58	7.56	4.54	0
observed moment $/\mu_B$	2.3– 2.5	3.4– 3.6	3.5– 3.6		1.4– 1.7	3.3– 3.5	7.9– 8.0	9.5– 9.8	10.4– 10.6	10.4– 10.7	9.4– 9.6	7.1– 7.5	4.3– 4.9	0

In actinides spin-orbit coupling is strong and the coupling approximates to *j j* coupling.

This means that it is difficult to calculate the effective moment. For example, uranium(IV),  $f^2$ , in the complex  $[UCl_6]^{2-}$  has a measured effective moment of 2.2  $\mu_B$ , which includes a contribution from temperature-independent paramagnetism.

### Main group elements and organic compounds

Very few compounds of main group elements are paramagnetic. Notable examples include: oxygen,  $O_2$ ; nitric oxide, NO; nitrogen dioxide, NO<sub>2</sub> and chlorine dioxide, ClO<sub>2</sub>. In organic chemistry, compounds with an unpaired electron are said to be free radicals. Free radicals, with some exceptions, are short-lived because one free radical will react rapidly with another, so their magnetic properties are difficult to study. However, if the radicals are well separated from each other in a dilute solution in a solid matrix, at low temperature, they can be studied byelectron paramagnetic resonance (EPR). Such radicals are generated by irradiation. Extensive EPR studies have revealed much about electron delocalization in free radicals. The simulated spectrum of the CH<sub>3</sub>• radical shows hyperfine splitting due to the interaction of the electron with the 3 equivalent hydrogen nuclei, each of which has a spin of 1/2.

Spin labels are long-lived free radicals which can be inserted into organic molecules so that they can be studied by EPR.<sup>[29]</sup> For example, the nitroxide MTSL, a functionalized derivative of TEtra Methyl Piperidine Oxide, TEMPO, is used in site-directed spin labeling.

### **Applications**

The gadolinium ion,  $Gd^{3+}$ , has the  $f^7$  electronic configuration, with all spins parallel. Compounds of the  $Gd^{3+}$  ion are the most suitable for use as a contrast agent for MRI scans. The magnetic moments of gadolinium compounds are larger than those of any transition metal ion. Gadolinium is preferred to other lanthanide ions, some of which have larger effective moments, due to its having anon-degenerate electronic ground state.

For many years the nature of oxyhemoglobin, Hb-O<sub>2</sub>, was highly controversial. It was found experimentally to be diamagnetic. Deoxy-hemoglobin is generally accepted to be a complex of iron in the +2 oxidation state, that is a d<sup>6</sup> system with a high-spin magnetic moment near to the spin-only value of 4.9  $\mu_B$ . It was proposed that the iron is oxidized and the oxygen reduced to superoxide.

Fe(II)Hb (high-spin) +  $O_2 \rightleftharpoons [Fe(III)Hb]O_2^-$ 

Pairing up of electrons from  $\text{Fe}^{3+}$  and  $\text{O}_2^-$  was then proposed to occur via an exchange mechanism. It has now been shown that in fact the iron(II) changes from high-spin to low-spin when an oxygen molecule donates a pair of electrons to the iron. Whereas in deoxy-hemoglobin the iron atom lies above the plane of the heme, in the low-spin complex the effective ionic radius is reduced and the iron atom lies in the heme plane.

 $Fe(II)Hb + O_2 \rightleftharpoons [Fe(II)Hb]O_2 (low-spin)$ 

This information has an important bearing on research to find artificial oxygen carriers.

Compounds of gallium(II) were unknown until quite recently. As the atomic number of gallium is an odd number (31),  $Ga^{2+}$  should have an unpaired electron. It was assumed that it would act as a free radical and have a very short lifetime. The non-existence of Ga(II) compounds was part of the so-called inert pair effect. When salts of the anion with empirical formula such as

# CLASS: IIIB.Sc CHEMISTRY COURSENAME: PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602 **UNIT: II** (MAGNETIC PROPERTY OF MOLECULES) BATCH-2015-2018

 $[GaCl_3]^-$  were synthesized they were found to be diamagnetic. This implied the formation of a Ga-Ga bond and a dimeric formula,  $[Ga_2Cl_6]^{2-}$ .

# **POSSIBLE QUESTIONS**

### **PART-A** (One Mark)

### (Multiple Choice Questions)

- 1. For vacuum the value of magnetic permeability is **a.One** b. 5 c. 8 d. 2.3
- 2. If the magnetic lines of force are repelled from the substance, the substances is called

a. Diamagnetic	b. paramagnetic	c. ferromagnetic	d. Polymers
----------------	-----------------	------------------	-------------

- 3. The strength of the magnetic field present in the material is called
  - a. Magnetic induction b. Magnetic susceptibility
  - c. Magnetic permeability d. dipole moment
- 4. Molar magnetic susceptibility is an a.Intensive property b. Extensive property
  - d. surface property c. Constitutive property
- 5. If the magnetic lines of force prefer to pass through the vacuum than through the substance comprising the medium, then value of  $\mu$  is
  - a. 1 b. 0 c. less than one d. greater than one
- 6. The magnetic moment per volume is called a. Magnetic induction b. Magnetic susceptibility c. Magnetic permeability d. Intensity of magnetization
- 7. The relative tendency of the magnetic lines of force to pass through the medium as compared to that in the vacuum is called

### a.Magnetic permeability

- b. Magnetic susceptibility c. Dipole moment d. magnetic moment
- 8. The strength of the magnetic field present in the material is called
  - a. Magnetic induction b. Magnetic susceptibility
  - d. dipole moment c. Magnetic permeability

CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602 UNIT: II (MAGNETIC PROPERTY OF MOLECULES) BATCH-2015-2018

- 9. Gouy's method is used to determine
  - a. Magnetic permeability b. Magnetic susceptibility
  - c. Magnetic flux d. Intensity of magnetization
- 10. The value of atomic susceptibility of carbon atom is
  - a.-2.93 b. -**6.00**
- c. -11.5

d. -30.6

PART-B (Eight Mark)

### **Either or Type questions**

1. Explain the terms

(i) Magnetic susceptibility

- (ii) Magnetic induction
- (iii) Specific magnetic susceptibility
- 2. How magnetic susceptibility is determined experimentally by Gouy's method
- 3. How magnetic susceptibility values are used to find the molecular structures
- 4. Using Magnetic susceptibility values

i)Establish the structure of methyl acetate

- ii)Confirm the structure of benzoic acid
- 5. Explain the molecular interpretation of diamagnetism and paramagnetism.

6. Explain the application of Magnetic susceptibility measurements in Conforming the structure of a given molecule

7. Explain the application of Magnetic susceptibility measurements in calculation of the number of unpaired electrons in a molecule

8. Explain the application of Magnetic susceptibility measurements in the study of coordination compounds

9. What is meant by magnetic permeability, diamagnetism, paramagnetism and ferromagnetism 10. Give adetailed note on diamagnetism.

CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602 UNIT: II (MAGNETIC PROPERTY OF MOLECULES) BATCH-2015-2018

Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 20/19

Subject : Physical methods and Chemical structures				
Subject Code : 15CHU602				
Class : III B.Sc Chemistry				
Batch : 2015-2018 Batch				
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UNIT-II

#### Multiple Choice Questions(Each Carry One Mark)

Questions	Option 1	Option 2	Option 3	Option 4	Answer
The relative tendency of the magnetic lines of force to pass through the					
medium as compared to that in the vacuum is called	Magnetic permeability	Magnetic susceptibility	Dipole moment	magnetic moment	Magnetic permeability
The strength of the magnetic field present in the material is called	Magnetic induction	Magnetic susceptibility	Magnetic permeability	dipole moment	Magnetic induction
Gouy's method is used to determine	Magnetic permeability	Magnetic susceptibility	Magnetic flux	Intensity of magnetization	Magnetic susceptibility
The value of atomic susceptibility of carbon atom is	-2.93	-6	-11.5	-30.6	-6
For vacuum the value of magnetic permeability is	One	5	8	2.3	One
If the magnetic lines of force are repelled from the substance, the					
substances is called	Diamagnetic	paramagnetic	ferromagnetic	Polymers	Diamagnetic
The strength of the magnetic field present in the material is called	Magnetic induction	Magnetic susceptibility	Magnetic permeability	dipole moment	Magnetic induction
Molar magnetic susceptibility is an	Intensive property	Extensive property	Constitutive property	surface property	Constitutive property
If the magnetic lines of force prefer to pass through the vacuum than					
through the substance comprising the medium, then value of $\mu$ is	1	0	less than one	greater than one	less than one
The magnetic moment per volume is called	Magnetic induction	Magnetic susceptibility	Magnetic permeability	Intensity of magnetization	Intensity of magnetization
Molar magnetic susceptibility is an	Intensive property	Extensive property	Additive property	surface property	Additive property
				through which the magnetic	
				lines of force can pass very	
A permeable substance is one	which is a good conductor	which is a bad conductor	which is a strong magnet	easily	which is a strong magnet
The materials having low retentivity are suitable for making	weak magnets	temporary magnets	permanent magnets	Diamagnet	temporary magnets
A magnetic field exists around	iron	copper	aluminium	moving charges	moving charges
Ferrites are materials.	paramagnetic	diamagnetic	ferromagnetic	non-ferromagnetic	ferromagnetic
			from one end of the magnet to		
The direction of magnetic lines of force is	from south pole to north pole	from north pole to south pole	another	No effect	from north pole to south pole
Which of the following is a vector quantity	Relative permeability	Magnetic field intensity	Flux density	Magnetic potential	Magnetic field intensity
A material which is slightly repelled by a magnetic field is known as	ferromagnetic material	diamagnetic material	paramagnetic material	conducting material	diamagnetic material
	the magnetic lines of force	the magnetic lines of force	ř – – –		the magnetic lines of force
	will bend away from their	will bend away from their			will bend away from their
	usual paths in order to go	usual paths in order to pass	the magnetic field will not be		usual paths in order to pass
When an iron piece is placed in a magnetic field	away from the piece	through the piece	affected	the iron piece will break	through the piece
The ratio of intensity of magnetisation to the magnetisation force is known					
as	flux density	susceptibility	relative permeability	dipole moment	susceptibility
Magnetising steel is normals difficult because	it corrodes easily	it has high permeability	it has high specific gravity	it has low permeability	it has low permeability
The unit of relative permeability is	henry/metre	henry	henry/sq. m	it is dimensionless	it is dimensionless
The force between two long parallel conductors is inversely proportional			product of current in two	distance between the	distance between the
to	radius of conductors	current in one conductor	conductors	conductors	conductors
		high permeability and low	high co-ercivity and high	high co-ercivity and low	high permeability and low
Materials subjected to rapid reversal of magnetism should have	large area oiB-H loop	hysteresis loss	reten-tivity	density	hysteresis loss
Indicate which of the following material does not retain magnetism					
permanently.	Soft iron	Stainless steel	Hardened steel	Rought iron	Soft iron
The main constituent of permalloy is	cobalt	chromium	nickel	tungsten	nickel
The use of permanent magnets is, not made in	magnetoes	energy meters	transformers	loud-speakers	transformers
	5	65		equal to that ferromagnetic	
Paramagnetic materials have relative permeability	slightly less than unity	equal to unity	slightly more than unity	mate rials	slightly more than unity
Substances which have permeability less than the permeability of free		<u> </u>			
space are known as	ferromagnetic	paramagnetic	diamagnetic	bipolar	diamagnetic
Which of the following is a ferromagnetic material	Tungsten	Aluminium	Copper	Nickel	Nickel
0			1		1

Nickel is an	ferromagnetic material	paramagnetic material	diamagnetic material	bipolar material	ferromagnetic material
Susceptibility is positive for	non-magnetic substances	diamagnetic substances	ferromagnetic substances	para magnetic	ferromagnetic substances
The commonly used material for shielding or screening magnetism is	copper	aluminium	soft iron	brass	soft iron
If a copper disc is rotated rapidly below a freely suspended magnetic	less than that of disc but in o	equal to that of disc	equal to that of disc and in the	less than that of disc and in	less than that of disc and in
needle, the magnetic needle shall start rotating with a velocity)	pposite direction	and in the same direction	opposite direction	the same direction	the same direction
				attracts ferromagnetic	
	attracts some substances and	attracts all paramagnetic	attracts only ferromagnetic	substances and repels all	attracts some substances and
A permanent magnet	repels others	substances and repels others	substances	others	repels others
The material which attracts some substance but repels others is called	bipolar	ferromagnetic material	magnetoes	permanent magnet	permanent magnet
The soft iron is used as a	de-magneting agent	maneting agent	paramagnetic material	ferromagnetic material	de-magneting agent
The ferromangnetic substances have	positive susceptibility	negative susceptibility	low susceptibility	high susceptibility	positive susceptibility
	force between two parllal	force between two	hight between two parllal	width between two parllal	force between two parllal
The distance between conductors inversly proportinal to	conductors	perpendicular conductors	conductors	conductors	conductors
Th repeltion of diamagnetic substance is	high	zero	low	Very high	low
The Magnetic field intensity is a	physical property	vector property	qualicative property	Electrical property	vector property
Magnetic moment is a	pole strength	universal constant	scalar quantity	vector quantity	vector quantity
The change of cross-sectional area of conductor in magnetic field will	reluctance of conductor	resistance of conductor	a and b but b>in the same way	No resistance	a and b but b>in the same way
affect			5		
	the field of a set of parallel	the field of a single conductor	the field in which all lines of	a field of perpendicular	the field in which all lines of
	conductors	e e	magnetic flux are parallel and	conductor	magnetic flux are parallel and
The uniform magnetic field is			equidistant		equidistant
	decreases with increasing cros	increases with increasing cros	does not vary with increasing	increases with decreasing cros	decreases with increasing cros
	s sectional area of material	s-sectional area of material	cross-sectional area of	s sectional area of material	s sectional area of material
The magnetic reluctance of a material			material		
	the highest permeability of the	the lowest permeability of the	the permeability at the end of	the permeability almost in non	the permeability almost in non-
The initial permeability of an iron rod is	iron rod	iron rod	the iron rod	magnetised state	magnetised state
	equal to temperature	directionaly proportional to	inversly proportional to	not equal to temperature	equal to temperature
The susceptibility of paramagnetic substance is		temperature	temperature		· · · · · · · · · · · · · · · · · · ·
	equal to temperature	directionaly proportional to	inversiv proportional to	not equal to temperature	not equal to temperature
The susceptibility of diamagnetic substance is	· · · · · · · · · · · · · · · · · · ·	temperature	temperature	r in the second s	r in the second se
Which of the following substance have negative susceptibility	paramagnetic	ferromagnetic	diamagnetic	ceramic	diamagnetic
Materials which can store electrical energy are called.	magnetic materials	semi conductors	dielectric materials	super conductors	magnetic materials
The critical temperature above which the ferromagnetic materials loose	hysterisis	Curie point	transition temperature	standard temperature	Curie point
their magnetic property is known as		p			F
The diamagnetic substance have	positive susceptibility	negative susceptibility	zero susceptibility	constant susceptibility	negative susceptibility
Permanent magnets are made of	soft magnetic materials	hard magnetic materials	semi conductors	super conductors	hard magnetic materials
Materials, which provide a path to the magnetic flux, are classified as	insulating materials	semi conducting materials	magnetic materials	super conductors	magnetic materials
Dielectric constant of vacuum is	infinity	100	one	zero	one
The relative permeability of a paramagnetic substance is	unity	slightly more than unity	zero	less than unity	slightly more than unity
	Transformer cores	Electrical machinery	High frequency equipment	Light weight permanent	Light weight permanent
Hard ferrites are used for making.		Lieeurour muenmery	ingi nequency equipment	magnets	magnets
Hard magnetic materials are used for making	Permanent magnets	Temporary magnets	Conductors	Insulator	Permanent magnets
Magnetic materials .	provide path to magnetic flux	are good insulators	are semiconductors	conductors	provide path to magnetic flux
In a ferromagnetic material the state of flux density is as follows when	Increased	Decreased	Remains unchanged	Becomes zero	Remains unchanged
external magnetic field is applied to it			gea		geu
Which of the following is ferromagnetic material	Ferroites	Rought iron	ceramics	Insulator	Ferroites
Which of the following is ferromagnetic material	Ferroites	Rought iron	ceramics	Insulator	Ferroites

# CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)

### <u>UNIT-III</u>

### **SYLLABUS**

**Spectroscopy**: Absorption spectra- Fundamental concepts of electromagnetic spectrum- The various regions of the spectrum and the relative energies of the radiation in each region-Type of changes induced by the interaction of the radiation with matter. Theory of rotation spectra – Diatomic molecule as rigid rotor and non rigid rotor - Intensities of spectral lines.

Theories of IR spectra – simple harmonic oscillator, model anharmonic oscillator, model of diatomic molecules information on molecular constitution from IR spectra; Application of IR spectra.

### Unit-III

### The Electromagnetic Spectrum

The electromagnetic spectrum is a continuum of all electromagnetic waves arranged according to frequency and wavelength. The sun, earth, and other bodies radiate electromagnetic energy of varying wavelengths. Electromagnetic energy passes through space at the speed of light in the form of sinusoidal waves. The wavelength is the distance from wavecrest to wavecrest.



Light is a particular type of electromagnetic radiation that can be seen and sensed by the human eye, but this energy exists at a wide range of wavelengths. The micron is the basic unit for

# CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)

measuring the wavelength of electomagnetic waves. The spectrum of waves is divided into sections based on wavelength. The shortest waves are gamma rays, which have wavelengths of 10e<sup>-6</sup> microns or less. The longest waves are radio waves, which have wavelengths of many kilometers. The range of visible consists of the narrow portion of the spectrum, from 0.4 microns to 0.7 microns.



### **Electromagnetic radiation.**

Light waves and other types of energy that radiate (travel out) from where they're produced are called **electromagnetic radiation**. Our eyes can see only a limited part of the electromagnetic spectrum—the colorful rainbow we see on sunny-rainy days, which is an *incredibly tiny* part of all the electromagnetic radiation that zaps through our world. We call the energy we can see **visible light** and, like radio waves, microwaves, and all the rest, it's made up of **electromagnetic waves**. The light we can see stretches in a spectrum from red (the lowest frequency and longest wavelength of light our eyes can register) through orange, yellow, green, blue, and indigo to violet (the highest frequency and shortest wavelength we can see).

CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)

# Magnetic vibration Megnetic vibration Electrical vibration Waves move together at speed of light

### Kinds of energy make up the electromagnetic spectrum.

- **Radio waves**: If our eyes could see <u>radio</u> waves, we could (in theory) watch <u>TV</u>programs . Typical size: 30cm–500m. Radio waves cover a huge band of frequencies, and their wavelengths vary from tens of centimeters for high-frequency waves to hundreds of meters (the length of an athletics track) for lower-frequency ones. That's simply because any electromagnetic wave longer than a microwave is called a radio wave.
- Microwaves: Obviously used for cooking in <u>microwave ovens</u>, but also for transmitting information in <u>radar</u> equipment. Microwaves are like short-wavelength radio waves. Typical size: 15cm (the length of a pencil).
- **Infrared**: Just beyond the reddest light we can see, with a slightly shorter frequency, there's a kind of invisible "hot light" called**infrared**. Although we can't see it, we can feel it warming our skin when it hits our face—it's what we think of as radiated <u>heat</u>. If, like rattlesnakes, we could see infrared radiation, it would be a bit like having <u>night-vision</u> lenses built into our heads. Typical size: 0.01mm (the length of a cell).
- Visible light: The light we can actually see is just a tiny slice in the middle of the spectrum.
- Ultraviolet: This is a kind of blue-ish light just beyond the highest-frequency violet light our eyes can detect. The Sun transmits powerful ultraviolet radiation that we can't see: that's why you can get sunburned even when you're <u>swimming</u> in the sea or on cloudy

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# CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)

days—and why <u>sunscreen</u> is so important. Typical size: 500 nanometers (the width of a typical bacteria).

- **X rays**: A very useful type of high-energy wave widely used in medicine and security. Find out more in our main article on <u>X rays</u>. Typical size: 0.1 nanometers (the width of an atom).
- Gamma rays: These are the most energetic and dangerous form of electromagnetic waves. Gamma rays are a type of harmful radiation. Typical size: 0.000001 nanometers (the width of an atomic nucleus).



All the different kinds of electromagnetic radiation are essentially the same "stuff" as light: they're forms of energy that travel in straight lines, at the speed of light (300,000 km or 186,000 miles per second), when <u>electrical</u> and <u>magnetic</u> vibrations wiggle from side to side. Together, these forms of energy as the **electromagnetic spectrum**.

James Clerk Maxwell (1831–1879) was able to come up with a single theory that explained both electricity and magnetism. He realized that electromagnetism could travel in the form of waves, at the speed of light, and concluded that light itself had to be a kind of electromagnetic wave. About a decade after Maxwell's death, a brilliant German physicist named Heinrich Hertz (1857–1894) became the first person to produce electromagnetic waves in a laboratory. That piece of

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# CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)

work led to the development of <u>radio</u>, <u>television</u>, and—much more recently—things like <u>wireless</u> Internet.

If we want to "see" beyond the electromagnetic limits of our own eyes, we can use telescopes "tuned" to higher or lower wavelengths. Astronomers use all kinds of telescopes—some on Earth, some in space—to glean information about distant objects from the electromagnetic radiation they give off.

### **ELECTROMAGNETIC RADIATION & ELECTROMAGNETIC SPECTRUM**

The word light usually makes one think of the colors of the rainbow or light from the Sun or a lamp. This light, however, is only one type of electromagnetic radiation. Electromagnetic radiation comes in a range of energies, known as the electromagnetic spectrum. The spectrum consists of radiation such as gamma rays, x-rays, ultraviolet, visible, infrared and radio.



Electromagnetic radiation travels in waves, just like waves in an ocean. The energy of the radiation depends on the distance between the crests (the highest points) of the waves, or the wavelength. In general the smaller the wavelength, the higher the energy of the radiation. Gamma rays have wavelengths less than ten trillionths of a meter which is about the size of the nucleus of an atom. This means that gamma rays have very high-energy. Radio waves, on the other hand, have wavelengths that range from less than one centimeter to greater than 100 meters (this is bigger than the size of a football field). The energy of radio waves is much lower than the energy of other types of electromagnetic radiation. The only type of light detectable by the

# CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)

human eye is visible light. It has wavelengths about the size of a bacteria cell, and its energies fall between those of radio waves and gamma rays.

### Moment of Inertia of a Diatomic Molecule

In stable equilibrium position, the two atoms in a diatomic molecule are separated by a certain distance  $r_0$ . This distance is called intermolecular distance or bond length.

Let us imagine the diatomic molecule as a system of two tiny spheres at either end of a thin weightless rod.

Let C be the centre of mass of the molecule. Let  $r_1$  and  $r_2$  be the distances of the two atoms from the centre of mass C of the molecule.



Now,  $r_1 + r_2 = r_0$  ------ (1)

and  $m_1r_1 = m_2r_2$  ----- (2)

where  $m_1$  and  $m_2$  are the masses of the two atoms.

From equation (1)

 $\mathbf{r}_2 = \mathbf{r}_0 - \mathbf{r}_1$ 

From equation (2)

 $m_1r_1 = m_2 (r_0 - r_1) \text{ or } m_1r_1 = m_2r_0 - m_2r_1$ 

$$r_1(m_1 + m_2) = m_2 r_0 \text{ or } r_1 = \frac{m_2}{m_1 + m_2} r_0$$

Similarly 
$$r_2 = \frac{m_1}{m_1 + m_2} r_0$$

Let I be the moment of inertia of the diatomic molecule about an axis passing through the centre of mass of the molecule and perpendicular to bond length.

Then,  $I = m_1 r_1^2 + m_2 r_2^2$ 

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# CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)

or I = 
$$m_1 \left[ \frac{m_2}{m_1 + m_2} r_0 \right]^2 + m_2 \left[ \frac{m_1}{m_1 + m_2} r_0 \right]^2$$
  
or I =  $\frac{m_1 m_2^2}{(m_1 + m_2)^2} r_0^2 + \frac{m_2 m_1^2}{(m_1 + m_2)^2} r_0^2$   
or I =  $\frac{m_1 m_2 (m_2 + m_1)}{(m_1 + m_2)^2} r_0^2$   
or I =  $\frac{m_1 m_2}{m_1 + m_2} r_0^2$   
But  $\frac{m_1 m_2}{m_1 + m_2} = \mu$  (reduced mass of molecule)  
 $\therefore$  I =  $\mu r_0^2$ 

Therefore, moment of inertia of a diatomic molecule about an axis passing through the centre of the diatomic molecule and perpendicular to bond length, is the product of reduced mass of the molecule and the square of bond length.

### The Rigid Rotor

The rigid rotor is a simple model of a rotating diatomic molecule. We consider the diatomic to consist of two point masses at a fixed internuclear distance. We then reduce the model to a one-dimensional system by considering the rigid rotor to have one mass fixed at the origin, which is

orbited by the reduced mass  $\mu$ , at a distance  $\underline{T}$ . The Schrödinger equation is

$$-\frac{\hbar^2}{2I} \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \psi(r) = E\psi(r) \tag{1}$$

After a little effort, the eigenfunctions can be shown to be the spherical harmonics , defined by

$$Y_J^M(\theta,\phi) = \left[\frac{(2J+1)}{4\pi} \frac{(J-|M|)!}{(J+|M|)!}\right]^{1/2} P_J^{|M|}(\cos\theta) e^{iM\phi}$$
(2)

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# CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)

# $P_J^{|M|}(x)$

where

are the associated Legendre functions. The eigenvalues are simply

$$E_J = \frac{\hbar^2}{2I}J(J+1) \tag{3}$$

Each energy level is -fold degenerate in M, since M can have  $-J, -J+1, \ldots, J-1, J$  values

### Non rigid rotor:

We have assumed so far that the bond length remains fixed during rotation of the molecule - this is the rigid rotor model. However, as the molecule rotates the atoms are subject to **centrifugal forces** which stretch the bonds - this is the non-rigid rotor model.

Hooke's law states for an elastic bond:

 $F = -k(r-r_{eq}) \qquad k = 4\pi^2 \omega^2 c^2 m$ 

- F = restoring force (N)
- $r = bond length; r_{eq} = equilibrium bond length (m)$
- $k = force constant (Nm^{-1})$
- c = vibrational frequency (cm<sup>-1</sup>)
- m = reduced mass (kg)

Non-rigid rotor model for diatomic molecules:

$$\epsilon_J = BJ(J+1) - DJ^2(J+1)^2$$
  
 $D = h^3 / 32 \pi^4 I^2 R^2 kc$ 

The first term is the rigid rotor model, and the second term is a correction for the centrifugal distortion. It is important to consider this for high values of J.

Centrifugal distortion leads to lowering of the given energy level (at high J). Consequently, spectral lines cluster together at high J and are no longer equally spaced.

# CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)

When greater accuracy is desired, the departure of the molecular rotational spectrum from that of the <u>rigid rotor</u> model can be described in terms of centrifugal distortion and the vibration-rotation interaction. To second order in the relevant quantum numbers, the rotation can be described by the expression



### The Harmonic Oscillator

V(x)

Now consider a particle subject to a restoring force , as might arise for a massspring system obeying Hooke's Law. The potential is then

$$\frac{-\int_{-\infty}^{\infty}(-kx)dx}{V_0 + \frac{1}{2}kx^2} \tag{1}$$

If we choose the energy scale such that  $V_0 = 0$  then  $V(x) = (1/2)kx^2$ . This potential is also appropriate for describing the interaction of two masses connected by an ideal spring. In this case, we let  $\underline{x}$  be the distance between the masses, and for the mass  $\underline{m}$  we substitute the

reduced mass  $\int$ . Thus the harmonic oscillator is the simplest model for the vibrational motion of the atoms in a diatomic molecule, if we consider the two atoms as point masses and the bond between them as a spring. The one-dimensional Schrödinger equation becomes

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# CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x)$$
(2)

After some effort, the eigenfunctions are

$$\psi_n(x) = N_n H_n(\alpha^{1/2} x) e^{-\alpha x^2/2} \qquad n = 0, 1, 2, \dots$$
(120)

(3)

where  $H_n$  is the Hermite polynomial of degree  $\underline{n}$ , and  $\underline{\alpha}$  and  $N_n$  are defined by

$$lpha = \sqrt{rac{k\mu}{\hbar^2}} \qquad \qquad N_n = rac{1}{\sqrt{2^n n!}} \left(rac{lpha}{\pi}
ight)^{1/4}$$

The eigenvalues are

$$E_n = \hbar \omega \left( n + 1/2 \right) \tag{4}$$
with  $\frac{\omega = \sqrt{k/\mu}}{2}$ 

### **IR Spectroscopy**

According to wave theory, light travels in the form of waves and radiant energy is emitted by fluctuation of electric charge and magnetic field. Just like light, there are various forms of electromagnetic radiations. These are radiations produced by the oscillation of electric charge and magnetic field residing on the atom.

These radiations are associated with a certain value of wave length and wave number. All types of radiations can travel in vacuum with same velocity. The sequence of all types of electromagnetic radiations in order of their increasing wavelength or decreasing frequencies is known as complete electromagnetic spectrum.

CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)



The interaction between matter and electromagnetic radiation is defined as spectroscopy. When a light radiation passed through a sample of organic compound, some of the wavelengths are absorbed. A molecule can absorbed a certain frequency of light and electrons get excited. The absorption of energy changes the vibration, rotational and electronic levels of molecule. The amount of wavelength absorbed is measured by using spectrometer.

### **Principle of IR Spectroscopy**

Infra-red spectroscopy is an important spectroscopy which gives almost complete information about the structure of a compound. The infra-red spectrum is containing a large number of absorption bands which provides much information about the molecule's structure.

The infra-red region extends from 2.5 $\lambda\lambda$  to 50 $\lambda\lambda$ , out of this; from 0.8 $\lambda\lambda$  to 2.5 $\lambda\lambda$  is known as near infrared, from 15 $\lambda\lambda$  to 200 $\lambda\lambda$  is called as far infra red region.

Region	Wavelength range (λλm)	Wave number range (cm <sup>-1</sup> )
Near	0.78 - 2.5	12800 - 4000
Middle	2.5 - 50	4000 - 200
Far	50 - 1000	200 - 10

Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 11/20

# CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)

The absorption of infrared radiations can be expresses either in terms of wavelength or wave number.

Wave length = 1/wave length (cm)

The intensity of bands observed in IR spectrum is expressed in terms of transmittance (T) or absorbance (A).

### $A = \log_{10} (1/T)$

Because of absorption of infra-red radiation, molecules become excited and move to lower to higher vibrational level. Each vibrational level is associated with a number of spaced rotational levels. Hence the absorption of infra-red caused to effect vibrational as well as rotational level and also called as vibrational- rotational spectra.

he absorption of infrared radiations is possible by only those bonds of molecule which can show a change in dipole moment by the absorption of radiations. Such types of vibrational transitions which involve the change in dipole moment are known as infra-red transitions.

However those vibrational transitions which are not accompanied by the change in dipole moment are not directly observed and called as infra-red inactive transition. For example; the vibrational transitions of C=O, O-H, N-H etc. bands are accompanied by the change in dipole moment, hence absorbed strongly in IR region.

While some other transitions like C-C bond in symmetrical alkene and alkyne are IR inactive transitions. Hence some of the fundamental vibrations are infra-red active and some are not. It governed by the selection rule.

- 1. If a molecule has a center of symmetry, then the vibrations are Centro symmetric and are inactive in the infra-red region but active in Raman, known as active vibrations.
- 2. The vibrations which are not Centro symmetric are active in infra-red region but inactive in Raman, called as forbidden vibrations.
- 3. Since the absorption of infra-red region is quantized, a molecule of the organic compound will show a number of peaks in the infrared region.

CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)



When light beam passed through the substance, it absorbs some of light with frequency v. Due to this absorption, the energy of molecule increases and can be shown as

 $\mathbf{E} = \mathbf{h}\lambda\lambda$ 

Where

If the falling radiations are belong to mid-infrared region than the energy would be just equivalent to the molecular vibration energy level. Hence molecules in the ground state of vibration absorb this radiation and transit to the first excitation state of vibration. However, it is not necessary that absorption takes place with the given energy of mid-infra red region. There are two important selection principles.

- 1. Only those transitions are permitted in which the vibrational quantum number (v) changes by +/-1. The transitions correspond this change are known as fundamental vibration tones. However vibrations of +/-2, +/-3, etc. equivalent to harmonic tones are known as forbidden transitions, which are not permitted.
- 2. The absorption of radiation can be possible only when the dipole moment of the whole molecule changes due to certain molecular vibrations.

### **Applications of IR Spectroscopy**

The Infra-red spectroscopy can be employed to establish the identity of two compounds or to determine the structure of a new compound. This technique is quite useful to predict the presence of certain functional groups which absorb at definite frequencies. It is widely used in different industries like organic synthesis, agriculture soil analysis and biochemical industries for the

h = Plank's constant

# CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)

analysis of complex biological molecules like proteins, nucleic acid and lipids.

The main benefit of this technique is that some of the applications of IR spectroscopy are as follows.

### Identification of functional group and structure elucidation

- 1. The identity of an organic compound can be established by using its finger print region (1400-1900 cm<sup>-1</sup>).
- 2. The identity of an organic compound is confirmed of its finger print region exactly matches with the known spectrum of that compound.
- 3. As compounds contain same functional group may have similar absorptions above 1500 cm-1 but they differ considerably in finger print region.
- 4. Each functional group absorbs a certain frequency of radiation and show corresponding peak. Hence the position of peak gives the information regarding the presence of certain functional group.

### Identification of structure of substances

- 1. Infra red spectroscopy is used to establish the structure of an unknown compound.
- 2. All functional groups present in molecule absorbed at their characteristic wave number and the shift due to environment effect can be easily observed in spectrum.
- 3. Form the data available, the whole structure of molecule can be predicated.
- 4. If the IR spectrum of two compounds is exactly same, it shows that they are identical compounds. Hence must be samples of the same substances.
- 5. IR spectrum cannot identify the presence of Enantiomers as they show similar IR spectrum.

### Study of the progress of a chemical reaction

- 1. Infra red spectroscopy is quite useful for studying the rate and progress of a chemical reaction.
- 2. For example the reduction of ketone to secondary alcohol can be detected easily. As the absorption band of ketone is observed at about 1710 cm-1.
- 3. With the progress of reaction the band of >C=O group diminished and band of -O-H group at 3300 cm<sup>-1</sup> appears.
- 4. The progress of reaction can be determined by using the rate of disappearance of a certain absorption band of the reactant molecule and the rate of appearance of the absorption band of the product group.
- 5. IR spectroscopy is also used to predict the products formed in photochemical reaction.

Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 14/20

CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)

#### **Detection of impurities Infra-red**

- 1. Infra red spectroscopy is also useful in the detection of the impurity in a compound by comparing its spectrum with the spectrum of the authentic sample of the compound.
- 2. A pure sample always consists of sharp peaks and bands while the impure sample will have poor bands with some additional bands.

#### **Quantitative analysis**

The quantitative analysis of an organic mixture can be done by measuring the intensities of the absorption bands of each component and by knowing the optical density of the absorption bands for the pure substance.

For example, Xylene exits as mixture of three isomers, ortho, para and meta. The separation of mixture is not easy but percentage composition can be determined by using IR spectrum as all three isomers show different absorption bands.

- ortho-Xylene at 740 cm<sup>-1</sup>
- meta-Xylene at 880 cm<sup>-1</sup>
- para-Xylene at 830 cm<sup>-1</sup>

The presence of certain bands decide the isomer of Xylene and the optical density values gives information about the percentage composition of each isomer in given sample.

The presence of certain bands decide the isomer of Xylene and the optical density values gives information about the percentage composition of each isomer in given sample.



Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 15/20

# CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)



### Distinction between two type of hydrogen bonding

Infra red spectroscopy can be detect the presence of H-bonding as well as the type of hydrogen bonding; Intermolecular or Intramolecular. The molecules of the substance which contain asctive hydrogen groups like -OH, -COOH etc. undergo self association. For example, when hydroxy groups get associate like in solid or liquid state, the absorption band shifted towards lower frequency. But when such substances dissolved in non-polar solvents, the aggregates get

Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 16/20

# CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)

dissociate to monomers and the absorption bands shifted towards high frequency and bands become sharper. The formation of intramolecular hydrogen bonding does not show any shift in absorption on dilation which intermolecular does.

### Study of Keto-enol isomerism

The infra-red spectrum of diketons or ketoesters which can show keto-enol isomerism also known as tautomerism due to C=O, C=C and O-H bonds.

For example; ethyl acetoacetic ester exits in keto-enol form. The lowering in the absorption band of >C=O (straching) in the enolic form is because of intra-molecular hydrogen bonding which established by resonance.

#### keto enol tautomerism in acetoacetic ester



### Study of complex formation Infra red

Infra red spectroscopy is useful in prediction of structure of complex molecules like penicillin . There are two possibilities for penicillin structure;  $\alpha$ -lactum and Oxazolone. Infra red absorption bands conform the penicillin structure as  $\alpha$ -lactum and ruled out Oxazolone structure. As  $\alpha$ -lactum and penicillium both show strong band at 1770 cm<sup>-1</sup>.



### **Forensic Analysis and Crime Investigation**

- 1. Infrared spectroscopy is useful in prediction of unknown compound and presence of certain functional groups.
- 2. Hence this method is quite beneficial in forensic analysis. Ur technique plays an important role in crime investigation by locating the criminal offenders.

### **Conformation analysis**

Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 17/20

# CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)

IR technique is useful in determination of relative stability of various conformations of cyclic compounds. For example, cyclohexane can exhibit in chair and boat conformation. There are 18 infra-red active C-C and CH<sub>2</sub> rocking and twisting vibrations for boat conformation while chair conformation show only 5 absorption bands in the region of 1350-700 cm<sup>-1</sup>. This shows the greater stability of chair conformation over boat form.



Similarly IR spectroscopy helps in detection of Gauche and staggered conformations. Like both conformations of 1, 2-Dichloroethane show two bands at 1235 cm<sup>-1</sup> and 1291 cm<sup>-1</sup> in IR spectrum. Due to more stability, the staggered form predominant at lower temperature whereas gauche form dominates at high temperature.



### **Geometrical Isomerism**

Only those vibrations are IR active which involves the change in dipole moment of the molecule and the intensity of absorption bands depends upon the change in dipole moment of molecule. Since there is a change in dipole moment in case of cis-isomer whereas trans-isomers are nonpolar in nature, therefore both geometrical isomers show different bands in IR spectrum.

Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 18/20

CLASS : IIIB.Sc CHEMISTRY COURSENAME : PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE :15CHU602 BATCH-2015-2018

# UNIT: III (SPECTROSCOPY)

### **POSSIBLE QUESTIONS**

### **UNIT III**

### PART-A (One Mark)

### (Multiple Choice Questions)

1.	Unit of frequency is
	a. Hertz b. Nanometers c. $cm^{-1}$ d. Km/sec
2.	In the selection rules for rotational spectra $\Delta J$ = -1 corresponds to
	b. Absorption b. <b>Emission</b> c. Positive intensity d. Negative intensity
3.	Pure rotational spectrum is obtained for those molecules having
	a. Permanent dipole moment b. Magnetic susceptibility
	c. Rest mass d. Zero point energy
4.	Rotational spectra is observed in the area
	a. Micro-wave region b. Infra red region
	c. Ultraviolet region d. Radio wave region
5.	Which is having greater reduced mass
	a. C-F b. C-Cl c. <b>C-Br</b> d. C-H
6.	Which molecules does not exhibit Pure rotational spectrum
	a. $N_2 O$ b. <b>Carbon dioxide</b> c. NO d. water
7.	. The restrictions applied on the transition between energy levels is
	a. Selection rules b. Allowed transition
	c. Forbidden transition d. Band system
8.	A shift of the maximum absorption to shorter wavelength is called
	a. Bathochromic shift b. <b>Hypsochromic shift</b>
	c. Hyperchromic shift d. Hypo chromic shift
9.	The absorption frequency for the stretching frequency for C-O bond (cm <sup>-1</sup> )
	a. 2850-2960b. 1350-1470c. 1000-1300d. 540-785
10.	IR spectra cannot be recorded for
	a. H-Cl b. H-Br c. Methyl bromide d. <b>Oxygen</b>
11.	The absorption frequency of 1600 cm <sup>-1</sup> shows the presence of
	a. Carbonyl group b. <b>C=C group</b> c. O-H group d. Nitrile group
CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602BATCH-2015-2018UNIT: III (SPECTROSCOPY)

### **PART-B** (Eight Mark )

### **EITHER OR TYPE QUESTIONS**

- 1. Discuss about the vibrational energy levels in a simple harmonic oscillator. What is meant by zero point energy?
- 2. Using the study of IR spectrum explain calculation of moment of inertia and bond length
- 3. Using the study of IR spectrum explain calculation of force constant.
- 4. Name the different types of molecular spectra. Explain each of them briefly in which

region of the electromagnetic spectrum are this obtained.

- 5. What do you understand by degrees of freedom of motion of a molecule. Briefly explain the different types of degrees pf freedom possessed by linear and non linear molecules.
- 6. Briefly explain the term absorption and emission spectroscopy. Why absorption spectroscopy is preferred. Give its experimental set-up.
- 7. Explain in detail about the different types of molecular spectra
- 8. How IR spectroscopy is used to find the following molecules. A. alcohols b. carboxylic acids c. amines d. aldehydes
- 9. What are the basic components of a spectrometer. Show them diagrammatically
- 10. What are the applications of IR spectroscopy

Subject : Physical methods and Chemical structures
Subject Code : 15CHU602
Class : III B.Sc Chemistry
Batch : 2015-2018 Batch
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### UNIT-III

### Multiple Choice Questions(Each Carry One Mark)

Questions	Option 1	Option 2	Option 3	Option 4	Answer
The branch of science associated with the interaction of radiations of different	spectroscopy	Magnetic susceptibility	Dipole moment	Current Electricity	spectroscopy
wavelengths with matter					
The number of successive crests which pass through a stationary point in one second is called	Wave number	Frequency	wavelength	Debye	Frequency
The distance between successive crests	Wave number	Frequency	wavelength	Debye	wavelength
Reciprocal of wavelength is called	Wave number	Frequency	wavelet	Debye	wavenumber
Unit of frequency is	Hertz	nanometers	cm <sup>-1</sup>	Kilometres/sec	Hertz
Unit of wavelength is	Hertz	nanometers	cm <sup>-1</sup>	Kilometres/sec	nanometers
Unit of wave number	Hertz	nanometers	cm <sup>-1</sup>	Kilometres/sec	cm <sup>-1</sup>
If the energy absorbed by the molecule is such that it can cause transition only from one rotational level to another within the same vibrational level. It is called	Rotational spectra	Vibrational-rotational spectra	Raman spectra	Electronic band spectra	Rotational spectra
Rotational spectra is observed in the area	Micro-wave region	Infra red region	Ultraviolet region	Radio wave region	Microwave region
If the incident energy is sufficiently large so that it can cause a transition from different vibrational levels within an electronic level	Rotational spectra	Vibrational-rotational spectra	Raman spectra	Electronic band spectra	Rotational spectra
Vibrationall spectra is observed in the area	Micro-wave region	Infra red region	Ultraviolet region	Radio wave region	Infra red region
If the incident energy is sufficiently large so that it can cause a transition between different electronic levels	Rotational spectra	Vibrational-rotational spectra	Raman spectra	Electronic band spectra	Electronic band spectra
Electronic spectra is observed in the area	Micro-wave region	Infra red region	Ultraviolet region	Radio wave region	Infra red region
A type of spectrum based on the scattering of light	Rotational spectra	Vibrational-rotational spectra	Raman spectra	Electronic band spectra	Raman spectra
Spectrum arises from the transitions between the nuclear spin energy levels of the molecule	Rotational spectra	Vibrational-rotational spectra	Nuclear magnetic spectra	Electronic band spectra	Nuclear magnetic spectra
Raman spectra is observed in the area	Micro-wave region	Infra red region	Ultraviolet region	Visible region	visible region
NMR spectra is observed in the area	Micro-wave region	Infra red region	Ultraviolet region	Radio wave region	Radio wave visible region
Spectrum arises from the transitions between the electron spin energy levels of the molecule	Rotational spectra	Vibrational-rotational spectra	Nuclear magnetic spectra	Electron spin spectra	Electron spin spectra
ESR spectra is observed in the area	Micro-wave region	Infra red region	Ultraviolet region	Radio wave region	Micro-wave region
The restrictions applied on the transition between energy levels is	Selection rules	Allowed transition	Forbidden transition	Band system	Selection rules
Transition of electron can take place in a	Allowed transition	Forbidden transition	NMR spectra	IR spectra	Allowed transition
Transition of electron from one electroic level to the other is not allowed in a	Allowed transition	Forbidden transition	NMR spectra	IR spectra	Forbidden transition
In the selection rules for rotational spectra $\Delta J = +1$ corresponds to	absorption	Emission	Positive intensity	Negative intensity	absorption
A molecule can be excited to only the next higher rotational level by	Absorption of energy	Release of energy	The electric current	Applying magnetic field	Absorption of energy
In the selection rules for rotational spectra $\Delta J$ = -1 corresponds to	absorption	Emission	Positive intensity	Negative intensity	emission
The IR spectra of a compound helps in	Providing the identity of a compound	Finding functional groups	Determining total structure of a molecule	To determine the dipole moment	Finding functional groups
The Raman spectra can tell us whether	The molecule is linear or not linear	The molecule is dextrorotatory	The molecule is levorotatory or not	Chiral or not	The molecule is linear or not linear
The Raman spectra can tell us whether	The molecule is symmetrical or assymetrical	The molecule is dextrorotatory	The molecule is levorotatory or not	Chiral or not	The molecule is symmetrical or assymetrical
TheIR spectra can tell us whether	The molecule is linear or not linear	The molecule is dextrorotatory	The molecule is levorotatory or not	Chiral or not	The molecule is linear or not linear
The IR spectra can tell us whether	The molecule is symmetrical or assymetrical	The molecule is dextrorotatory	The molecule is levorotatory or not	Chiral or not	The molecule is symmetrical or assymetrical
In the Raman spectrum, the middle line is called	Raman line	Rayleigh line	Functional group line	Broglie line	Raman line
The rotational spectra involve	A very high energy changes	Small enegy changes	No energy change	Zero point energy	Small enegy changes
The electronic spectra consists of	A larger number of absorption bands	A large number of closely packed lines	A large number of peaks	Close bands	A large number of closely packed lines
The electromagnetic radiation of higher wavelength has	Higher energy	Lower energy	Intermediate energy	Zero energy	Lower energy
The vibrational frequency is smaller in the excited state than in the ground state of	It is proportional to the force	Depends upon the rest mass	It depends on the zero point	It depends on the wavelength	It is proportional to the force constant
the molecule because	constant		energy		
The vibrational frequency is smaller in the excited state than in the ground state of	The force constant is smaller in the	Depends upon the rest mass	It depends on the zero point	It depends on the wavelength	The force constant is smaller in the
the molecule because	excited state		energy		excited state

The rotational constant B of a diatomic molecule depends upon the electronic	B depends on the moment of inertia	B depends upon dipole moment	B depends upon magnetic	B depends upon intensity of magnetiation	depends on the moment of inertia
state of the molecule, because			susceptibility		
The rotational constant B of a diatomic molecule depends upon the electronic state of the molecule, because	B depends on the inter nuclear distance r	B depends upon dipole moment	B depends upon magnetic susceptibility	B depends upon intensity of magnetiation	depends on the inter nuclear distance r
The rotational constant B of a diatomic molecule depends upon the electronic state of the molecule, because	The inter nuclear distance r is different for different electronic states of a molecule	B depends upon dipole moment	B depends upon magnetic susceptibility	B depends upon intensity of magnetiation	The inter nuclear distance r is different for different electronic states of a molecule
The vibration-rotation spectrum of HCl, each individual line found to consists of doublets because	Hyperfine splitting	Presence of two isotopes of chlorine	Chemical coupling	Different coupling constants	Presence of two isotopes of chlorine
The vibration-rotation spectrum of HCl, each individual line found to consists of doublets because	Hyperfine splitting	The two isotopes of chlorine results in different moment of inertia	Chemical coupling	Different coupling constants	The two isotopes of chlorine results in different moment of inertia
Which is having greater reduced mass	C-F	C-Cl	C-Br	С-Н	C-Br
Which is having greater absorption frequency	C-F	C-Cl	C-Br	С-Н	C-H
Which is having greater force constant	C-C	C=C	C to C triple bond	C-H	C to C triple bond
Pure rotational spectrum is obtained for those molecules having	Permanent dipole moment	Magnetic susceptibility	Rest mass	Zero point energy	Permanent dipole moment
Which is having greater absorption frequency	C-C	C=C	C to C triple bond	C-H	C to C triple bond
Pure rotational spectrum is obtained for	Non-polar molecules	Polar molecules	Diamagnetic molecules	Paramagnetic molecules	Polar molecules
Which molecules exhibit Pure rotational spectrum	Carbon dioxide	benzene	Carbon tetrachloride	water	Water
Which molecules exhibit Pure rotational spectrum	Carbon dioxide	benzene	Carbon tetrachloride	NO	NO
Which molecules exhibit Pure rotational spectrum	Carbon dioxide	benzene	Carbon tetrachloride	N <sub>2</sub> O	N <sub>2</sub> O
Which molecules does not exhibit Pure rotational spectrum	N <sub>2</sub> O	benzene	NO	water	benzene
Which molecules does not exhibit Pure rotational spectrum	N <sub>2</sub> O	Carbon dioxide	NO	water	Carbon dioxide
Which molecules does not exhibit Pure rotational spectrum	N <sub>2</sub> O	Carbon tetra chloride	NO	water	Carbon tetrachloride
Which molecules does not exhibit Pure rotational spectrum	Non-polar molecules	Polar molecules	Water	NO	Non-Polar molecules
The total degree of freedom in acetylene molecule is	3	4	12	7	12
The total degree of freedom in water molecule is	3	9	12	6	9
The total translational degree of freedom in acetylene molecule is	3	4	12	7	3
The total translational degree of freedom in water molecule is	3	9	12	6	3
The total rotational degree of freedom in acetylene molecule is	3	2	12	7	2
The total vibrational degree of freedom in acetylene molecule is	3	4	12	7	7

CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602UNIT: IV (RAMAN SPECTRA AND NMR SPECTROSCOPY)BATCH-2015-2018

### UNIT-IV

### **SYLLABUS**

Theory of Raman spectra – Comparison of IR and Raman spectra - Theory of UV and visible spectra–Franck-Condon principle-Application of UV spectra to simple molecules.

NMR spectra – Basic principles – Chemical shift – Application of NMR spectra to simple molecules. High resolution Raman spectra (details not expected). Examples-Ethanol and o, m & p-xylenes.

### RAMAN SPECTRA AND NMR SPECTROSCOPY



### Raman spectroscopy

Energy-level diagram showing the states involved in Raman spectra.

**Raman spectroscopy** is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system.<sup>[1]</sup> Raman spectroscopy is commonly used in chemistry to provide a fingerprint by which molecules can be identified.

It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with

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molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system. Infrared spectroscopy yields similar, but complementary, information.

Typically, a sample is illuminated with a laser beam. Electromagnetic radiation from the illuminated spot is collected with alens and sent through a monochromator. Elastic scattered radiation at the wavelength corresponding to the laser line (Rayleigh scattering) is filtered out by either a notch filter, edge pass filter, or a band pass filter, while the rest of the collected light is dispersed onto a detector.

Spontaneous Raman scattering is typically very weak, and as a result the main difficulty of Raman spectroscopy is separating the weak inelastically scattered light from the intense Rayleigh scattered laser light. Historically, Ramanspectrometers used holographic gratings and multiple dispersion stages to achieve a high degree of laser rejection. In the past, photomultipliers were the detectors of choice for dispersive Raman setups, which resulted in long acquisition times. However, modern instrumentation almost universally employs notch or edge filters for laser rejection and spectrographs either axial transmissive (AT), Czerny–Turner (CT) monochromator, or FT (Fourier transform spectroscopy based), and CCDdetectors.

There are a number of advanced types of Raman spectroscopy, including surfaceenhanced Raman, resonance Raman, tip-enhanced Raman, polarized Raman, stimulated Raman (analogous tostimulated emission), transmission Raman, spatially offset Raman, and hyper Raman.

### **Theoretical basis**

The Raman effect occurs when electromagnetic radiation impinges on a molecule and interacts with the polarizable electron density and the bonds of the molecule in the phase (solid, liquid or gaseous) and environment in which the molecule finds itself. For the spontaneous Raman effect, which is a form of inelastic light scattering, a photon (electromagnetic radiation of

a specific wavelength) excites (interacts with) the molecule in either the ground rovibronic state (lowest rotational and vibrational energy level of the ground electronic state) or an excited rovibronic state. This results in the molecule being in a so-called virtual energy state for a short period of time before an inelastically scattered photon results. The resulting inelastically scattered photon which is "emitted"/"scattered" can be of either lower (Stokes) or higher (anti-Stokes) energy than the incoming photon. In Raman scattering the resulting rovibronic state of the molecule is a different rotationalor vibrational state than the one in which the molecule was originally, before interacting with the incoming photon (electromagnetic radiation). The difference in energy between the original rovibronic state and this resulting rovibronic state leads to a shift in the emitted photon's frequency away from the excitation wavelength, the so-called Rayleigh line. The Raman effect is due to inelastic scattering and should not be confused with emission (fluorescence or phosphorescence) where a molecule in an excited electronic state emits a photon of energy and returns to the ground electronic state, in many cases to a vibrationally excited state on the ground electronic state potential energy surface.

S.No.	Raman	IR
1	It is due to the scattering of light by the vibrating molecules	It is the result of absorption of light by vibrating molecules.
2	The vibration is Raman active if it causes a change in polarisability.	Vibration is IR active if there is change in dipole moment.
3	The molecule need not possess a permanent dipole moment	The vibration concerned should have a change in dipole moment due to that vibration
4	Water can be used as a solvent	Water cannot be used due to its intense absorption of IR

### **Differences between IR and Raman methods**

5	Sample preparation is not very elaborate, it can be	Sample preparation is elaborate
	in any state.	Gaseous samples can rarely be used
6	Gives an indication of covalent character in the molecule.	Gives an indication of ionic character in the molecule.
7	Cost of instrumentation is very high	Comparatively inexpensive

### <u>Ultraviolet–Visible Spectroscopy</u>

**Ultraviolet–visible spectroscopy** or **ultraviolet-visible spectrophotometry** (**UV-Vis** or **UV/Vis**) refers to absorption spectroscopy or reflectance spectroscopy in the ultravioletvisible spectral region. This means it uses light in the visible and adjacent (near-UV and nearinfrared [NIR]) ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions.

### Franck-Condon principle



Figure. Franck–Condon principle energy diagram.

Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates. The potential wells are shown favoring transitions between v = 0 and v = 2.

The **Franck–Condon principle** is a rule in spectroscopy and quantum chemistry that explains the intensity of vibronic transitions. Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photonof the appropriate energy. The principle states that during an electronic transition, a change from one vibrational energy level to another will be more likely to happen if the two vibrational wave functions overlap more significantly.

### **Development of the principle**

In a report published in 1926 in Transactions of the Faraday Society, James Franck was concerned with the mechanisms of photon-induced chemical reactions. The presumed mechanism was the excitation of a molecule by a photon, followed by a collision with another molecule during the short period of excitation. The question was whether it was possible for a molecule to break into photoproducts in a single step, the absorption of a photon, and without a collision. In order for a molecule to break apart, it must acquire from the photon a vibrational energy exceeding the dissociation energy, that is, the energy to break a chemical bond. However, as was known at the time, molecules will only absorb energy corresponding to allowed quantum transitions, and there are no vibrational levels above the dissociation energy level of thepotential well. High-energy photon absorption leads to a transition to a higher electronic state instead of dissociation. In examining how much vibrational energy could be enough to immediately break apart the molecule, he drew three diagrams representing the possible changes in binding energy between the lowest electronic state and higher electronic states.

Diagram shows a great weakening of the binding on a transition from the normal state *n* to the excited states *a* and *a'*. Here we have D > D' and D' > D''. At the same time the equilibrium position of the nuclei moves with the excitation to greater values of *r*. If we go from the equilibrium position (the minimum of potential energy) of the *n* curve **vertically** [emphasis added] upwards to the a curves in Diagram I. the particles will have a potential energy greater than D' and will fly apart. In this case we have a very great change in the oscillation energy on excitation by light...

### —James Franck, 1926

James Franck recognized that changes in vibrational levels could be a consequence of the instantaneous nature of excitation to higher electronic energy levels and a new equilibrium position for the nuclear interaction potential. Edward Condon extended this insight beyond photoreactions in a 1926 Physical Review article titled "A Theory of Intensity Distribution in Band Systems". Here he formulates the semiclassical formulation in a manner quite similar to its modern form. The first joint reference to both Franck and Condon in regards to the new principle appears in the same 1926 issue of Physical Review in an article on the band structure of carbon monoxide by Raymond Birge.



Fig. 1. Typical relation of the potential energy curves, illustrating graphical method of finding favored transitions.

**Figure .** Above Figure in Edward Condon's first publication on what is now the Franck–Condon principle [Condon 1926]. Condon chose to superimpose the potential curves to illustrate the method of estimating vibrational transitions.

CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602UNIT: IV (RAMAN SPECTRA AND NMR SPECTROSCOPY)BATCH-2015-2018

### Application of UV spectra

UV/Vis spectroscopy is routinely used in analytical chemistry for of different the quantitative determination analytes, such astransition metal ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied.

- Solutions of transition metal ions can be colored (i.e., absorb visible light) because d electrons within the metal atoms can be excited from one electronic state to another. The colour of metal ion solutions is strongly affected by the presence of other species, such as certain anions or ligands. For instance, the colour of a dilute solution of copper sulfate is a very light blue; adding ammonia intensifies the colour and changes the wavelength of maximum absorption ( $\lambda_{max}$ ).
- Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of theelectromagnetic spectrum. The solvents for these determinations are often water for water-soluble compounds, or ethanol for organic-soluble compounds. (Organic solvents may have significant UV absorption; not all solvents are suitable for use in UV spectroscopy. Ethanol absorbs very weakly at most wavelengths.) Solvent polarity and pH can affect the absorption spectrum of an organic compound. Tyrosine, for example, increases in absorption maxima and molar extinction coefficient when pH increases from 6 to 13 or when solvent polarity decreases.
- While charge transfer complexes also give rise to colours, the colours are often too intense to be used for quantitative measurement.

The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length.<sup>[3]</sup> Thus, for a fixed path length, UV/Vis spectroscopy can be used to determine the concentration of the absorber in a

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solution. It is necessary to know how quickly the absorbance changes with concentration. This can be taken from references (tables of molar extinction coefficients), or more accurately, determined from a calibration curve.

A UV/Vis spectrophotometer may be used as a detector for HPLC. The presence of an analyte gives a response assumed to be proportional to the concentration. For accurate results, the instrument's response to the analyte in the unknown should be compared with the response to a standard; this is very similar to the use of calibration curves. The response (e.g., peak height) for a particular concentration is known as the response factor.

The wavelengths of absorption peaks can be correlated with the types of bonds in a given molecule and are valuable in determining the functional groups within a molecule. TheWoodward-Fieser rules, for instance, are a set of empirical observations used to predict  $\lambda_{max}$ , the wavelength of the most intense UV/Vis absorption, for conjugated organic compounds such as dienes and ketones. The spectrum alone is not, however, a specific test for any given sample. The nature of the solvent, the pH of the solution, temperature, high electrolyte concentrations, and the presence of interfering substances can influence the absorption spectrum. Experimental variations such as the slit width (effective bandwidth) of the spectrophotometer will also alter the spectrum. To apply UV/Vis spectroscopy to analysis, these variables must be controlled or accounted for in order to identify the substances present.<sup>[4]</sup>

UV-Vis spectroscopy is also used in the semiconductor industry to measure the thickness and optical properties of thin films on a wafer. UV-Vis spectrometers are used to measure the reflectance of light, and can be analyzed via the Forouhi-Bloomer dispersion equations to determine the Index of Refraction (n) and the Extinction Coefficient (k) of a given film across the measured spectral range.

To understand why some compounds are colored and others are not, and to determine the relationship of conjugation to color, we must make accurate measurements of light absorption at different wavelengths in and near the visible part of the spectrum. Commercial optical

spectrometers enable such experiments to be conducted with ease, and usually survey both the near ultraviolet and visible portions of the spectrum.

The visible region of the spectrum comprises photon energies of 36 to 72 kcal/mole, and the near ultraviolet region, out to 200 nm, extends this energy range to 143 kcal/mole. Ultraviolet radiation having wavelengths less than 200 nm is difficult to handle, and is seldom used as a routine tool for structural analysis.



"electronic spectroscopy". A diagram showing the various kinds of electronic excitation that may occur in organic molecules is shown on the left. Of the six transitions outlined, only the two lowest energy ones (left-most, colored blue) are achieved by the energies available in the 200 to 800 nm spectrum. As a rule, energetically favored electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and the resulting species is called an **excited state**. For a review of molecular orbitals.

orbital.

is

called

When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The

resulting spectrum is presented as a graph of absorbance (A) versus wavelength, as in the isoprene spectrum shown below. Since isoprene is colorless, it does not absorb in the visible part of the spectrum and this region is not displayed on the graph. **Absorbance** usually ranges from 0 (no absorption) to 2 (99% absorption), and is precisely defined in context with spectrometer operation.

Because the absorbance of a sample will be proportional to the number of absorbing molecules in the spectrometer light beam (e.g. their molar concentration in the sample tube), it is necessary to correct the absorbance value for this and other operational factors if the spectra of different compounds are to be compared in a meaningful way. The corrected absorption value is called "molar absorptivity", and is particularly useful when comparing the spectra of different compounds and determining the relative strength of light absorbing functions (chromophores). **Molar absorptivity** ( $\epsilon$ ) is defined as:

### Molar Absorptivity, $\varepsilon = A / c l$

(where A= absorbance, **c** = sample concentration in moles/liter & **l** = length of light path through the sample in cm.)

If the isoprene spectrum on the right was obtained from a dilute hexane solution ( $c = 4 * 10^{-5}$  moles per liter) in a 1 cm sample cuvette, a simple calculation using the above formula indicates a molar absorptivity of 20,000 at the maximum absorption wavelength. Indeed the entire vertical absorbance scale may be changed to a molar absorptivity scale once this information about the sample is in hand. Clicking on the spectrum will display this change in units.

Chromophore	Example	Excitation	$\lambda_{\max}$ , nm	3	Solvent
C=C	Ethene	$\pi \longrightarrow \pi^*$	171	15,000	hexane
C≡C	1-Hexyne	π> π*	180	10,000	hexane

Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 10/22

CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602UNIT: IV (RAMAN SPECTRA AND NMR SPECTROSCOPY)BATCH-2015-2018

С=О		Ethanal	n -> π*	290	15	hexane
			$\pi \longrightarrow \pi^*$	180	10,000	hexane
N=O		Nitromethane	n —> $\pi^*$	275	17	ethanol
			$\pi \longrightarrow \pi^*$	200	5,000	ethanol
C-X X	K=Br	Methyl bromide	n -> σ*	205	200	hexane
X=I		Methyl Iodide	n -> σ*	255	360	hexane

From the chart above it should be clear that the only molecular moieties likely to absorb light in the 200 to 800 nm region are pi-electron functions and hetero atoms having non-bonding valence-shell electron pairs. Such light absorbing groups are referred to as **chromophores**. A list of some simple chromophores and their light absorption characteristics is provided on the left above. The oxygen non-bonding electrons in alcohols and ethers do not give rise to absorption above 160 nm. Consequently, pure alcohol and ether solvents may be used for spectroscopic studies.

The presence of chromophores in a molecule is best documented by UV-Visible spectroscopy, but the failure of most instruments to provide absorption data for wavelengths below 200 nm makes the detection of isolated chromophores problematic. Fortunately, conjugation generally moves the absorption maxima to longer wavelengths, as in the case of isoprene, so conjugation becomes the major structural feature identified by this technique. Molar absorptivities may be very large for strongly absorbing chromophores (>10,000) and very small if absorption is weak (10 to 100). The magnitude of reflects both the size of the chromophore and the probability that light of a given wavelength will be absorbed when it strikes the chromophore.

### Principles of NMR.

The nuclei of all elements carry a charge. When the spins of the protons and neutrons comprising these nuclei are not paired, the overall spin of the charged nucleus generates a magnetic dipole along the spin axis, and the intrinsic magnitude of this dipole is a fundamental nuclear property called the nuclear magnetic moment,  $\mu$ . The symmetry of the charge distribution in the nucleus is a function of its internal structure and if this is spherical (ie analogous to the symmetry of a 1s hydrogen orbital), it is said to have a corresponding spin angular momentum number of I=1/2, of which examples are <sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N, <sup>19</sup>F, <sup>31</sup>P etc. Nuclei which have a non-spherical charge distribution (analogous to e.g. a hydrogen 3d orbital) have higher spin numbers (eg <sup>10</sup>B, <sup>14</sup>N etc) outside the scope of this particular lecture course.

In quantum mechanical terms, the nuclear magnetic moment of a nucleus can align with an externally applied magnetic field of strength **Bo** in only 2I+1 ways, either re-inforcing or opposing **Bo**. The energetically preferred orientation has the magnetic moment aligned parallel with the applied field (spin +1/2) and is often given the notation  $\alpha$ , whereas the higher energy anti-parallel orientation (spin -1/2) is referred to as  $\beta$ . The rotational axis of the spinning nucleus cannot be orientated exactly parallel (or anti-parallel) with the direction of the applied field **Bo** (defined in our coordinate system as about the *z* axis) but must precess about this field at an angle (for protons about 54) with an angular velocity given by the expression;

 $\omega_0 = \gamma \mathbf{B} \mathbf{0} \dots (1)$  (the Larmor frequency, in Hz)

The constant  $\gamma$  is called the magnetogyric ratio and relates the magnetic moment  $\Box$  and the spin number I for any specific nucleus;

 $\gamma = 2\pi\mu/hI$  ...(2) (h is Planck's constant)

CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602UNIT: IV (RAMAN SPECTRA AND NMR SPECTROSCOPY)BATCH-2015-2018



For a single nucleus with I=1/2 and positive  $\gamma$ , only one transition is possible ( $\Delta$ I=1, a single quantum transition) between the two energy levels;



NMR is all about how to interpret such transitions in terms of chemical structure. We will first consider the energy of a typical NMR transition. If angular velocity is related to frequency by  $B_0 = 2^{1/4}v$ , then

$$v = \gamma Bo/2^{1}/4 ...(3)$$

It follows that proton NMR transitions ( $\Delta I=1$ ) have the following energy;

$$hv = \Delta E = h\gamma Bo./2\pi ...(4)$$

For a proton  $\gamma = 26.75 \times 10^7$  rad T<sup>-1</sup> s<sup>-1</sup> and **Bo** ~ 2T,  $\Delta E = 6 \times 10^{-26}$  J. The relative populations of the higher (n<sup>2</sup>) and lower (n<sup>1</sup>) energy levels at room temperature are given by the Boltzmann law;

 $n^2/n^1 = e^{-\Delta}E/kT \sim 0.99999....(5)$ 

For NMR, this means that the probability of observing a transition from  $n^1$  to  $n^2$  is only slightly greater than that for a downward transition, *ie* the overall probability of observing absorption of energy is quite small. This relationship also explains why a larger **Bo** favours sensitivity in NMR measurements, increasing as it does the difference between the two Boltzmann levels, and why NMR becomes more sensitive at lower temperatures.

### Applications of <sup>1</sup>H NMR.

In contrast to carbon, proton spectra tend to be much more complicated in appearance due to a) the smaller chemical shift range found for typical compounds (~ 20 ppm at most) and the wide variation in the magnitude of the coupling constants. You should by now be aware of typical chemical shift values found for protons;

H-C-C, 0-2 ppm; H-C-C=O, ~2 ppm; H-C-N, ~3 ppm; H-C-O, ~4 ppm; H-C=C, ~5 ppm; H-aromatic, 6-7 ppm; H-C=O, ~9 ppm; H-O-C=O, ~12 ppm (for more extensive tables, see the recommended text).

This information supplements that obtainable from <sup>13</sup>C spectra. In this lecture we will focus on the type of information **not** obtainable from <sup>13</sup>C spectra, namely stereochemical information derived from the numerical values of coupling constants and the techniques used to derive this information.

As noted above, the coupling J is a manifestation of the splitting of **Bo** by the essentially equal populations of the ground and excited energy levels of a spin 1/2 nucleus. As such, it

depends *not* on the absolute value of **Bo** but on the characteristics of the nuclei involved and in particular of the bonding electrons between them. Chemical shifts on the other hand are directly related to relative Larmor frequencies, and so*do* depend on **Bo**. Let us illustrate this with part of the spectrum of *trans*3-phenyl propenoic acid, which gives rise to a so called two-spin system. The spin system is referred to as **AB** if the chemical shifts are quite close together, and **AX** if



The spectra are shown at different values of **Bo**, corresponding to Larmor proton frequencies of Bo=60, 100, 300 and 600 MHz (the practical limit for a spectrometer is around 1000 MHz, of which only one is currently installed, in the United States). Each proton signal is split into two by the presence of the other (2nI+1, n=1, I=1/2), the splitting being given by J =  $\delta * \omega/10^6$ , which in each spectrum is approximately 16 Hz. Before we discuss the chemical interpretation of this value, we note that a) the 600 MHz spectrum appears simpler than the 60

Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 15/22

### CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602UNIT: IV (RAMAN SPECTRA AND NMR SPECTROSCOPY)BATCH-2015-2018

MHz version and b) the 60 MHz relative peak intensities are dramatically different from those at 600 MHz. As J (in Hz) becomes numerically similar to the difference in Larmor frequencies (in Hz) between the two protons ( $\Delta\omega o = \delta * \omega_{average}/10^6$ ) the spectra are said to become more "second order", the prime manifestation of which is the "tilting" of the intensities of each doublet towards the other. It is actually possible to solve the equations describing this behaviour. You can do this for yourself using a program called **gNMR**, available on both Macs and PC systems.

Since J coupling depends on the intervening bonds and electrons, its value is highly characteristic of these bonds. In this case the coupling arises from three intervening bonds, and hence we term it <sup>3</sup>JH-H coupling. Typical values for alkenes are;



The last example is actually a <sup>2</sup>J coupling at a sp <sup>2</sup> carbon.

The next spectrum is slightly more complex;



### CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602UNIT: IV (RAMAN SPECTRA AND NMR SPECTROSCOPY)BATCH-2015-2018

Here three different protons all couple to one another (described as an **ABX** spin system), and the 2nI+1 rule must be applied in stages as follows;

Each proton is described as a double doublet, since the two couplings involved are numerically different. The actual values when measured from the spectrum are; **da 2.72**, **db 3.25**, **dc 4.38 ppm; Jab = 18 Hz, Jac = 2, Jbc = 10 Hz.** To see what the spectrum for this system looks like, you can simulate it using the geNMR program. Instructions will be issued during the lecture



Whereas in the alkene example previously only two angles between the H-C bonds are possible, here values ranging from 0 -  $180^{*}$  may occur. A theoretical relationship describing the value of J in terms of the angle between the two bonds involved in such <sup>3</sup>J coupling was derived by Karplus.



From this one can immediately conclude that  $J_{ac}$  must correspond to a gauche coupling (~60š) and  $J_{bc}$  to an anti coupling (~180š). Note also that at about 90š, J~0 a situation often encountered in many molecules. The largest coupling of +/-18 Hz is typical of the two bond <sup>2</sup>J H-C-H system (compare that with the <sup>2</sup>J H-C-H coupling in alkenes, where J is close to zero), and from other experiments can actually be shown to be negative! The NMR data therefore allows the conformation shown above to be proposed, and illustrates the powerful utility of NMR in such conformational analysis.

Before we leave this system, we ask why the  ${}^{2}J$  H-C-H coupling in this compound is visible, whereas that in *eg* bromoethane is not. If a CH2 group is close to a chiral centre in the molecule, the two methylene protons are said to be *diastereotopic* and are likely to have differing chemical shifts and different coupling to adjacent protons. This effect arises NOT from any restricted rotation about the C-C single bond, but from the absence of any possible plane of symmetry bisecting the methylene group. As can be seen from the Newman projection above, in all possible conformations for this molecule, Ha and Hb are always in a different environment; this would not be true of *eg* bromoethane.

### **Other Types of Coupling.**

<sup>4</sup>J for allylic coupling, **H**-C=C-C-**H** varies from -3 to +2 Hz, depending again on the angle between the two H-C bonds. In aromatic systems, <sup>3</sup>J or *ortho* coupling ~ 7-8; <sup>4</sup>J or *meta* coupling

 $\sim 2$  Hz; <sup>5</sup>J or*para* coupling  $\sim 0.5$  Hz. Large long range coupling is not often observed, but one type of system does reveal a dramatic dependence on geometry, often called "W" coupling because of the relationship between the two protons;



**Coupling Between Protons and Other Nuclei.** We have seen previously how <sup>1</sup>H-<sup>13</sup>C coupling can help in understanding <sup>13</sup>C spectra but such coupling is not apparently observed in <sup>1</sup>H (thank goodness) because on average there is only a 1% probability that a given proton will be adjacent to a <sup>13</sup>C nucleus. However, if you look about <sup>2</sup>JH-C/2 ~ 65 Hz away from a strong proton peak (eg methanol) you may see a small peak about 0.5% of the intensity of the central proton peak. This is the so called carbon satellite arising from just such hetero-nuclear coupling. Observing such satellites can sometimes have uses. Another satellite due to <sup>2</sup>J29Si-CH coupling is often observed (but rarely correctly attributed) as a small peak +/-3 Hz of the proton TMS signal and about 2.5% the height. Satellites are commonly observed in spectra of many other elements where the isotopic abundance is not 100%.

Finally if either <sup>19</sup>F or <sup>31</sup>P are present in a molecule, both are likely to couple to protons since these isotopes are 100% abundant. Typical couplings are <sup>1</sup>JH-P ~ 200-700 Hz, <sup>2</sup>JHC-P ~ 0.5 - 20 Hz; <sup>2</sup>JHC-F ~ 45 Hz, <sup>3</sup>JHC-F ~ 5-20 Hz. Heteronuclear spectra can be simulated using the gNMR program.

### CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602UNIT: IV (RAMAN SPECTRA AND NMR SPECTROSCOPY)BATCH-2015-2018

### Simplification of Spectra.

The three spin proton system discussed above had 12 lines, but even so the "tilting" and closeness of the peaks frequently results in spectra that are very difficult to interpret. Many modern techniques are available for dealing with this problem. Here we will deal with only a few to give some flavour of how these problems are approached.

### **POSSIBLE QUESTIONS**

### PART-A (One Mark)

### (Multiple Choice Questions)

- 1. An electronic transition takes place so rapidly that a vibrating molecule does not change its inter nuclear distance during transition
  - a. Frank condon principle b. Zeeman effect
  - c. Peltier effect d. Joule Thomson effect
- 2. Vibrational spectra is observed in the area
- a. Micro-wave region b. Infra red region
- c. Ultraviolet region d. Radio wave region
- 3. The reference compound used in NMR
- a. Chloroform b. Acetone c. TMS d. methanol
- 4. If the induced field opposes the applied field, the effective field strength experienced by the proton decreases. It means
- a. **The proton absorbs Upfield** b. The proton absorbs down field c. The intensity of the signal increases d. Protons are deshielded
- 5. .The area under the signal in NMR spectra is proportional to the number of
- a. **Protons** b. Environment of protons c. Non-equivalent protons d. Asymmetric protons

### 6. The Raman spectra can tell us whether

	a.The molecule is linear or not linear		ar b. The molec	b. The molecule is dextrorotatory		
	molecule is levore	ule is levorotatory or not d. Chiral or not		ot		
7	In contribute the m					
1.	In acetylene the p	rotons are				
	a. Shielded	b. deshielded	c. Non-equivalent	d. asymmetric		
8.	The unsaturated pro	otons appear at				
a.	10 -11 ppm	b. 6-8 ppm	c.4-6 ppm	d. 1-2 ppm		
0	The breader signal	of hydroxyl protons i	s duo to			
9.	The broader signal	of figuroxyl protons i	s due to			
a.	Shielding	b. deshielding	c. H-bonding	d. Reacting nature		
10.	The area under the	signal is proportiona	l to the number of			
a.	Protons	b. Envi	ronment of protons			
c.N	Ion-equivalent proto	ns d. Asyr	nmetric protons			

### PART-B (Eight Mark)

### (Either or type Questions)

1. What is Raman spectrum? Name the different types of lines present in it and explain the

reasons for observing these lines.

2.Explain in detail the principle of Nuclear Magnetic Resonance spectroscopy.

3.Discuss the applications of UV-Visible spectroscopy in the identification of organic molecules.

4.Explain the terms following terms in NMR spectroscopy

- (i) splitting of signals
- (ii) Coupling constant
- (iii) Chemical shift

5.Explain Raman effect on the basis of polarizability of molecules.

6. What are the characteristics of the solvent used in NMR.

7.Explain in detail about the NMR spectrophotometer.

### CLASS: IIIB.Sc CHEMISTRYCOURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURESCOURSECODE:15CHU602UNIT: IV (RAMAN SPECTRA AND NMR SPECTROSCOPY)BATCH-2015-2018

8. What is meant by Franck-Condon Principle. Explain the different types of excitations in the electromagnetic spectrum.

9.Explain about the various factors affecting the chemical shift of protons in NMR spectra

10.What is Raman spectrum? Name the different types of lines present in it and explain the reasons for observing these lines.

Subject : Physical methods and Chemical structures
Subject Code : 15CHU602
Class : III B.Sc Chemistry
Batch : 2015-2018 Batch
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UNIT-IV

### Multiple Choice Questions(Each Carry One Mark)

Questions	Option 1	Option 2	Option 3	Option 4	Answer
The total rotational degree of freedom in water molecule is	3	9	12	6	3
The total vibrational degree of freedom in water molecule is	3	9	5	6	3
A shift of the maximum absorption to longer wavelength is called	Bathochromic shift	Hypsochromic shift	Hyperchromic shift	Hypo chromic shift	Bathochromic shift
A shift of the maximum absorption to longer wavelength is called	Red shift	Hypsochromic shift	Hyperchromic shift	Hypo chromic shift	Red shift
A shift of the maximum absorption to longer wavelength is called	Red shift	Blue shift	Green shift	Yellow shift	Red shift
A shift of the maximum absorption to shorter wavelength is called	Bathochromic shift	Hypsochromic shift	Hyperchromic shift	Hypo chromic shift	Hypsochromic shift
A shift of the maximum absorption to shorter wavelength is called	Bathochromic shift	Blue shift	Hyperchromic shift	Hypo chromic shift	Hypsochromic shift
A shift of the maximum absorption to shorter wavelength is called	Red shift	Blue shift	Green shift	Yellow shift	Blue shift
An increase in the intensity of the absorption band is called	Bathochromic shift	Hypsochromic shift	Hyperchromic shift	Hypo chromic shift	Hyperchromic shift
An decrease in the intensity of the absorption band is called	Bathochromic shift	Hypsochromic shift	Hyperchromic shift	Hypo chromic shift	Hypo chromic shift
An increase in the molar coefficient of the absorption band is called	Bathochromic shift	Hypsochromic shift	Hyperchromic shift	Hypo chromic shift	Hyperchromic shift
An decrease in the molar coefficient of the absorption band is called	Bathochromic shift	Hypsochromic shift	Hyperchromic shift	Hypo chromic shift	Hypo chromic shift
An electronic transition takes place so rapidly that a vibrating molecule	Frank condon principle	Zeeman effect	Peltier effect	Joule Thomson effect	Frank condon principle
does not change its inter nuclear distance during transition					
The selection rule for rotation-vibration Raman spectra is	Polarisation has to change as the molecule vibrates	Magnetic moment has to change	Spin has to change	Intensity should change	Polarisation has to change as the molecule vibrates
IR spectra cannot be recorded for	H-Cl	H-Br	Methyl bromide	Oxygen	Oxygen
The force constant value for C-C bond	$4.6 \times 10^5$ dynes/cm	9.6 x 10 <sup>5</sup> dynes/cm	15.8 x 10 <sup>5</sup> dynes/cm	$7.6 \times 10^5$ dynes/cm	$4.6 \times 10^5$ dynes/cm
The force constant value for C=C bond	4.6 x 10 <sup>5</sup> dynes/cm	9.6 x 10 <sup>5</sup> dynes/cm	15.8 x 10 <sup>5</sup> dynes/cm	$7.6 \times 10^5$ dynes/cm	9.6 x 10 <sup>5</sup> dynes/cm
The force constant value for C to C triple bond	4.6 x 10 <sup>5</sup> dynes/cm	9.6 x 10 <sup>5</sup> dynes/cm	15.8 x 10 <sup>5</sup> dynes/cm	$7.6 \times 10^5$ dynes/cm	15.8 x 10 <sup>5</sup> dynes/cm
The restoring force per unit displacement of a harmonic oscillator is	Frank condon principle	Force constant	Moment of inertia	Band centre	Force constant
The absorption frequency for the stretching frequency for C-H bond (cm <sup>-1</sup> )	2850-2960	1350-1470	1000-1300	540-785	2850-2960
The absorption frequency for the bending frequency for C-H bond (cm <sup>-1</sup> )	2850-2960	1350-1470	1000-1300	540-785	1350-1470
The absorption frequency for the stretching frequency for C-O bond (cm <sup>-1</sup> )	2850-2960	1350-1470	1000-1300	540-785	1000-1300
The absorption frequency for the stretching frequency for C-Cl bond (cm <sup>-1</sup> )	2850-2960	1350-1470	1000-1300	540-785	540-785
The absorption frequency for the stretching frequency for C=O bond (cm <sup>-1</sup> )	2850-2960	1350-1470	1720	540-785	1720
The absorption frequency for the stretching frequency for C=C bond $(cm^{-1})$	2850-2960	1600	1000-1300	540-785	1600
The absorption frequency of 1720 cm <sup>-1</sup> shows the presence of	Carbonyl group	C=C	O-H group	Nitrile group	Carbonyl group
The absorption frequency of 1600 cm <sup>-1</sup> shows the presence of	Carbonyl group	C=C group	O-H group	Nitrile group	C=C group
The absorption frequency of 3400 cm <sup>-1</sup> shows the presence of	Carbonyl group	C=C	O-H group	Nitrile group	O-H group
The absorption frequency of 2240 cm <sup>-1</sup> shows the presence of	Carbonyl group	C=C	O-H group	Nitrile group	Nitrile group
Which among the solvents can act as a NMR solvent	Chloroform	Deuterio chloroform	methanol	ether	Deuterio chloroform
Which among the solvents can act as a NMR solvent	Chloroform	Deuteriated methanol	methanol	ether	Deuteriated methanol
Which among the solvents can act as a NMR solvent	Chloroform	Deuteri acetone	methanol	ether	Deuteri acetone
Which among the solvents can act as a NMR solvent	Chloroform	Deuterium oxide	methanol	ether	Deuterium oxide
Protons in a molecule having the same environment are called	Equivalent protons	Isoelectronic protons	Neo protons	Assymetric protons	Equivalent protons

The scale in the frequency axis is denoted as	delta	cm	lamda	pascal	Delta
The scale in the frequency axis is denoted as	ppm	cm	lamda	pascal	ppm
The reference compound used in NMR	chloroform	Acetone	TMS	methanol	TMS
The number of different types of protons in 2,2-dibromopropane	one	two	three	four	one
The number of different types of protons in isopropyl chloride	one	two	three	four	two
If the induced field opposes the applied field, the effective field strength	The proton absorbs Upfield	The proton absorbs down	The intensity of the signal	Protons are deshielded	The proton absorbs Upfield
experienced by the proton decreases. It means		field	increases		
If the induced field opposes the applied field, the effective field strength	The protons are Shielded	The proton absorbs down	The intensity of the signal	Protons are deshielded	The protons are Shielded
experienced by the proton decreases. It means		field	increases		
If the induced field aligns the applied field, the effective field strength	The proton absorbs down	The proton absorbs down	The intensity of the signal	Protons are shielded	The proton absorbs down field
experienced by the proton increases . It means	field	field	increases		
If the induced field opposes the applied field, the effective field strength	The protons are deShielded	The proton absorbs down	The intensity of the signal	Protons are shielded	The protons are deShielded
experienced by the proton decreases. It means		field	increases		
In acetylene the protons are	shielded	deshielded	Non-equivalent	assymetric	shielded
In benzene the protons are	shielded	deshielded	Non-equivalent	assymetric	deshielded
The aldehydes protons are	shielded	deshielded	Non-equivalent	assymetric	dshielded
The aldehydes protons appear at	10 -11 ppm	6-8 ppm	4-6 ppm	1-2 ppm	10-11 ppm
The Phenolic protons appear at	10 -11 ppm	6-8 ppm	4-6 ppm	1-2 ppm	10-11 ppm
The aromatic protons appear at	10 -11 ppm	6-8 ppm	4-6 ppm	1-2 ppm	6-8 ppm
The unsaturated protons appear at	10 -11 ppm	6-8 ppm	4-6 ppm	1-2 ppm	4-6 ppm
The alkyl group protons appear at	10 -11 ppm	6-8 ppm	4-6 ppm	1-2 ppm	1-2 ppm
The broader signal of hydroxyl protons is due to	shielding	deshielding	H-bonding	Reacting nature	H-bonding
The area under the signal is proportional to the number of	protons	Environment of protons	Non-equivalent protons	Asymmetric protons	protons
TMS is used as a reference compound because	Chemically inert	No protons present	Gives a broad signal	High boiling point	Chemically inert
TMS is used as a reference compound because	Low boiling point	No protons present	Gives a broad signal	High boiling point	Low boiling point
TMS is used as a reference compound because	Contains 12 equivalent	No protons present	Gives a broad signal	High boiling point	Contains 12 equivalent protons
	protons and gives a sharp				and gives a sharp signal
	signal				
The solvent used in NMR should be	Highly reactive	Highly exchangeable	Highly inert	Should have protons	Highly inert
The solvent used in NMR should be	Highly reactive	Highly exchangeable	Should not have protons	Should have protons	Should not have protons
A group of signals appeared at 6-7 ppm, the group present is	unsaturated	phenolic	hydroxy	aromatic	aromatic
A group of signals appeared at 8-10 ppm, the group present is	unsaturated	phenolic	hydroxy	aromatic	Phenolic

### CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

### <u>UNIT-V</u>

### **SYLLABUS**

Chromatography – classification- Principles of Column, Paper and Thin Layer chromatography.

### Chromatography

**Chromatography** (Greek*chroma* "color" and *graphein* "to write") is the collective term for a set of laboratory techniques for the separation of mixtures. The mixture is dissolved in a fluid called the *mobile phase*, which carries it through a structure holding another material called the *stationary phase*. The various constituents of the mixture travel at different speeds, causing them to separate. The separation is based on differential partitioning between the mobile and stationary phases. Subtle differences in a compound's partition coefficient result in differential retention on the stationary phase and thus changing the separation.

Chromatography may be preparative or analytical. The purpose of preparative chromatography is to separate the components of a mixture for more advanced use (and is thus a form of purification). Analytical chromatography is done normally with smaller amounts of material and is for measuring the relative proportions of analytes in a mixture. The two are not mutually exclusive.



Thin layer chromatography is used to separate components of a plant extract, illustrating the experiment with plant pigments that gave chromatography its name

### CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

Chromatography was first employed in Russia by the Italian-born scientist Mikhail Tsvet in 1900. He continued to work with chromatography in the first decade of the 20th century, primarily for the separation of plant pigments such as chlorophyll, carotenes, and xanthophylls. Since these components have different colors (green, orange, and yellow, respectively) they gave the technique its name. New types of chromatography developed during the 1930s and 1940s made the technique useful for many separation processes.

Chromatography technique developed substantially as a result of the work of Archer John Porter Martin and Richard Laurence Millington Synge during the 1940s and 1950s. They established the principles and basic techniques of partition chromatography, and their work encouraged the rapid development of several chromatographic methods: paper chromatography, gas chromatography, and what would become known as high performance liquid chromatography. Since then, the technology has advanced rapidly. Researchers found that the main principles of Tsvet's chromatography could be applied in many different ways, resulting in the different varieties of chromatography described below. Advances are continually improving the technical performance of chromatography, allowing the separation of increasingly similar molecules.

### **Chromatography terms**

- The **analyte** is the substance to be separated during chromatography. It is also normally what is needed from the mixture.
- Analytical chromatography is used to determine the existence and possibly also the concentration of analyte(s) in a sample.
- A **bonded phase** is a stationary phase that is covalently bonded to the support particles or to the inside wall of the column tubing.
- A **chromatogram** is the visual output of the chromatograph. In the case of an optimal separation, different peaks or patterns on the chromatogram correspond to different components of the separated mixture.

### CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018



Plotted on the x-axis is the retention time and plotted on the y-axis a signal (for example obtained by a spectrophotometer, mass spectrometer or a variety of other detectors) corresponding to the response created by the analytes exiting the system. In the case of an optimal system the signal is proportional to the concentration of the specific analyte separated.

- A **chromatograph** is equipment that enables a sophisticated separation, e.g. gas chromatographic or liquid chromatographic separation.
- **Chromatography** is a physical method of separation that distributes components to separate between two phases, one stationary (stationary phase), the other (the mobile phase) moving in a definite direction.
- The **eluate** is the mobile phase leaving the column.
- The **eluent** is the solvent that carries the analyte.
- An eluotropic series is a list of solvents ranked according to their eluting power.
- An **immobilized phase** is a stationary phase that is immobilized on the support particles, or on the inner wall of the column tubing.
- The **mobile phase** is the phase that moves in a definite direction. It may be a liquid (LC and Capillary Electrochromatography (CEC)), a gas (GC), or a supercritical fluid (supercritical-fluid chromatography, SFC). The mobile phase consists of the sample being separated/analyzed and the solvent that moves the sample through the column. In the case of HPLC the mobile phase consists of a non-polar solvent(s) such as hexane in normal phase or polar solvents in reverse phase chromatography and the sample being separated. The mobile phase moves through the chromatography column (the stationary phase) where the sample interacts with the stationary phase and is separated.

Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 3/23

### CLASS: IIIB.Sc CHEMISTRY

COURSENAME: PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE: 15CHU602UNIT: V (Chromatography) BATCH-2015-2018

- **Preparative chromatography** is used to purify sufficient quantities of a substance for further use, rather than analysis.
- The **retention time** is the characteristic time it takes for a particular analyte to pass through the system (from the column inlet to the detector) under set conditions. See also: Kovats' retention index
- The **sample** is the matter analyzed in chromatography. It may consist of a single component or it may be a mixture of components. When the sample is treated in the course of an analysis, the phase or the phases containing the analytes of interest is/are referred to as the sample whereas everything out of interest separated from the sample before or in the course of the analysis is referred to as waste.
- The **solute** refers to the sample components in partition chromatography.
- The **solvent** refers to any substance capable of solubilizing another substance, and especially the liquid mobile phase in liquid chromatography.
- The **stationary phase** is the substance fixed in place for the chromatography procedure. Examples include the silica layer in thin layer chromatography
- The **detector** refers to the instrument used for qualitative and quantitative detection of analytes after separation.

Chromatography is based on the concept of partition coefficient, any solute partitions between two immiscible solvents. When we make one solvent immobile (by adsorption on a solid support matrix) and another mobile it results in most common applications of chromatography. If matrix support is polar (e.g. paper, silica etc.) it is forward phase chromatography, and if it is non-polar (C-18) it is reverse phase.

### Techniques by chromatographic bed shape

### **Column chromatography**

Column chromatography is a separation technique in which the stationary bed is within a tube. The particles of the solid stationary phase or the support coated with a liquid stationary phase may fill the whole inside volume of the tube (packed column) or be concentrated on or along the inside tube wall leaving an open, unrestricted path for the mobile phase in the middle part of the tube (open tubular column). Differences in rates of movement through the medium are calculated to different retention times of the sample.

In 1978, W. Clark Still introduced a modified version of column chromatography called **flash column chromatography** (flash). The technique is very similar to the traditional column chromatography, except for that the solvent is driven through the column by applying positive pressure. This allowed most separations to be performed in less than 20 minutes, with improved separations compared to the old method. Modern flash chromatography systems are sold as prepacked plastic cartridges, and the solvent is pumped through the cartridge. Systems may also be linked with detectors and fraction collectors providing automation. The introduction of gradient pumps resulted in quicker separations and less solvent usage.

### CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

In expanded bed adsorption, a fluidized bed is used, rather than a solid phase made by a packed bed. This allows omission of initial clearing steps such as centrifugation and filtration, for culture broths or slurries of broken cells.

Phosphocellulose chromatography utilizes the binding affinity of many DNA-binding proteins for phosphocellulose. The stronger a protein's interaction with DNA, the higher the salt concentration needed to elute that protein.

### **Planar chromatography**

**Planar chromatography** is a separation technique in which the stationary phase is present as or on a plane. The plane can be a paper, serving as such or impregnated by a substance as the stationary bed (paper chromatography) or a layer of solid particles spread on a support such as a glass plate (thin layer chromatography). Different compounds in the sample mixture travel different distances according to how strongly they interact with the stationary phase as compared to the mobile phase. The specific Retention factor ( $R_f$ ) of each chemical can be used to aid in the identification of an unknown substance.

### Paper chromatography

Paper chromatography is a technique that involves placing a small dot or line of sample solution onto a strip of *chromatography paper*. The paper is placed in a container with a shallow layer of solvent and sealed. As the solvent rises through the paper, it meets the sample mixture, which starts to travel up the paper with the solvent. This paper is made of cellulose, a polar substance, and the compounds within the mixture travel farther if they are non-polar. More polar substances bond with the cellulose paper more quickly, and therefore do not travel as far.

### Thin layer chromatography

Thin layer chromatography (TLC) is a widely employed laboratory technique and is similar to paper chromatography. However, instead of using a stationary phase of paper, it involves a stationary phase of a thin layer of adsorbent like silica gel, alumina, or cellulose on a flat, inert substrate. Compared to paper, it has the advantage of faster runs, better separations, and the choice between different adsorbents. For even better resolution and to allow for quantification, high-performance TLC can be used. An older popular use had been to differentiate chromosomes by observing distance in gel (separation of was a separate step).

### Techniques by physical state of mobile phase

### Gas chromatography

Gas chromatography (GC), also sometimes known as gas-liquid chromatography, (GLC), is a separation technique in which the mobile phase is a gas. Gas chromatographic separation is always carried out in a column, which is typically "packed" or "capillary". Packed columns are

### CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

the routine work horses of gas chromatography, being cheaper and easier to use and often giving adequate performance. Capillary columns generally give far superior resolution and although more expensive are becoming widely used, especially for complex mixtures. Both types of column are made from non-adsorbent and chemically inert materials. Stainless steel and glass are the usual materials for packed columns and quartz or fused silica for capillary columns.

Gas chromatography is based on partition equilibrium of analyte between a solid or viscous liquid stationary phase (often a liquid silicone-based material) and a mobile gas (most often helium). The stationary phase is adhered to the inside of a small-diameter (commonly 0.53 - 0.18mm inside diameter) glass or fused-silica tube (a capillary column) or a solid matrix inside a larger metal tube (a packed column). It is widely used in analytical chemistry; though the high temperatures used in GC make it unsuitable for high molecular weight biopolymers or proteins (heat denatures them), frequently encountered in biochemistry, it is well suited for use in the petrochemical, environmental monitoring and remediation, and industrial chemical fields. It is also used extensively in chemistry research.



### Liquid chromatography

Liquid chromatography (LC) is a separation technique in which the mobile phase is a liquid. It can be carried out either in a column or a plane. Present day liquid chromatography that generally utilizes very small packing particles and a relatively high pressure is referred to as high performance liquid chromatography (HPLC).

In HPLC the sample is forced by a liquid at high pressure (the mobile phase) through a column that is packed with a stationary phase composed of irregularly or spherically shaped particles, a porous monolithic layer, or a porous membrane. HPLC is historically divided into two different sub-classes based on the polarity of the mobile and stationary phases. Methods in which the stationary phase is more polar than the mobile phase (e.g., toluene as the mobile phase, silica as the stationary phase) are termed normal phase liquid chromatography (NPLC) and the

### CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

opposite (e.g., water-methanol mixture as the mobile phase and C18 = octadecylsilyl as the stationary phase) is termed reversed phase liquid chromatography (RPLC).

Specific techniques under this broad heading are listed below.

### Affinity chromatography

Affinity chromatography is based on selective non-covalent interaction between an analyte and specific molecules. It is very specific, but not very robust. It is often used in biochemistry in the purification of proteins bound to tags. These fusion proteins are labeled with compounds such as His-tags, biotin or antigens, which bind to the stationary phase specifically. After purification, some of these tags are usually removed and the pure protein is obtained.

Affinity chromatography often utilizes a biomolecule's affinity for a metal (Zn, Cu, Fe, etc.). Columns are often manually prepared. Traditional affinity columns are used as a preparative step to flush out unwanted biomolecules.

However, HPLC techniques exist that do utilize affinity chromatogaphy properties. Immobilized Metal Affinity Chromatography (IMAC) is useful to separate aforementioned molecules based on the relative affinity for the metal (I.e. Dionex IMAC). Often these columns can be loaded with different metals to create a column with a targeted affinity.

### Techniques by separation mechanism

### Ion exchange chromatography

Ion exchange chromatography (usually referred to as ion chromatography) uses an ion exchange mechanism to separate analytes based on their respective charges. It is usually performed in columns but can also be useful in planar mode. Ion exchange chromatography uses a charged stationary phase to separate charged compounds including anions, cations, amino acids, peptides, and proteins. In conventional methods the stationary phase is an ion exchange resin that carries charged functional groups that interact with oppositely charged groups of the compound to retain. Ion exchange chromatography is commonly used to purify proteins using FPLC.

### Size-exclusion chromatography

Size-exclusion chromatography (SEC) is also known as **gel permeation chromatography** (GPC) or **gel filtration chromatography** and separates molecules according to their size (or more accurately according to their hydrodynamic diameter or hydrodynamic volume). Smaller molecules are able to enter the pores of the media and, therefore, molecules are trapped and removed from the flow of the mobile phase. The average residence time in the pores depends upon the effective size of the analyte molecules. However, molecules that are larger than the average pore size of the packing are excluded and thus suffer essentially no retention;

Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 7/23

### CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

such species are the first to be eluted. It is generally a low-resolution chromatography technique and thus it is often reserved for the final, "polishing" step of a purification. It is also useful for determining the tertiary structure and quaternary structure of purified proteins, especially since it can be carried out under native solution conditions.

### Expanded Bed Adsorption (EBA) Chromatographic Separation

Expanded Bed Adsorption (EBA) Chromatographic Separation captures a target protein from a crude feed stream when it passes through a chromatography column system containing adsorbent beads. With this technique the crude feedstock can be treated directly in the chromatographic column, avoiding the traditional clarification and pre-treatment steps. EBA Chromatographic Separation is highly scalable, from laboratory-based 1 cm diameter columns to large production columns up to 2 meter in diameter. These columns can typically handle feed stock throughput of more than 1,000,000 liter per day with a production capacity of 1000 MT protein per year.

### **Column chromatography**



A chemist in the 1950s using column chromatography. The Erlenmeyer receptacles are on the floor.

### CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018



Automated fraction collector and sampler for chromatographic techniques

**Column chromatography** in chemistry is a method used to purify individual chemical compounds from mixtures of compounds. It is often used for preparative applications on scales from micrograms up to kilograms. The main advantage of column chromatography is the relatively low cost and disposability of the stationary phase used in the process. The latter prevents cross-contamination and stationary phase degradation due to recycling.

The classical preparative chromatography column is a glass tube with a diameter from 5 mm to 50 mm and a height of 5 cm to 1 m with a tap and some kind of a filter (a glass frit or glass wool plug - to prevent the loss of the stationary phase) at the bottom. Two methods are generally used to prepare a column: the dry method and the wet method.

- For the dry method, the column is first filled with dry stationary phase powder, followed by the addition of mobile phase, which is flushed through the column until it is completely wet, and from this point is never allowed to run dry.
- For the wet method, slurry is prepared of the eluent with the stationary phase powder and then carefully poured into the column. Care must be taken to avoid air bubbles. A solution of the organic material is pipetted on top of the stationary phase. This layer is usually topped with a small layer of sand or with cotton or glass wool to protect the shape of the organic layer from the velocity of newly added eluent. Eluent is slowly passed through the column to advance the organic material. Often a spherical eluent reservoir or an eluent-filled and stoppered separating funnel is put on top of the column.

The individual components are retained by the stationary phase differently and separate from each other while they are running at different speeds through the column with the eluent. At

Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 9/23
# CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

the end of the column they elute one at a time. During the entire chromatography process the eluent is collected in a series of fractions. Fractions can be collected automatically by means of fraction collectors. The productivity of chromatography can be increased by running several columns at a time. In this case multi stream collectors are used. The composition of the eluent flow can be monitored and each fraction is analyzed for dissolved compounds, e.g. by analytical chromatography, UV absorption, or fluorescence. Colored compounds (or fluorescent compounds with the aid of an UV lamp) can be seen through the glass wall as moving bands.

### Stationary phase



Photografic sequence of a column chromatography

The *stationary phase* or *adsorbent* in column chromatography is a solid. The most common stationary phase for column chromatography is silica gel, followed by alumina. Cellulose powder has often been used in the past. Also possible are ion exchange chromatography, reversed-phase chromatography (RP), affinity chromatography or expanded bed adsorption (EBA). The stationary phases are usually finely ground powders or gels and/or are microporous for an increased surface; though in EBA a fluidized bed is used. There is an important ratio between the stationary phase weight and the dry weight of the analyte mixture that can be applied onto the column. For silica column chromatography, this ratio lies within 20:1 to 100:1, depending on how close to each other the analyte components are being eluted.

## Mobile phase (eluent)

The *mobile phase* or *eluent* is either a pure solvent or a mixture of different solvents. It is chosen so that the retention factor value of the compound of interest is roughly around 0.2 - 0.3 in order to minimize the time and the amount of eluent to run the chromatography. The eluent has also been chosen so that the different compounds can be separated effectively. The eluent is optimized in small scale pretests, often using thin layer chromatography (TLC) with the same stationary phase.

Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 10/23

# CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

There is an optimum flow rate for each particular separation. A faster flow rate of the eluent minimizes the time required to run a column and thereby minimizes diffusion, resulting in a better separation. However, the maximum flow rate is limited because a finite time is required for the analyte to equilibrate between the stationary phase and mobile phase, see Van Deemter's equation. A simple laboratory column runs by gravity flow. The flow rate of such a column can be increased by extending the fresh eluent filled column above the top of the stationary phase or decreased by the tap controls. Faster flow rates can be achieved by using a pump or by using compressed gas (e.g. air, nitrogen, or argon) to push the solvent through the column (flash column chromatography).

The particle size of the stationary phase is generally finer in flash column chromatography than in gravity column chromatography. For example, one of the most widely used silica gel grades in the former technique is mesh  $230 - 400 (40 - 63 \mu m)$ , while the latter technique typically requires mesh  $70 - 230 (63 - 200 \mu m)$  silica gel.

A spreadsheet that assists in the successful development of flash columns has been developed. The spreadsheet estimates the retention volume and band volume of analytes, the fraction numbers expected to contain each analyte, and the resolution between adjacent peaks. This information allows users to select optimal parameters for preparative-scale separations before the flash column itself is attempted.

# Automated systems



An automated ion chromatography system.

Column chromatography is an extremely time consuming stage in any lab and can quickly become the bottleneck for any process lab. Therefore, several manufacturers like Buchi, Teledyne Isco, have developed automated flash chromatography systems (typically referred to as LPLC, low pressure liquid chromatography, around 350–525 kPa or 50.8–76.1 psi) that minimize human involvement in the purification process. Automated systems will include components normally found on more expensive high performance liquid chromatography (HPLC) systems such as a gradient pump, sample injection ports, a UV detector and a fraction collector to collect the eluent. Typically these automated systems can separate samples from a few milligrams up to an industrial many kilogram scale and offer a much cheaper and quicker solution to doing multiple injections on prep-HPLC systems.

Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 11/23

# CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

The resolution (or the ability to separate a mixture) on an LPLC system will always be lower compared to HPLC, as the packing material in an HPLC column can be much smaller, typically only 5 micrometre thus increasing stationary phase surface area, increasing surface interactions and giving better separation. However, the use of this small packing media causes the high back pressure and is why it is termed high pressure liquid chromatography. The LPLC columns are typically packed with silica of around 50 micrometres, thus reducing back pressure and resolution, but it also removes the need for expensive high pressure pumps. Manufacturers are now starting to move into higher pressure flash chromatography systems and have termed these as medium pressure liquid chromatography (MPLC) systems which operate above 1 MPa (150 psi).

# Thin-layer chromatography



Separation of black ink on a TLC plate

**Thin-layer chromatography** (TLC) is a chromatography technique used to separate non-volatile mixtures. Thin-layer chromatography is performed on a sheet of glass, plastic, or aluminium foil, which is coated with a thin layer of adsorbent material, usually silica gel, aluminium oxide, or cellulose. This layer of adsorbent is known as the stationary phase.

After the sample has been applied on the plate, a solvent or solvent mixture (known as the mobile phase) is drawn up the plate via capillary action. Because different analytes ascend the TLC plate at different rates, separation is achieved.



TLC of three standards (ortho-, meta- and para-isomers) and a sample

# CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

Thin-layer chromatography can be used to monitor the progress of a reaction, identify compounds present in a given mixture, and determine the purity of a substance. Specific examples of these applications include: analyzing ceramides and fatty acids, detection of pesticides or insecticides in food and water, analyzing the dye composition of fibers in forensics, assaying the radiochemical purity of radiopharmaceuticals, or identification of medicinal plants and their constituents.

A number of enhancements can be made to the original method to automate the different steps, to increase the resolution achieved with TLC and to allow more accurate quantitative analysis. This method is referred to as HPTLC, or "high-performance TLC".

### **Plate preparation**

TLC plates are usually commercially available, with standard particle size ranges to improve reproducibility. They are prepared by mixing the adsorbent, such as silica gel, with a small amount of inert binder like calcium sulfate (gypsum) and water. This mixture is spread as a thick slurry on an unreactive carrier sheet, usually glass, thick aluminum foil, or plastic. The resultant plate is dried and *activated* by heating in an oven for thirty minutes at 110 °C. The thickness of the absorbent layer is typically around 0.1 - 0.25 mm for analytical purposes and around 0.5 - 2.0 mm for preparative TLC.

## Technique



Chromatogram of 10 essential oilscoloured with vanillin reagent.

The process is similar to paper chromatography with the advantage of faster runs, better separations, and the choice between different stationary phases. Because of its simplicity and speed TLC is often used for monitoring chemical reactions and for the qualitative analysis of reaction products.

To run a thin layer chromatography, the following procedure is carried out:

# CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

- A small spot of solution containing the sample is applied to a plate, about 1.5 centimeters from the bottom edge. The solvent is allowed to completely evaporate off, otherwise a very poor or no separation will be achieved. If a non-volatile solvent was used to apply the sample, the plate needs to be dried in a vacuum chamber.
- A small amount of an appropriate solvent (eluent) is poured into a glass beaker or any other suitable transparent container (separation chamber) to a depth of less than 1 centimeter. A strip of filter paper (aka "wick") is put into the chamber so that its bottom touches the solvent and the paper lies on the chamber wall and reaches almost to the top of the container. The container is closed with a cover glass or any other lid and is left for a few minutes to let the solvent vapors ascend the filter paper and saturate the air in the chamber. (Failure to saturate the chamber will result in poor separation and non-reproducible results).
- The TLC plate is then placed in the chamber so that the spot(s) of the sample do not touch the surface of the eluent in the chamber, and the lid is closed. The solvent moves up the plate by capillary action, meets the sample mixture and carries it up the plate (elutes the sample). The plate should be removed from the chamber before the solvent front reaches the top of the stationary phase (continuation of the elution will give a misleading result) and dried.

# **Separation Process and Principle**

Different compounds in the sample mixture travel at different rates due to the differences in their attraction to the stationary phase and because of differences in solubility in the solvent. By changing the solvent, or perhaps using a mixture, the separation of components (measured by the  $R_{\rm f}$  value) can be adjusted. Also, the separation achieved with a TLC plate can be used to estimate the separation of a flash chromatography column.



Development of a TLC plate, a purple spot separates into a red and blue spot



Surface of a freshly cut plank of *Eucalyptus camaldulensis* displaying thin-layer chromatography. The horizontal blue strip is from a reaction between the iron bandsaw supports and the acidic timber

Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 14/23

# CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

Separation of compounds is based on the competition of the solute and the mobile phase for binding places on the stationary phase. For instance, if normal-phase silica gel is used as the stationary phase, it can be considered polar. Given two compounds that differ in polarity, the more polar compound has a stronger interaction with the silica and is, therefore, more capable to dispel the mobile phase from the binding places. As a consequence, the less polar compound moves higher up the plate (resulting in a higher  $R_{\rm f}$  value). If the mobile phase is changed to a more polar solvent or mixture of solvents, it is more capable of dispelling solutes from the silica binding places, and all compounds on the TLC plate will move higher up the plate. It is commonly said that "strong" solvents (eluents) push the analyzed compounds up the plate, whereas "weak" eluents barely move them. The order of strength/weakness depends on the coating (stationary phase) of the TLC plate. For silica gel-coated TLC plates, the eluent strength increases in the following order: perfluoroalkane (weakest), hexane, pentane, carbon tetrachloride, benzene/toluene, dichloromethane, diethyl ether, ethyl acetate, acetonitrile, acetone, 2-propanol/n-butanol, water, methanol, triethylamine, acetic acid, formic acid (strongest). For C18-coated plates the order is reverse. This means that if a mixture of ethyl acetate and hexane as the mobile phase is used, adding more ethyl acetate results in higher  $R_{\rm f}$ values for all compounds on the TLC plate. Changing the polarity of the mobile phase will normally not result in reversed order of running of the compounds on the TLC plate. An eluotropic series can be used as a guide in selecting a mobile phase. If a reversed order of running of the compounds is desired, an apolar stationary phase should be used, such as C18functionalized silica.

# Analysis

As the chemicals being separated may be colorless, several methods exist to visualize the spots:

- fluorescent analytes like quinine may be detected under blacklight (366 nm)
- Often a small amount of a fluorescent compound, usually manganese-activated zinc silicate, is added to the adsorbent that allows the visualization of spots under UV-C light (254 nm). The adsorbent layer will thus fluoresce light-green by itself, but spots of analyte quench this fluorescence.
- Iodine vapors are a general unspecific color reagent
- Specific color reagents into which the TLC plate is dipped or which are sprayed onto the plate exist.
  - Potassium permanganate oxidation
  - Bromine
- In the case of lipids, the chromatogram may be transferred to a PVDF membrane and then subjected to further analysis, for example mass spectrometry, a technique known as Far-Eastern blotting.

Once visible, the  $R_f$  value, or retardation factor, of each spot can be determined by dividing the distance the product traveled by the distance the solvent front traveled using the initial spotting

# CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

site as reference. These values depend on the solvent used and the type of TLC plate and are not physical constants.

## Applications

### Characterization

In organic chemistry, reactions are qualitatively monitored with TLC. Spots sampled with a capillary tube are placed on the plate: a spot of starting material, a spot from the reaction mixture, and a cross-spot with both. A small (3 by 7 cm) TLC plate takes a couple of minutes to run. The analysis is qualitative, and it will show if the starting material has disappeared, i.e. the reaction is complete, if any product has appeared, and how many products are generated (although this might be underestimated due to co-elution). Unfortunately, TLCs from low-temperature reactions may give misleading results, because the sample is warmed to room temperature in the capillary, which can alter the reaction—the warmed sample analyzed by TLC is not the same as what is in the low-temperature flask. One such reaction is the DIBALH reduction of ester to aldehyde.

In one study TLC has been applied in the screening of organic reactions, for example in the fine-tuning of BINAP synthesis from 2-naphthol. In this method, the alcohol and catalyst solution (for instance iron(III) chloride) are placed separately on the base line, then reacted, and then instantly analyzed.

### Isolation

Since different compounds will travel a different distance in the stationary phase, chromatography can in effect be used as an isolation technique. The separated compounds each occupying a specific area on the plate, they can be scraped away, put in another solvent to separate them from the stationary phase and used for further analysis. As an example, in the chromatography of an extract of green leaves (for example spinach) in 7 stages of development, Carotene elutes quickly and is only visible until step 2. Chlorophyll A and B are halfway in the final step and lutein the first compound staining yellow. Once the chromatography is over, the carotene can be removed from the plate, put back into a solvent and ran into a spectrophotometer to characterize its wavelength absorption.

### **Paper Chromatography**

The paper is suspended in a container with a shallow layer of a suitable solvent or mixture of solvents in it. It is important that the solvent level is below the line with the spots on it. The next diagram doesn't show details of how the paper is suspended because there are too many possible ways of doing it and it clutters the diagram. Sometimes the paper is just coiled into a loose cylinder

## CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

and fastened with paper clips top and bottom. The cylinder then just stands in the bottom of the container.

The reason for covering the container is to make sure that the atmosphere in the beaker is saturated with solvent vapour. Saturating the atmosphere in the beaker with vapour stops the solvent from evaporating as it rises up the paper.



As the solvent slowly travels up the paper, the different components of the ink mixtures travel at different rates and the mixtures are separated into different coloured spots.

The diagram shows what the plate might look like after the solvent has moved almost to the top.



It is fairly easy to see from the final chromatogram that the pen that wrote the message contained the same dyes as pen 2. You can also see that pen 1 contains a mixture of two different blue dyes - one of which might be the same as the single dye in pen 3.

# **Rf values**

Some compounds in a mixture travel almost as far as the solvent does; some stay much closer to the

## CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

base line. The distance travelled relative to the solvent is a constant for a particular compound as long as you keep everything else constant - the type of paper and the exact composition of the solvent, for example.

The distance travelled relative to the solvent is called the Rfvalue. For each compound it can be worked out using the formula:

# $R_f = \frac{\text{distance travelled by compound}}{\text{distance travelled by solvent}}$

For example, if one component of a mixture travelled 9.6 cm from the base line while the solvent had travelled 12.0 cm, then the Rf value for that component is:

$$R_{f} = \frac{9.6}{12.0}$$
  
= 0.80

In the example we looked at with the various pens, it wasn't necessary to measure Rf values because you are making a direct comparison just by looking at the chromatogram.

You are making the assumption that if you have two spots in the final chromatogram which are the same colour and have travelled the same distance up the paper, they are most likely the same compound. It isn't necessarily true of course - you could have two similarly coloured compounds with very similar Rf values. We'll look at how you can get around that problem further down the page.

What if the substances you are interested in are colourless?

In some cases, it may be possible to make the spots visible by reacting them with something which produces a coloured product. A good example of this is in chromatograms produced from amino acid mixtures.

Suppose you had a mixture of amino acids and wanted to find out which particular amino acids the mixture contained. For simplicity we'll assume that you know the mixture can only possibly contain five of the common amino acids.

A small drop of a solution of the mixture is placed on the base line of the paper, and similar small spots of the known amino acids are placed alongside it. The paper is then stood in a suitable solvent and left to develop as before. In the diagram, the mixture is M, and the known amino acids are

## CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

labelled 1 to 5.

The position of the solvent front is marked in pencil and the chromatogram is allowed to dry and is then sprayed with a solution of ninhydrin. Ninhydrin reacts with amino acids to give coloured compounds, mainly brown or purple.

The left-hand diagram shows the paper after the solvent front has almost reached the top. The spots are still invisible. The second diagram shows what it might look like after spraying with ninhydrin.





before spraying with ninhydrin

after spraying with ninhydrin

There is no need to measure the Rf values because you can easily compare the spots in the mixture with those of the known amino acids - both from their positions and their colours.

In this example, the mixture contains the amino acids labelled as 1, 4 and 5.

And what if the mixture contained amino acids other than the ones we have used for comparison? There would be spots in the mixture which didn't match those from the known amino acids. You would have to re-run the experiment using other amino acids for comparison.

# Two way paper chromatography

Two way paper chromatography gets around the problem of separating out substances which have very similar Rf values.

I'm going to go back to talking about coloured compounds because it is much easier to see what is happening. You can perfectly well do this with colourless compounds - but you have to use quite a lot of imagination in the explanation of what is going on!

This time a chromatogram is made starting from a single spot of mixture placed towards one end of the base line. It is stood in a solvent as before and left until the solvent front gets close to the top of the paper.

## CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

In the diagram, the position of the solvent front is marked in pencil before the paper dries out. This is labelled as SF1 - the solvent front for the first solvent. We shall be using two different solvents.

	SF1	
•		
•		
M		

If you look closely, you may be able to see that the large central spot in the chromatogram is partly blue and partly green. Two dyes in the mixture have almost the same Rf values. They could equally well, of course, both have been the same colour - in which case you couldn't tell whether there was one or more dye present in that spot.

What you do now is to wait for the paper to dry out completely, and then rotate it through 90°, and develop the chromatogram again in a different solvent. It is very unlikely that the two confusing spots will have the same Rf values in the second solvent as well as the first, and so the spots will move by a different amount.

The next diagram shows what might happen to the various spots on the original chromatogram. The position of the second solvent front is also marked.



You wouldn't, of course, see these spots in both their original and final positions - they have moved! The final chromatogram would look like this:

# CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018



wo way chromatography has completely separated out the mixture into four distinct spots.

If you want to identify the spots in the mixture, you obviously can't do it with comparison substances on the same chromatogram as we looked at earlier with the pens or amino acids examples. You would end up with a meaningless mess of spots. You can, though, work out the Rf values for each of the spots in both solvents, and then compare these with values that you have measured for known compounds under exactly the same conditions.

How does paper chromatography work?

Although paper chromatography is simple to do, it is quite difficult to explain compared with thin layer chromatography. The explanation depends to some extent on what sort of solvent you are using, and many sources gloss over the problem completely. If you haven't already done so, it would be helpful if you could read the explanation for how thin layer chromatography works (link below). That will save me a lot of repetition, and I can concentrate on the problems.

Prepared by Dr.M.Makeswari&Mrs.R.Sharmila Devi, Asst Prof, Dept. of Chemistry, KAHE Page 21/23

# CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

POSSIBLE QUESTIONS					
	PART-A (One Mark)				
	(Multiple Choice Questions)				
1. a)	Chromatography is a technique used for compoundsSeparationb)identificationc) measured) analysis				
2. a)	Column chromatography is a type of Partitionc) Absorptiond) thin layer				
3. a) c)	Thin layer chromatography is Ionizationb) partition chromatography d) adsorption chromatography				
4. a)	<ul> <li>4. In gas chromatography, the basis for separation of the components of the volatile material is the difference in</li> <li>a) partition coefficients b) conductivity c) molecular weight d) elements percentage</li> </ul>				
5. a)	<ul> <li>5. In reverse phase chromatography, the stationary phase is made</li> <li>a) non-polar</li> <li>b) either non-polar or polar</li> <li>c) polar</li> <li>d) low polar</li> </ul>				
6. a) b)	<ul> <li>6. Ion exchange chromatography is based on the</li> <li>a) electrostatic attraction</li> <li>b) electrical mobility of ionic species</li> <li>b) electrical mobility of ionic species</li> <li>c) partition chromatography</li> </ul>				
7. a)	<ul> <li>7. The general expression for the appearance of a solute in an effluent is (where V is the elution volume of a substance, V<sub>0</sub> void volume, k<sub>D</sub> distribution constant and V<sub>i</sub> internal water volume)</li> <li>a) V = V<sub>0</sub> + k<sub>D</sub>V<sub>i</sub>b)V = V<sub>0</sub>/V<sub>i</sub> = C)V = V<sub>0</sub> - k<sub>D</sub>V<sub>i</sub> = d)V/V<sub>0</sub> = k<sub>D</sub>V<sub>i</sub></li> </ul>				
8. <b>a</b> ) b)	<ul> <li>A combination of paper chromatography and electrophoresis involves</li> <li>a) Absorption</li> <li>b) electrical mobility of the ionic species</li> <li>b) Ionization</li> <li>d) adsorption chromatography</li> </ul>				
9. a) b)	Which of the following is not used for detection in GC?Infrared spectroscopyb) NMRFlame ionizationd) Electrical conductivity				
10 a) b)	<ul> <li>10. Which of these effects result from slow injection of a large sample volume?</li> <li>a) Increased resolution</li> <li>b) Decreased resolution</li> <li>b) Non-linear detector response</li> <li>d) Constant resolution</li> </ul>				

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# CLASS: IIIB.Sc CHEMISTRY COURSENAME:PHYSICAL METHODS AND CHEMICAL STRUCTURES COURSECODE:15CHU602UNIT: V (Chromatography)BATCH-2015-2018

# PART-B (Eight Mark)

## **Either or Type Questions**

- **1.** What is chromatography? What are the basic principles of chromatography? Explain the classifications of chromatography.
- 2. Describe the instrumentation and working of paper chromatography.
- 3. Describe in detail ascending and descending paper chromatography.
- 4. Explain the application of paper chromatography.
- 5. Give a brief account of column chromatography.
- 6. Explain the applications of column chromatography.
- **7.** What is the principle of column chromatography? Describe the instrumentation and working of Column chromatography.
- 8. How will you Describe the instrumentation and working of Thin layer Chromatography?
- 9. Write notes on the applications of Thin layer chromatography.
- **10.** Give a brief account of TLC.

Subject : Physical methods and Chemical structures		
Subject Code : 15CHU602		
Class : III B.Sc Chemistry		
Batch : 2015-2018 Batch		
Staff Incharge : Dr.M.Makeswari and Mrs.R.Sharmila Devi		

### UNIT-V

### Multiple Choice Questions(Each Carry One Mark)

Questions	Option 1	Option 2	Option 3	Option 4	Answer
Chromatography is a technique used for compounds	separation	identification	measure	analysis	separation
Column chromatography is atype of	partition	adsorption	Absorption	thin layer	adsorption
Thin layer chromatography is	ionization	partition chromatography	electrical mobility of ionic species	adsorption chromatography	adsorption chromatography
In gas chromatography, the basis for separation of the components of the volatile material is the difference in	partition coefficients	conductivity	molecular weight	elements percentage	partition coefficients
In reverse phase chromatography, the stationary phase is made	non-polar	either non-polar or polar	polar	low polar	non-polar
Ion exchange chromatography is based on the	electrostatic attraction	electrical mobility of ionic species	adsorption chromatography	partition chromatography	electrostatic attraction
The general expression for the appearance of a solute in an effluent is (where V is the elution volume of a substance, $V_0$ void volume, $k_0$ distribution constant and V, internal water volume)	$V = V_0 + k_D V_i$	$V = V_0 / V_i$	$V = V_0 - k_D V_i$	$V/V_0 = k_D V_i$	$V = V_0 + k_D V_i$
A combination of paper chromatography and electrophoresis involves	Absorption	electrical mobility of the ionic species	ionization	adsorption chromatography	electrical mobility of the ionic species
Which of the following is not used for detection in GC?	Infrared spectroscopy	NMR	Flame ionisation	Electrical conductivity	NMR
Which of these effects result from slow injection of a large sample volume?	Increased resolution	Decreased resolution	Non-linear detector response	Constant resolution	Decreased resolution
The GC trace obtained after an experiment is called a	chromatograph	chromatogram	chromatophore	graph	chromatogram
Which of the following detectors give concentration-dependent signals?	Electron-capture detector	non thermal conductivity	UV detector	Scintillation counter	Electron-capture detector
What useful information can be found from a Van Deemter plot?	The selectivity factor	Optimum mobile phase flow rate	Optimum column temperature	Optimum column length	Optimum mobile phase flow rate
What is the typical internal diameter of fused silica capillary columns?	0.2-0.3 mm	0.3-0.5mm	0.5-1.0 mm	1.0-2.0 mm	0.2-0.3 mm
Resolution is proportional to the	number of theoretical plates in a	square root of the number of theoretical	square of the number of theoretical	cube root of the number of theoretical	square root of the number of theoretical plates
Derivatisation of a sample is carried out to	reduce polarity of the analytes	decrease the detector response	decrease volatility of the analytes	irreducible polarity	reduce polarity of the analytes
	Gas chromatography is notused to	Gas chromatography is used to analyse	Gas chromatography is not used to	Gas chromatography is not used to analyse	
which of the statements is correct?	analyse gases	solids	analyse gases, solutions	solid , gases	Gas chromatography is used to analyse solids
In column switching chromatography	compounds trapped on one column are eluted to another column	one column is removed and replaced by another	the flow to the column is switched on and off repeatedly	compounds does not move	compounds trapped on one column are eluted to another column
A retention gap is placed between the injector and the front of the column to	retain contaminants and prevent them from reaching the column	retain the sample and release it gradually to the column	prevent backflush of the injected solution	release random to the column	retain contaminants and prevent them from reaching the column
Which of the following detectors give mass flow-dependent signals?	Electron capture detector	Field ionisation detector	Thermal conductivity detector	Proton capture	Field ionisation detector
Headspace analysis is carried out in order to	analyse volatile compounds from solid or liquid samples	determine the psychological state of the tutor	analyse the column contents ahead of the sample	determine non-volatiles	analyse volatile compounds from solid or liquid samples
Split injection is carried out by	splitting the sample into smaller portions to inject sequentially	splitting the sample into smaller portions to inject at the same time through parallel ports	splitting off some of the sample so that it does not enter the column	It does not splitting the sample portions	splitting off some of the sample so that it does not enter the column
What does the retention factor, k', describe?	The distribution of an analyte between the stationary and the mobile phase	The migration rate of an analyte through a column	The velocity of the mobile phase	The velocity of the stationary phase	The migration rate of an analyte through a column
Theoretical plates are used to	estimate the efficiency of a column	determine the thickness of the stationary phase	measure the distribution of the analyte between mobile and stationary phases	Estimate the compounds	estimate the efficiency of a column
What does the selectivity factor describe?	The proportional difference in widths of two chromatographic peaks	The maximum number of different species which a column can separate simultaneously	The relative separation achieved between two species	does not separate the species	The relative separation achieved between two species
Hellum is generally preferred as carrier gas over nitrogen and hydrogen because	it is inert	it has a high viscosity	it not doubles up as a party gas for balloons and funny voices	it is reactive	it is inert
The column is heated to	prevent analyte condensation within the column	control elution of the same analytes	irreduce band broadening to get	control elution of the different analytes	control elution of the different analytes
What are the benefits of decreasing the column internal diameter?	Increased sample capacity	Increased resolution	Reduced risk of column overloading	non-Reduced risk of column overloading	Increased resolution
Sample retention in the column is measured by	retention time	factor	index	co-efficient	retention time
Column bleeding occurs when	elution of the analyte is extended over time	the column is cracked and stationary phase leaks out	traces of the stationary phase are eluted	the column breaks during installation and causes personal injury	traces of the stationary phase are eluted
Which of the following are not used as stationary phases in a GC column?	Polysiloxanes	Silica	Cyclodextrins	None are used as stationary phases	Silica
Doubling the column's length increases resolution by a factor of	(2) <sup>0.5</sup>	3	2	4	(2) <sup>0.5</sup>
Sample injection is considered successful if	all of the sample in the injector has	the sample is concentrated at the start of the column	the sample is spread evenly along the column	the sample is homogenously spread along	the sample is concentrated at the start of the
Which of the following gases is unsuitable for use as a GC carrier gas?	Nitrogen	Helium	Oxygen	Hydrogen	Oxygen
characteristic feature of any form of chromatography is the	use of molecules that are soluble in water	. use of an inert carrier gas.	. calculation of an R <sub>f</sub> value for the	use of a mobile and a stationary phase.	use of a mobile and a stationary phase.
food dye on the origin. After six minutes the solvent has moved 12 food dye on the origin. After six minutes the solvent has moved 12 cm and a blue spot has advanced 9 cm. After fourteen minutes the solvent has advanced a further 8 cm. How many cm from the origin is the blue spot likely to be?	26	8	18	15	15
different amino acids. If a particular amino acid has low solubility in the mobile phase used, then the amino acid	will have a low R <sub>f</sub> value.	will spend more time dissolved in the mobile phase than attached to the stationary phase.	must have a high molecular mass.	will move at a speed close to that of the solvent.	will have a low R <sub>r</sub> value.
Which of the following is the most suitable gas to use as a carrier gas in a gas chromatogram?	Helium	Oxygen	Methane	Carbon dioxide	Helium

A new youth drink contains sugar, salt, alcohol and vitamin C. A gas	alcohol content only.	alcohol, sugar and vitamin C content only.	concentration of all ingredients in the	alcohol and sugar content only.	alcohol content only.
chromatogram could be used to determine the			drink.		
components of a mixture is	by the components.	both stationary and mobile phases.	different mass in an electric field.	magnetic field.	stationary and mobile phases.
Acetone is an organic molecule with a semi-structural formula of CH <sub>3</sub> COCH <sub>3</sub> . A student runs a sample of acetone through a gas chromatogram at 50°C. The acetone produces a peak after 4.2 minutes. The student then injects a mixture of unknown organic substances into the same column at the same temperature. There are peaks after 3.1, 4.2 and 7.4 minutes. From this information. it can be concluded that	the mixture has three componenets, one of which must be acetone.	the mixture has at least three components, one of which might be acetone.	the mixture has at least three components, one of which must be acetone.	the mixture has three componenets, but acetone is not one of them.	the mixture has at least three components, one of which might be acetone.
A mixture of ethanior (L <sub>2</sub> n <sub>6</sub> O) and butanoi (L <sub>4</sub> n <sub>10</sub> O) is approximately 90% ethanol and 10% butanol. The mixture is passed through a gas liquid chromatogram. The printout obtained is likely to show that, compared to butanol, the ethanol has	a shorter retention time and a smaller area under the peak.	a shorter retention time and a larger area under the peak.	a longer retention time and a larger area under the peak.	a smaller retardation factor and a larger area under the peak.	a shorter retention time and a larger area under the peak.
High performance liquid chromatography (HPLC) cannot be used to	separate types of organic pesticides.	determine the mercury content of a fish sample.	identify the various pigments from a leaf extract.	determine the caffeine content of coffee samples.	determine the mercury content of a fish sample.
Which of the following statements about paper and gas chromatography is correct?	The $R_f$ and $R_t$ values of a substance are determined solely by the interaction of the substance with the stationary phase.	A substance with a long retention time in gas chromatography is likely to have a high $R_f$ value in paper chromatography.	A high $R_r$ value is indicative of a substance that adsorbs strongly onto the stationary phase.	A long retention time in gas chromatography is indicative of a substance with a strong adsorption on to the stationary phase.	d
The example of bulk property detector used in HPLC is	Refractive index detector	UV detector	fluorescence detector	UV-visible detector	а
In-vitro hydrolysis studies of drugs & kinetic studies of reaction can be performed					
by	Polarimetry	Refractometry	Potentiometry	Conductometry	Conductometry
The alkenes and aromatic compounds can be suitably detected using	Refractive index detector	conductivity detector	Spectrophotometric detector	Potentiometric detector	Spectrophotometric detector
Formic acid is an example of	protogenic solvent	protophillic solvent	amphiprotic solvent	Aprotic solvent	protogenic solvent
The relationship between concentration, temperature & potential of a solution is given by	Ilkovic equation	Henderson equation	Nernst equation	Hassalbach equation	Nernst equation
In refractometric analysis, if temperature is increased by 1 BC then refractive index decreases by	0.001 to 0.002	0.002 to 0.003	0.003 to 0.004	0.004 to 0.005	0.004 to 0.005
Sucrose can be determined after silylation using which chromatographic technique	HPLC	Gel chromatography	Gas liquid chromatography	Paper chromatography	Gas liquid chromatography
R <sub>f</sub> is refered as	retention time	retard factor	resistant value	reduced value	retention time
The composition of Silica gel G is	silica gel without binder	silica gel + CaSO <sub>4</sub>	Silica gel + alumina	silica gel + MaSO <sub>4</sub>	Silica gel + alumina
The formula for resolution (R) between peaks in gas chromatography is (where d = distance between peak 1 and 2; W1 and W2 are width of peak 1 and 2, respectively)	2d / (W1+W2)	d / (W1+W2)	2d / (W1-W2)	d / (W1-W2)	2d / (W1+W2)
Oxygenbe used as carrier gas in gas chromatography	can	cannot	often	always	can
Snells law is related to	Refractometry	Potentiometry	Non-aqueous titrations	Chromatography	Refractometry
Relative flow (Rf) value ranges from	0 to 1	0 to 2.0	+2 to -2	+1 to -1	0 to 1
Electrostatic attraction is a function present in chromatography	column	paper	ion exchange	gas	ion exchange
TLC means	thinlayer chromatography	thicklayer chromatography	thermolinear chromatography	therotical layer chromatography	thinlayer chromatography
The mechanism present in the ion exchange chromatography	reversible	irreversible	ionisation	bromination	reversible



### (Under Section 3 of UGC Act 1956)

### COIMBATORE-641 021

(For the candidates admitted from 2015 & onwards)

### **B.Sc. DEGREE EXAMINATION, JANUARY 2018**

### Sixth Semester

### CHEMISTRY PHYSICAL METHODS & CHEMICAL STRUCTURES

#### Date : .01.2018

Copies: 80 Nos

NO OF

Time: 2 Hours	Maximum : 50 mar		
PART- A	$(20 \times 1 = 20 \text{ Marks})$		

- A pentaatomic molecule having zero dipole moment and having a tetrahedral shape a. CCl<sub>4</sub> b. CH<sub>3</sub>Cl c. CH<sub>3</sub>Br d. CH<sub>3</sub>I
- 2. The isomer which shows zero value for dipole moment
  - a. Cis-dichloro ethane b. trans-dichloroethene c. chloroethene d. trichloro ethene
- The bond length of H-I is 1.60 A. Which of the following is the correct value for its dipole moment, if it were present in the completely ionic form
- a 7.68 D b. 3.00 D c. 3.20 D d. 2.77D
- 4 The shape of ammonia molecule is
- a Linear b. V shaped c. Tetrahedral d. Pyramidal

### 5. The dipole moment is zero for

- a Carbon dioxide b. ethyl bromide c. methyl iodide d. chlorobenzene
- 6. Dipole moment is a vector quantity ,since it has -----

a. direction only b. magnitude only c. direction and magnitude d. neither direction nor magnitude

- 7. The dipole moment if HF is
  - a. 2.0 b. 1.03 c. 0.78 d. 0.38
- 8. The high dipole moment of HF among hydrogen halides is due to

a.High electron affinity of fluorine b. Low electron affinity of fluorine c. very low electron affinity of fluorine d. no electron affinity of fluorine

- 9. Which compound will have lower dipole moment
  - a. ortho disubstituted compound b. m- disubstituted compound
  - c. p- disubstituted compound d. tri substituted compound
- The molar polarization is constant and independent of temperature for a.Nitrogen b. Nitro benzene c. chloroform d. HCl
- In Ebert's method, the polar molecules in gaseous state, (or liquid state) if subjected to electrical field, will suffer ------
- a. orientation polarisation only b. distortion polarisation only c.molar olarization only
- d both orientation and distortion polarization
- 12. Molar magnetic susceptibility is an

a. Intensive property b. Extensive property c. Additive property d. surface property

13. If the magnetic lines of force prefer to pass through the vacuum than through the substance comprising the medium, then value of  $\mu$  is

a. 1 b. 0 c. less than one d. greater than one

14. The magnetic moment per volume is called

a. Magnetic induction b. Magnetic susceptibility c. Magnetic permeability d. Intensity of magnetization

15. Gouy's method is used to determine

a Magnetic permeability b. Magnetic susceptibility c. Magnetic flux d. Intensity of magnetization

16. If the magnetic lines of force are repelled away from the substance, the substances are called

- a Diamagnetic b. paramagnetic c ferromagnetic d. Polymers
- 17. The value of atomic susceptibility of carbon atom is

a - 2.93 b. -6.00 c. -11.5 d. -30.6

18. One among the following is a polar molecule

a. H<sub>2</sub> b. CH<sub>4</sub> c. CCl<sub>4</sub> d. H-Cl

19. In dichloroethylene cis form has been found to have a dipole moment of -----

a 1.9D b. zero c. 1.2D d. 1.4D

289 (18) : 1917a

20. The materials having low retentivity are suitable for making

a. weak magnets b. temporary magnets c. permanent magnets d. Diamagnet

PART-B

### (3x10=30 Marks)

### ANSWER ALL THE QUESTIONS:

21. a. Describe Orientation polarization

b. What is dipole moment? How dipole moment is used to find the structure of molecules.

Or

22. a. How to determine magnetic susceptibility by Gouy's method.

b. Explain molar polarization in detail.

Lang Distantial

23. a. Discuss about polar and non-polar molecules.

Or

b. What is meant by magnetic moment, diamagnetism, paramagnetism and ferromagnetism

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