

# GENERAL CHEMISTRY

M.Sc., Chemistry 1st Year, PAPER - I

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# FOREWORD

Since its establishment in 1976, Acharya Nagarjuna University has been forging ahead in the path of progress and dynamism, offering a variety of courses and research contributions. I am extremely happy that by gaining a B++ (80-85) grade from the NAAC in the year 2003, the University has achieved recognition as one of the front rank universities in the country. At present Acharya Nagarjuna University is offering educational opportunities at the UG, PG levels apart from research degrees to students from about 300 affiliated colleges spread over the three districts of Guntur, Krishna and Prakasam.

The University has also started the Centre for Distance Education with the aim to bring higher education within reach of all. The Centre will be a great help to those who cannot join in colleges, those who cannot afford the exorbitant fees as regular students, and even housewives desirous of pursuing higher studies. With the goal of bringing education to the doorstep of all such people, Acharya Nagarjuna University has started offering B.A., and B.Com courses at the Degree level and M.A., M.Com., M.Sc., M.B.A. and L.L.M. courses at the PG level from the academic year 2003-2004 onwards.

To facilitate easier understanding by students studying through the distance mode, these self-instruction materials have been prepared by eminent and experienced teachers. The lessons have been drafted with great care and expertise within the stipulated time by these teachers. Constructive ideas and scholarly suggestions are welcome from students and teachers involved respectively. Such ideas will be incorporated for the greater efficacy of this distance mode of education. For clarification of doubts and feedback, weekly classes and contact classes will be arranged at the UG and PG levels respectively.

It is my aim that students getting higher education through the Centre for Distance Education should improve their qualification, have better employment opportunities and in turn facilitate the country's progress. It is my fond desire that in the years to come, the Centre for Distance Education will grow from strength to strength in the form of new courses and by catering to larger number of people. My congratulations to all the Directors, Academic Co-ordinators, Editors and Lesson - writers of the Centre who have helped in these endeavours.

**Smt. B. Udayalakshmi, IAS**  
Vice - Chancellor, (i/c)

Acharya Nagarjuna University

M. Sc., CHEMISTRY, 1st Year

**PAPER - I : GENERAL CHEMISTRY**

**SPECTROSCOPY, DATA TREATMENT AND COMPUTERS FOR CHEMISTS**

**SYLLABUS**

**Unit - I**

**Introduction to Molecular Spectroscopy:**

Nature of radiation, quantization of energy, energy of molecules, types of molecular spectroscopy. Sources of different radiation.

**Microwave Spectroscopy :** Rotational Spectra of diatomic molecules - quantized energy levels in the rigid rotor - allowed transitions between rotational energy levels, isotopic effect in rotation spectra, spectra of rigid rotor, spectra of non-rigid rotor, spectra of linear molecules., Basic principles of N.M.R. and E.S.R. Spectroscopy.

**Unit - II**

**Visible and Ultraviolet Spectroscopy :** Electronic Spectra of diatomic molecules, vibrational structure of an electronic transition, classification of bands, rotational fine structure of electronic vibrational transitions.

**Infra-Red Spectroscopy :** Vibrational spectra of diatomic molecules, simple harmonic oscillator, quantization of vibrational motion, vibration spectra of anharmonic oscillator, diatomic vibrating rotator, vibrational and rotational spectra of diatomic molecules.

**Unit III**

**Sampling and Treatment of Analytical Data**

**Sampling :** Theory of sampling, techniques of sampling, sampling of gases, liquids and solids, transmission and storage of samples., Accuracy - precision - standard error of the mean - Measure of precision of a mean and of a standard deviation - confidence intervals - Tests of significance - "t" test F test-rejection of data - significant figures and computation rules - control charts - Regression analysis., method of least squares, Errors: Types of errors in analysis, propagation of errors, minimisation of errors., Gaussian distribution - Application to a finite sample - measures of central value and dispersion

**Unit IV**

**Elements of Computer Programming :**

Basic components of computers, comparison of micro, main-frame and super computers.,

**MS-FORTRAN :**

Flow charts, constants in FORTRAN, arithmetic expressions, arithmetic statements, assignment and replacement statements.



Control statements in FORTRAN (Logical and Arithmetic IF statements, GOTO-statement), DO statements with one Inner loop, list directed INPUT and OUTPUT statements, READ and WRITE with I, F, E formats multi record formats.

**Programmes to be practised :**

1. Rate constant of a first order reaction or Beer's law by least squares method (derivation not needed).
2. Roots of a quadratic equation - application to hydrogen ion concentration of a strong acid.
3. Solving Vander-Waal's equation
4. Standard deviation and variance of univariate data.
5. Summing a power series.

**BOOKS SUGGESTED**

1. Modern Spectroscopy, J.M.Hollas, John Wiley.
2. Applied Electron Spectroscopy for Chemical Analysis Ed.H. Windawi and F.L.Ho, Wiley interscience.
3. Introduction to Molecular Spectroscopy, G.M.Barrow, McGraw Hill.
4. Fundamentals of Molecular Spectroscopy By C.N. Banwell.
5. Computational Chemistry, A.C.Norris.
6. Computer Programming in FORTRAN IV, V. Rajaraman, Prentice Hall.
7. Quantitative Analysis -R.A.Day, Jr.and A.L.Underwood, Prentice Hall

M.Sc. (Previous) Degree Examination, May 2006  
First Year  
**Chemistry**  
**Paper I - GENERAL CHEMISTRY**

Time : Three hours

Maximum : 100 marks

**PART A - (4 x 10 = 40 marks)**

Answer any FOUR Questions.

1. What are the various forms of radiation and how are their energies quantized? Mention the forms of radiations used in molecular spectroscopy.
2. Discuss the quantized energy levels in the rigid rotor.
3. Mention and explain various forms of molecular vibrations.
4. Explain in rotational fine structure of electronic vibrational transitions.
5. Discuss the tests of significance with examples.
6. What is Gaussian distribution and what is its significance in least squares analysis?
7. Mention the functions of various hardware components of microcomputers.
8. Explain the working of logical IF. Write a program using logical IF.

**PART B - 4 x 15 = 60 marks)**

9. (a) Write the basic principles of NMR and ESR. Write the similarities and differences between the two techniques.  
Or  
(b) Interpret the microwave spectra of non-rigid rotors.
10. (a) Write an essay on anharmonic oscillator, with some typical examples.  
Or  
(b) Discuss the electronic spectra of diatomic molecules and assign the bands with various types of electronic transitions.
11. (a) Explain the theory and technique of sampling.  
Or  
(b) Write an essay on types of errors and remedies for them.
12. (a) Write an essay on control statements in FORTRAN. Explain their usage.  
Or  
(b) Write a Computer program in FORTRAN for solving van der Waals equation, with the help of a flow chart.

M.Sc.(Previous) DEGREE EXAMINATION, DECEMBER 2006

CHEMISTRY :: FIRST YEAR

Paper I - GENERAL CHEMISTRY

Time : Three hours

Maximum : 100 marks

PART A - ( 4 x 10 = 40 marks)

Answer any FOUR questions.

1. Explain the terms chemical shift and spin-spin splitting in NMR spectroscopy.
2. Discuss the allowed transitions between rotational energy levels.
3. Write a note on simple harmonic oscillator.
4. Discuss the classification of bands in Electronic spectroscopy.
5. Define, explain and compare accuracy and precision.
6. Write a note on regression analysis.
7. What are super computers and what are their applications?
8. Discuss the usage of various input and output statements in FORTRAN programming.

PART B - (4 x 15 = 60 marks)

Answer ALL questions.

9. (a) What is the isotopic effect on rotational spectra?  
(b) Discuss the quantized energy levels in the rigid rotor.  
Or  
(c) Compare the spectra of rigid rotor and non-rigid rotor.
10. (a) Write in detail the electronic spectra of diatomic molecules.  
Or  
(b) Explain the vibrational spectra of anharmonic oscillator.
11. (a) Discuss various methods of sampling of gases, liquids and solids.  
Or  
(b) Explain the terms:  
(i) Confidence intervals      (ii) Method of least squares      (iii) Gaussian distribution
12. (a) With the help of a flow chart, write a computer program in FORTRAN for the calculation of standard deviation and variance of univariate data.  
Or  
(b) With the help of a flow chart, Write a computer program in FORTRAN for the calculation of rate constant of a first order chemical reaction using least squares method.

(DCHE 01)

**M.Sc. (Previous) Chemistry DEGREE EXAMINATION, MAY 2007**

**Paper I - GENERAL CHEMISTRY**

Time : Three hours

Maximum : 100 marks

**PART A - (4 x 10 = 40 marks)**

Answer any FOUR questions

1. Discuss the types of molecular spectroscopic techniques and the sources of radiations used in them
2. Mention the basic principles of NMR and ESR techniques.
3. Write a note on electronic spectra of diatomic molecules.
4. Illustrate vibrational spectra of an harmonic oscillator.
5. Discuss the theory and techniques of sampling.
6. What is Gaussian distribution ? Discuss its applications.
7. Write a note on Computer Hardware.
8. Discuss the statements relevant to input and output of a computer program written in MS-FORTRAN.

**PART B - (4 x 15 = 60 marks)**

Answer ALL questions.

9. (a) Discuss the rotational spectra of diatomic molecules using rigid rotor model.  
Or  
(b) What are the selection rules for microwave spectroscopy ?  
(c) What is the isotopic effect on rotational spectra ?
10. (a) Describe the principle, selection rules and applications of vibrational spectroscopy.  
Or  
(b) Discuss the principle and applications of UV-visible spectroscopy.
11. (a) What are the various types of errors found sampling and data analysis and how are they minimized ?  
Or  
(b) Write an essay on regression analysis.
12. (a) Write a computer program in MS-FORTRAN for solving vander Waals equation.  
Or  
(b) Write a flow chart and computer program in MS-FORTRAN for the application of Beer's law by least square method.

(DCHE 01)

M.Sc. (Previous) Chemistry, DEGREE EXAMINATION, DECEMBER 2007.  
Paper I — GENERAL CHEMISTRY

Time : Three hours

Maximum : 100 marks

PART A — (4 × 10 = 40 marks)

Answer any FOUR questions.

1. NMR and ESR spectroscopies are complementary to each other. Explain.
2. Describe the quantized energy levels in the rigid rotor model.
3. Discuss the rotational fine structure of vibronic transitions.
4. Explain the nature of vibrational spectra of simple harmonic oscillator.
5. Explain the terms standard deviation, confidence interval and F-test. Mention their significance.
6. Discuss the methods to be adopted for minimization of errors.
7. Write a note on control statements in FORTRAN.
8. Write a flow chart and source code in MS FORTRAN for the determination of rate constant.

PART B — (4 × 15 = 60 marks)

Answer ALL questions.

9. (a) Discuss the instrumentation and applications of microwave spectroscopy.  
Or  
(b) Mention the theory behind rotational spectroscopy.
10. (a) How is infrared spectroscopy useful in identifying the compounds?  
Or  
(b) Write an essay on electronic spectroscopy of transition metal complexes.
11. (a) Describe the theory and techniques of sampling.  
Or  
(b) Discuss the role of statistical parameters in data analysis.
12. (a) Write the salient features of MS FORTRAN.  
Or  
(b) Write flow charts and source code in MS FORTRAN for the calculation of standard deviation and variance of univariate data.

(DCHE 01)

M.Sc. Chemistry (Previous) DEGREE EXAMINATION, MAY 2008.  
Paper I — GENERAL CHEMISTRY

Time : Three hours

Maximum : 100 marks

PART A — (4 × 10 = 40 marks)

Answer any FOUR questions.

1. Explain the allowed transitions between rotational energy levels.
2. Write short notes on ESR spectroscopy.
3. What is simple harmonic oscillator? Explain.
4. Write short notes on visible and ultraviolet spectroscopy.
5. Write short notes on Accuracy and Precision.
6. Explain the significance of 't' test and 'F' test.
7. Write short notes on super computers and applications of super computers.
8. Explain the basic components of a computer. Write a program for solving vander Waals equation.

PART B — (4 × 15 = 60 marks)

Answer ALL questions.

9. (a) What is the isotropic effect in rotational spectra? Compare the spectra of rigid rotor and non-rigid rotor.

Or

- (b) Explain the Rotational spectra of diatomic molecules. Discuss the Quantized energy levels in the rigid rotor.

10. (a) Explain the electronic spectra of diatomic molecules.

Or

- (b) Write short notes on Infra-red spectroscopy and its applications.

11. (a) Explain the various methods of sampling of gases, liquids and solids.

Or

- (b) Explain the terms :

(i) Regression analysis.

(ii) Gaussian distribution.

(iii) Significant Figures.

12. (a) Explain with the help of a flow chart, write a program in 'FORTRAN' for the calculation of rate constant of a first order chemical reaction using least squares method.

Or

- (b) Write programmes for

(i) Roots of a quadratic equation (ii) Solving vander- Waals equation

(iii) Standard deviation.

M.Sc. Chemistry (Previous) DEGREE EXAMINATION, DECEMBER 2008.  
Paper I — GENERAL CHEMISTRY

Time : Three hours

Maximum : 100 marks

PART A — (4 × 10 = 40 marks)

Answer any FOUR questions.

1. Write short notes on Rotational Spectra of diatomic molecules.
2. Explain the basic principle and applications of NMR spectroscopy.
3. Discuss the 'Classification of bands' in Electronic spectroscopy.
4. Write short note on vibrational spectra of an harmonic Oscillator.
5. Explain the methods of sampling of gases, liquids and solids.
6. Write short notes on regression analysis.
7. Explain the usage of various INPUT and OUTPUT statements in 'FORTRAN' Programming.
8. Explain the following micro, main Frame and super computers.

PART B — (4 × 15 = 60 marks)

9. (a) What is molecular spectroscopy? Explain the types of molecular spectroscopy and sources of different radiation.

Or

- (b) What is the Isotopic effect in rotational spectra? Compare the spectra of rigid rotor and non-rigid rotor.

10. (a) Explain the vibrational and rotational spectra of diatomic molecules.

Or

- (b) Write short notes on Electronic spectra of diatomic molecules and vibrational structure of an electronic transition.

11. (a) Write short notes on types of errors in analysis, propagation of errors, minimisation errors and Gaussian distribution.

Or

- (b) Explain the following :  
(i) Confidence intervals.  
(ii) Method of least squares.  
(iii) Accuracy and precision.

12. (a) Draw the Schematic diagram of a Basic computer and explain the functions of each component.

Or

- (b) Explain with the help of a flow chart, Write a computer program in 'FORTRAN' for the calculation of standard deviation and variance of univariate data.

M.Sc. Chemistry (Previous) DEGREE EXAMINATION, MAY 2009.  
Paper I — GENERAL CHEMISTRY

Time : Three hours

Maximum : 100 marks

PART A — (4 × 10 = 40 marks)  
Answer any FOUR questions.

1. Write a note on the energy of molecules in molecular spectroscopy.
2. Mention the basic principle of NMR and ESR techniques.
3. Describe the electronic transitions in UV and Visible spectroscopy.
4. Describe the quantization of vibrational motor in I.R. spectroscopy.
5. Write a note on the tests of significance.
6. Explain the regression analysis.
7. Describe the basic components of computers.
8. Write a Fortran programme for summing a power series.

PART B — (4 × 15 = 60 marks)  
Answer ALL questions.

9. (a) Explain the quantization of energy and sources of different radiation in molecular spectroscopy.

Or

- (b) Describe the basic principles of ESR spectroscopy.
10. (a) Explain the analytical applications of UV and visible spectroscopy with suitable examples.

Or

- (b) Explain the vibrational and rotational spectra of diatomic molecules.
11. (a) Describe the various methods of sampling of liquids and solids.

Or

- (b) Write short notes on :  
(i) Types of errors in analysis.  
(ii) Gaussian distribution.
12. (a) Describe the arithmetic expressions and arithmetic statements in Fortran.

Or

- (b) Write programmes for  
(i) Rate constant of a first order reaction.  
(ii) Solving Vander-Waals equations.



(DCHE 01)

M.Sc. Chemistry, (Previous) DEGREE EXAMINATION, DECEMBER 2009.

Paper I — GENERAL CHEMISTRY

Time : Three hours

Maximum : 100 marks

PART A — (4 × 10 = 40 marks)

Answer any FOUR questions.

1. Explain the rotational selection rules for linear, symmetric and asymmetric top molecules.
2. Write notes on the different types of bands which originate as a result of electronic transitions.
3. Explain the basic principles of NMR spectroscopy.
4. What is the effect of isotopic substitution in the study of rotational spectroscopy?
5. Explain the various techniques of sampling.
6. Write notes on student's t test and F-test.
7. What are conditional and unconditional statements? Describe the function of arithmetic, logical and block if statements.
8. Write the flow chart and Fortran program for calculating rate constant of a first order reaction using linear least squares method.

PART B — (4 × 15 = 60 marks)

Answer ALL questions.

9. (a) Compare the spectra of rigid rotor and non-rigid rotor.  
Or  
(b) Discuss the origin and significance of hyperfine coupling in ESR spectroscopy.
10. (a) Write notes on visible and ultraviolet spectroscopy.  
Or  
(b) (i) Write notes on vibrational spectra of anharmonic oscillator.  
(ii) Write the selection rules and explain the transitions in rotational-vibrational spectra.
11. (a) Write notes on :  
(i) Accuracy and precision (ii) Propagation of errors in analysis.  
Or  
(b) (i) Determinate and indeterminate errors. (ii) Regression analysis.
12. (a) With the help of a flow chart, write the important steps of a Fortran programme for obtaining hydrogen ion concentration of a strong acid.  
Or  
(b) Discuss arithmetic operations and hierarchy rules for IF, GO and DO statements.

(DCHE 01)

M.Sc. Chemistry (Previous) DEGREE EXAMINATION, JUNE 2010.

Paper I — GENERAL CHEMISTRY

Time : Three hours

Maximum : 100 marks

PART A — (4 × 10 = 40 marks)

Answer any FOUR questions.

1. Explain the nature of radiations in Molecular Spectroscopy.
2. Write a note on the isotopic effect in rotation spectra.
3. Describe the classification of bonds in UV and visible spectroscopy.
4. Explain the basic principles of I.R. Spectroscopy.
5. Discuss on T and F tests.
6. Give an account on theory of sampling.
7. Write a note on super-computers.
8. Explain the importance of a flow chart in FORTRAN with an example.

PART B — (4 × 15 = 60 marks)

Answer ALL questions.

9. (a) Explain the different types of molecular spectroscopy.  
Or  
(b) Describe the basic principles of NMR spectroscopy.
10. (a) Discuss on the electronic spectra of diatomic molecules.  
Or  
(b) Explain the basic principles of I.R. Spectroscopy and its applications in general chemistry.
11. (a) Write short notes on accuracy and precision and explain regression analysis.  
Or  
(b) Explain in detail about the types of errors in analysis.
12. (a) Describe the flow chart and FORTRAN programme for Beer's law by least squares method.  
Or  
(b) Discuss on the control statements in FORTRAN.

(DCHE 01)

M.Sc. Chemistry (Previous) DEGREE EXAMINATION, DECEMBER 2010.  
Paper I — GENERAL CHEMISTRY

Time : Three hours

Maximum : 100 marks

PART A — (4 × 10 = 40 marks)

Answer any FOUR questions.

1. Write notes on the spectra of rigid rotor.
2. Explain the basic principles of NMR spectroscopy.
3. What is the effect of isotopic substitution in the study of rotational spectroscopy?
4. Discuss the vibrational spectra of a harmonic oscillator.
5. Write notes on regression analysis and Gaussian distribution.
6. What are absolute and relative errors? How are they propagated?
7. What is the difference between an arithmetic statement and arithmetic expression? Explain how integer mode, real mode and mixed mode expressions are evaluated.
8. Write a Fortran program for summing a power series.

PART B — (4 × 15 = 60 marks)

Answer ALL questions.

9. (a) Write notes on spectra of rigid rotor and non-rigid rotor.  
Or  
(b) Explain the basic principles of ESR spectroscopy and discuss the significance of hyperfine coupling.
10. (a) Discuss the vibrational-rotational spectra of a diatomic molecule.  
Or  
(b) Explain the electronic spectra of diatomic molecules.
11. (a) Explain the terms precision and accuracy. Describe the various factors that quantify precision and accuracy.  
Or  
(b) Write notes on student's t-test and F-test.
12. (a) Write a flow chart and Fortran program for calculation of rate constant of a first order reaction.  
Or  
(b) What are control statements? Explain the syntax and use of conditional/unconditional statements.

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### GOLD MEDALS FOR MERITORIOUS STUDENTS OF CDE

**Prof. J. Ananthaswamy Memorial Gold Medal** for securing the highest number of marks in aggregate having passed **M.Sc. Chemistry** Examination at the first appearance under Distance Mode, offered by the Centre for Distance Education, Acharya Nagarjuna University.

# Lesson I Introduction To Molecular Spectroscopy

## Objectives

Introduction

Nature of radiation

Quantization of energy

Motions and Energy of molecules

Types of molecular spectroscopy

Sources of radiation .

### 1.1.i) Introduction:

In a study of molecular spectroscopy, we shall find that the principal tools used to obtain spectra do so by measuring the absorption of electromagnetic radiation by the molecules from an incident beam. It is important then, to consider the way in which one can describe this radiation. In general electromagnetic radiation is a term applied to the different types of radiation ranging from X-rays (short wave length) to radio waves (long wave length). These different regions taken together give rise to what is known as the Electromagnetic Spectrum.

### 1.1.ii) Nature of Radiation:

The radiation is pictured as travelling in space and time in the form of a wave. This wave nature is shown in fig: 1.1. The electric field intensity  $E$  of the wave arising from a source of radiation is plotted on the ordinate. The displacement  $x$  and the time  $t$  are plotted as abscissas. Both  $x$  and  $t$  are measured at a point distance from the source, compare the wavelength of the light. The wave extends from  $x=t=-\infty$  to  $x=t=+\infty$  in a continuous manner.

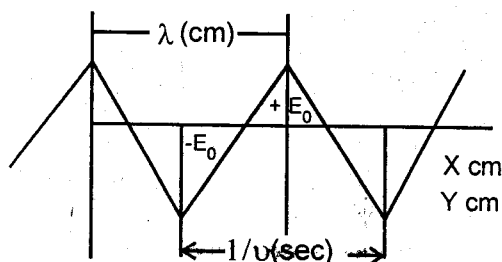


Fig: 1.1 wave nature of electromagnetic radiation.

The value of  $E$  repeats periodically in both  $x$  and  $t$ , as can be seen by the repetition of the maximum and minimum values of  $E$  in the figure. A wave with these properties is said to vary sinusoidally with both the displacement  $x$  and the time  $t$ . These wave properties can be represented by the equation.

$$E = E_0 \cos 2\pi \left( \nu t - \frac{x}{\lambda} \right) \text{ ----- (1.1)}$$

Where  $E$  = Electric field

$E_0$  = maximum displacement or amplitude

$\nu$  = frequency

$\lambda$  = wave length

(a) **Wavelength** : It is denoted by  $\lambda$ . And is the distance between two successive peaks of wave (fig: 1.1) that is the length of one wave.

Consider first the wave propagation at some arbitrary time ( $t = 0$ ), the equation 1.1 becomes

$$E = E_0 \cos(-2\pi x / \lambda) \text{ ----- (1.2)}$$

From trigonometry for any angle  $\theta$ ,  $\cos(-\theta) = \cos(\theta)$

$$E = E_0 \cos\left(\frac{2\pi x}{\lambda}\right) \text{ ----- (1.3)}$$

Now, vary  $x$  from  $x_1$  to  $x_1 + \lambda$ , then

$$E_{x_1} = E_0 \cos\frac{2\pi x_1}{\lambda} \text{ ----- (1.4a)}$$

$$E_{x_1 + \lambda} = E_0 \cos 2\pi \left( x_1 + \frac{\lambda}{\lambda} \right)$$

$$= E_0 \cos\left(\frac{2\pi x_1}{\lambda} + 2\pi\right) \text{ ----- (1.4b)}$$

From equation 1.4a and 1.4b, the effect of increasing  $x_1$  by the amount  $\lambda$ , is simply to increase the angle by  $2\pi$  ( $360^\circ$ ) i.e. the wave passes to complete one cycle. This shows that the wavelength  $\lambda$  is the distance correspond to one cycle of the variation of the electric field. So  $\lambda$  is measured in units of length normally in centimeters, cm. The other units are :

1. Angstrom

$$A^0 (1A^0 = 10^{-8} \text{ cm} = 10^{-10} \text{ m})$$

2. Nanometres  $\text{nm} (1 \text{ nm} = 1 \text{ m}\mu = 10^{-7} \text{ cm} = 10^{-9} \text{ m} = 10 \text{ \AA})$

3. Milli micron  $\text{m}\mu (1 \text{ nm} = 1 \text{ m}\mu = 10^{-7} \text{ cm} = 10^{-9} \text{ m} = 10 \text{ \AA})$

4. Micron  $\mu (1 \mu = 10^{-4} \text{ cm} = 10^{-6} \text{ m})$

**(b) Frequency:** It is denoted by  $\nu$  and is the number of cycles through which the wave goes per unit time. The meaning of  $\nu$  can be obtained in similar way by considering the wave propagation at some arbitrary point,  $x = 0$ . Using this equation 1.1 can be written as

$$E = E_0 \cos 2\pi \nu t \quad \text{-----} \quad (1.5)$$

Consider the change  $t_1$  to  $t_1 + \frac{1}{\nu}$ . Substituting the value for  $t$  in equation 1.5, it will show that the value of electric field will go through a complete cycle. i.e.  $E$  varies from  $+E_0$  through  $-E_0$  in one complete cycle.  $\frac{1}{\nu}$  is the period of wave motion and reciprocal of this quantity is  $\nu$ .

The unit of frequency is cycles per second (Hz). One cycle per second is some times called Hertz. A common unit is mega cycle per second or mega Hertz (M Hz). One mega Hertz =  $10^6$  cycles per second.

$\nu$  is the direct measure of energy since  $E = h\nu$ .

**(c) Velocity of light:** It is denoted by  $c$  and is the velocity of propagation of the wave, it is the number of waves passing any point in a given time, multiplied by the length of a single wave. In terms of  $\lambda$  and  $\nu$ . This definition yields for  $c$ , the velocity of Electromagnetic radiation

$$c = \nu \lambda, \nu = \frac{c}{\lambda} \text{ or } \lambda = \frac{c}{\nu} \quad \text{----} \quad (1.6)$$

The velocity has the constant value of  $3 \times 10^{10} \text{ cm. sec}^{-1}$  for all forms of radiation. The equation 1.6 shows that  $\nu$  and  $\lambda$  are inversely related.

**(d) Wave number:** It is denoted by  $\bar{\nu}$ . The wave number is proportional to the frequency. The proportionality constant being the velocity of light.

$$\nu = c \bar{\nu} \quad \text{-----} \quad (1.7)$$

The reason for defining  $\bar{\nu} \propto \nu$  will become clear when we consider energy from 1.6 one has  $\frac{\nu}{c} = \frac{1}{\lambda}$ , and therefore

$$\bar{\nu} = \frac{1}{\lambda} \quad (1.8)$$

The units of wave number are then reciprocal centimeters or  $\text{cm}^{-1}$  or Kariser.

### 1.1.ii) Electromagnetic Radiation:

Radiant energy is the energy transmitted from one body to another in the form of radiation. The term radiation includes electromagnetic vibration ranging from the electric waves of low frequency through U.V. rays, visible and infrared rays to the high frequency X - rays and  $\gamma$  - rays. According to Maxwell (1864), an alternating current of high frequency radiates in the form of waves, which travel in space with the same speed as that of light and these waves are known as electromagnetic waves or electromagnetic radiation.

### 1.1.iii) Regions of Electromagnetic Spectrum:

When a narrow beam of light is allowed to pass through a prism or grating, it is dispersed in to seven colors from red to violet and the set of colors or bands produced is called spectrum . Various regions of electromagnetic spectrum are given in table 1.1

**Table:1.1 regions of electromagnetic spectrum**

Region	Wavelength( $\text{A}^\circ$ )	FrequencyHz(cps)	Energy erg.
Radio waves	$10^3$	$3 \times 10^5$	$2 \times 10^{-21}$
MicroWaves	$10^9$	$3 \times 10^9$	$2 \times 10^{-17}$
Infrared	$10^6$	$5 \times 10^{11}$	$2 \times 10^{-16}$
Visible	7600	$4 \times 10^{14}$	$3 \times 10^{-12}$
Ultraviolet	3800	$7.9 \times 10^{14}$	$5 \times 10^{-12}$
X-rays	150	$2 \times 10^{16}$	$9 \times 10^{-10}$
$\gamma$ - rays	1	$3 \times 10^{18}$	$2 \times 10^{-8}$

### 1.1.iv) Quantization of Energy:

The earlier discussion of radiation assumes that the radiation is a wave with infinite extension in space and is characterized by a definite wavelength and frequency. Experiments with black-body radiation and photo-electric effect led to an alternate model of radiation. In order to explain the observation in the black body radiation experiments, Planck was forced to break away



from the previously hold view that the energy of the radiation could take on any value in the continuous manner. Planck (1900) assumed that radiation energy was not continuous, but could exists only in discrete multiples of a fundamental unit of energy, now called the quantum of energy. The magnitude of the quantum of energy  $E$  was shown by Planck to be directly proportional to the frequency of the radiation, i.e

$$E = h\nu \quad \text{--- (1.9)}$$

Where the proportionality constant  $h$ , known as Plancks constant has the value  $6.625 \times 10^{-27}$  ergs.sec.

Einstein, after successful explanation of photoelectric effect by Plancks quantum theory, postulated that radiation of given frequency consisted of energy packets called photons are propagated with the velocity of light. The interpretation of radiation as discrete quanta proved to be a powerful one in explaining the observed spectra of atoms .A simple experimental method for studying the spectrum of hydrogen atoms is shown in fig: 1.2.

A hydrogen discharge lamp, containing a hydrogen gas at low pressure, is energized by an external source of high voltage. This causes  $H_2$  molecules to dissociate in to hydrogen atoms, and these atoms are excited and emit light. This radiation formed into well defined beam by the entrance slit, made parallel by the lens. The collimated beam then falls on the dispersing element, prism. The prism disperses the radiation i.e. it spreads out the incident radiation is again collimated by lens and slit and falls on the detector.

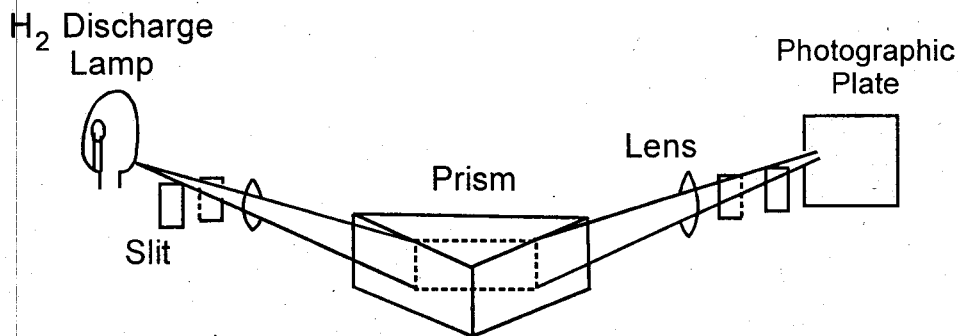


Fig : 1.2 A simple spectrograph.

Hydrogen Atom Spectrum consists of Lyman series , Balmer series, Paschan series, Bracket series and Pfund series of lines.

### 1.1.v) Motions and Energy of Molecules:

Let us consider in detail the nature of the molecular motions and the manner in which energy can be distributed among the various modes of motion. For this discussion we consider the state of matter in which the molecules composing the substance have minimum interaction .

#### Degrees of freedom :

The number of degrees of freedom that any body possess is related to the number of

independent coordinates needed to specify the position in space.

*For example :* Spherical ball to move randomly in space would require all the three cartesian coordinates X, Y, Z to specify its position. So spherical ball is said to have three degrees of freedom.

For a molecule with N atoms, the total number of degrees of freedom is equal to  $3N$ . The energy taken up by each degree of freedom is  $\frac{1}{2}kT$ , where k is Boltzman constant ( $1.38 \times 10^{-16} \text{ erg/}^{\circ}\text{K}$ ), T is the absolute temperature

**Types of Motion and Distribution of degrees of freedom:**

- (1) **Translational motion:** In a molecule, each atom is not free to move independently of others i.e., the molecule translates as a whole. Hence one can describe the translational motion of the entire molecule in terms of the three coordinates of the center of mass, the point in the mol. where all the mass can be considered to be concentrated. The number of translated degrees of freedom for mono atomic or poly atomic molecule is 3. The motions are shown in Fig:1.3 for non-linear tri atomic molecule.

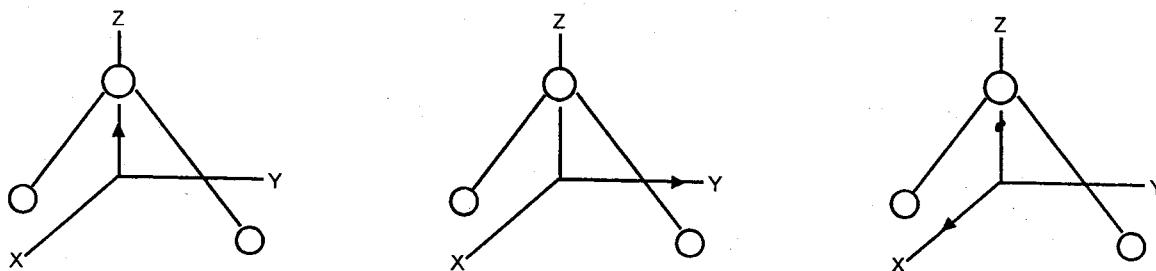


Fig. 1.3

- (2) **Rotational motion:** This is the internal mode of motion. The number of degrees of freedom left after translational motion is  $3N - 3$ , i.e. for triatomic molecule  $9 - 3 = 6$ . For rotational motion of linear molecule, the number of degrees of freedom are two, because motion about the, molecular axis will not contribute to the rotational energy of the molecule. The two degrees of freedom are shown in fig:1.4

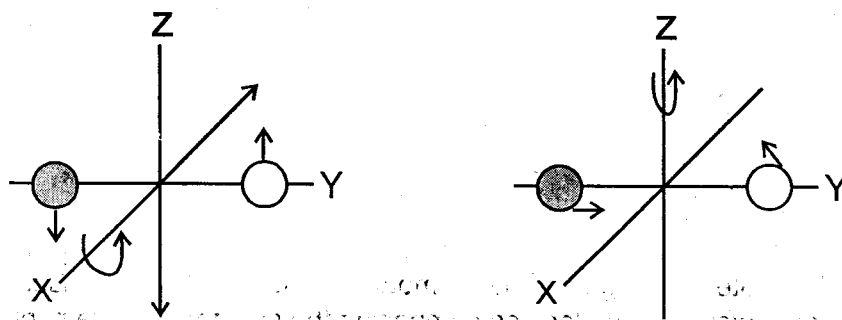


Fig : 1.4

For a non-linear triatomic molecule, the rotational degrees of freedom are three.

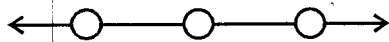
**(3) Vibrational motion:** This is also the internal mode of motion. The number of degrees of freedom left after rotational and translational motion of triatomic molecule is

For linear molecule  $9 - 5 = 4$ .

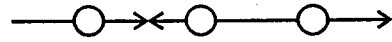
Non-linear molecule  $9 - 6 = 3$ .

The vibration modes for linear  $\text{CO}_2$  and non-linear  $\text{SO}_2$  are in shown in fig: 1.5 and 1.6 respectively.

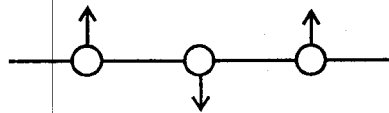
For  $\text{CO}_2$



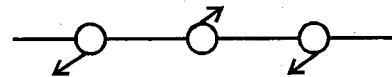
1. Symmetric stretching



2. Asymmetric stretching



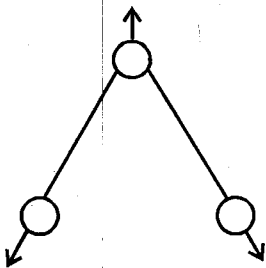
3. Inplane bending



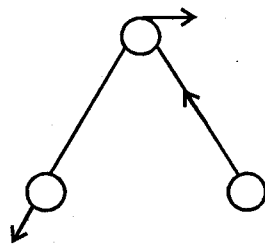
4. Out plane bending

Fig. 1.5

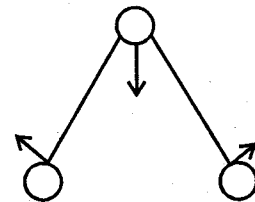
For  $\text{SO}_2$



1. Symmetric stretching



2. Asymmetric stretching



3. Bending

Fig. 1.6

**Energy of molecules:**

Energy for translational motion is given by

$$(K E)_{\text{tran}} = \frac{m u_x^2}{2} \dots\dots\dots (1.10)$$

Where  $m = \text{mass}$

$u_x = \text{component velocity of the particle in the X-direction}$

Energy for rotational motion is given by

$$(K E)_{\text{rot}} = \frac{I_x \omega_x^2}{2} \dots\dots\dots (1.11)$$

where  $I_x$  = moment of inertia

$\omega_x$  = angular velocity along X-direction.

Energy of vibrational motion is due to Kinetic energy as well as potential energy is given by

$$(K E)_{\text{vib}} = \frac{\mu u^2}{2} \dots\dots\dots (1.12)$$

where  $\mu$  = reduced mass =  $\frac{m_1 m_2}{m_1 + m_2}$

$u$  = vibrational velocity

$$(P.E.)_{\text{vib}} = \frac{K X^2}{2} \dots\dots\dots (1.13)$$

where  $X$  = displacement in the X - direction

$K$  = Force constant

The force constant is a measure of the ease with which the bond can be stretched or bent, the larger the  $K$ , the more stiff is the bond .

### Equipartition of energy principle:

When a molecule takes up energy, this energy is distributed into each of independent ways in which the molecule can absorb energy, i.e into each of the various modes of motion that the molecule can perform .

For a large number of mols, all the three energy terms have same average value but depends only on temperature.

### 1.1.vi) Types of molecular spectroscopy:

The vibrational, rotational and electronic motion of a molecule give quantised energy levels and that the absorbed spectra arise from allowed transitions between these levels. When a radiation of certain wavelength is passed through a sample, quanta energy are absorbed by the molecules of the sample. This energy can increase either the rotational, vibrational or electronic energy from one quantised level to another. The type of molecular energy that will increase depends on the energy of the radiation used .The spacing between adjacent levels increase in the order Rotational < Vibrational < Electronic

This means that lower energy is required to promote the molecules to higher rotational energy levels that is needed for either the vibrational or electronic transitions. This result in spectra due to rotational transitions require lower energy or lower frequency (longer  $\lambda$ ) than vibrational spectra. The experimental region in which these spectra occur are shown in Table 1.2.

Table: 1. 2.

Type of spectrum	Energy transition observed	Exptal $\lambda$ region
1. Rotation	Rotation	Microwave and far I.R
2. Vibration	Vibration and rotation	Infrared
3. Electronic	Vibration, rotation and electronic	Visible and Ultraviolet.

Molecular spectrum also called as band spectrum since bands are obtained in the spectrum and it is characteristic of molecule. Each band consists of band head (at long  $\lambda$ ) and shade or diffuse (at short  $\lambda$ ).

### 1.1.vii) Sources of Radiation:

The characteristics of the source of radiation are -

- It must generate a beam with sufficient power for ready detection and measurement.
- The source should provide continuous radiation in the region being studied.
- The source should be stable.
- The source must emit a measurable signal through out the region.

The sources for different radiations are -

- Visible** : Incandescent tungsten filament lamp, emitting capacity of which depends upon temperature of the filament and up on  $\lambda$  of emitted radiant energy.
- Ultra violet** : Hydrogen gas lamp and deuterium lamp.
- Infrared** : Nerst glower and globar, Nichrome wire coil. For near IR tungsten filament lamp.
- Absorption spectra** : (continuous source) - Incandescent and electric discharge in relatively high pressure gas of Xe or H<sub>2</sub> or O<sub>2</sub> etc.
- For discrete  $\lambda$ 's (line sources)** : An arc discharge in a gas containing excited metallic vapour or a noble gas.
- Lasers (visible or IR)** : Ruby laser consists of a carefully ground rod of ruby (Al<sub>2</sub>O<sub>3</sub>+Cr<sub>2</sub>O<sub>3</sub>) with parallel ends.

## 1.1.viii) problems:

1. Calculate the translational kinetic energy at 25°C and 35°C for a linear molecule.

Number of translational degrees of freedom = 3

Energy of each degree of freedom =  $1/2 kT$

$$\text{Therefore at 25°C energy i.e (T = 273+25)} = 3 \times 1/2 \times 1.38 \times 10^{-16} \times 298 \\ = 6.1686 \times 10^{-14}$$

$$\text{therefore at 35°C energy i.e (T = 273+35)} = 3 \times 1/2 \times 1.38 \times 10^{-16} \times 308 \\ = 6.3756 \times 10^{-14}$$

2. Calculate Wave number,  $\bar{\nu}$  of the radiation, if frequency is  $2.06 \times 10^{14}$  Hz

$$\nu = \frac{c}{\lambda} \quad \text{but} \quad \bar{\nu} = \frac{1}{\lambda} \quad \text{hence} \quad \bar{\nu} = \frac{\nu}{c}$$

$$\bar{\nu} = \frac{2.06 \times 10^{14}}{3 \times 10^{10}} = 6866 \text{ cm}^{-1}$$

3. Calculate the  $\nu$  and  $\bar{\nu}$  of the radiation where  $\lambda$  is 400 nm.

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^{10}}{4 \times 10^{-5}} = 7.5 \times 10^{15} \text{ Hz}$$

(  $\lambda$  is to be converted to be in cm in calculation )

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{4} \times 10^{-5} = 0.25 \times 10^5 \text{ cm}^{-1}$$

4. Calculate the energy of the molecule if  $\lambda$  is  $6 \times 10^4 \text{ \AA}$

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^{10}}{6 \times 10^4 \times 10^{-8}} = 5 \times 10^{13} \text{ Hz}$$

$$E = h\nu$$

The total energy absorbed one mol of gas is

$$E = N h \nu \quad \text{where N is avagadro number}$$

$$= (6.02 \times 10^{23}) (6.62 \times 10^{-27}) (5 \times 10^{13})$$

$$= 1.99 \times 10^{11} \text{ ergs.}$$

**1.1.ix) Model questions :**

1. Define frequency, wavelength and wave number. What is the relation of velocity with  $\nu$  or  $\lambda$ .
2. Write the units for  $\lambda$ ,  $\nu$ ,  $\bar{\nu}$ . Calculate the quantum energy for the radiation with the  $\lambda$  is 100 nm.
3. Mention different types of motions the molecule can perform and mention the no. of degrees of freedom associated with them.
4. What is equipartition energy principle ? write the energy expression for different motions in molecules.
5. Discuss the sources of radiation.
6. Define the electromagnetic radiation .Narrate different regions of radiation.
7. What is quantisation of energy ? Discuss about different types of spectra of the molecules.

**Recommended Books:**

- A.J. Sonessa : Introduction to molecular spectroscopy.  
B.K.Sharma : Spectroscopy,  
C.N.Banwell : Fundamentals of molecular spectroscopy.

## Objectives

- Introduction
- Rigid rotator model
- Quantisation of energy levels
- Allowed transition
- Selection rules of rotational spectra
- Isotopic effect
- Non-rigid rotator model
- Poly atomic molecular spectra

### 1.2.i. Introduction:

The molecule perform rotational motion at lower energy of radiation region i.e  $4 \times 10^{-4}$  (is the lower wavelength region). When this energy absorbed by the molecules, it can cause transition only from the rotational level to another. The spectrum obtained is known as rotational spectrum. These spectra are observed far infrared or microwave region. That is why it is called as microwave spectroscopy.

### 1.2.ii. Rigid rotator model:

Let us consider a diatomic molecule which may be regarded as rigid rotator i.e a rigid dumbbell (rigid bar) joined along its line of centers by a bond equal in length equal to the distance,  $r$  between the two nuclei.

Let us approach the rotational motion of a molecule by first considering rotation of a single particle. This motion consists of a particle of mass  $m$ , rotating in a fixed plane with a constant linear velocity ' $u$ ' and at fixed distance ' $r$ ' from the rotational axis (Fig: 1.8) and it is apparent that the path traced out by the particle is circle of radius ' $r$ '. so

$$K.E. = \frac{1}{2} mu^2 \quad \text{--- (1.14)}$$

For rotational motion, consider angular velocity as the rotational analog of linear velocity.



The angular velocity  $\omega$  is defined by

$$\omega = \frac{\theta}{t} \quad \text{--- (1.15)}$$

where  $\theta$  is the angle swept out by the particle in time  $t$ .

The rotational frequency  $\nu_{rot}$  is defined as the number of revolutions the particle makes in a second. Since there are  $2\pi$  radians ( $360^\circ$ ) in a complete revolution about the circle,  $\nu_{rot}$  is related to  $\omega$  by

$$\omega = 2\pi\nu_{rot} \quad \text{--- (1.16)}$$

The particle traveling in a circle of radius  $r$  cm, will cover the distance  $2\pi r$  cm for each revolution. Since it makes  $\nu_{rot}$  cm per second, it must travel a distance  $2\pi r\nu_{rot}$  cm per second. It is apparent from units this is the linear velocity  $u$ , hence

$$u = 2\pi r\nu_{rot} \quad \text{----- (1.17)}$$

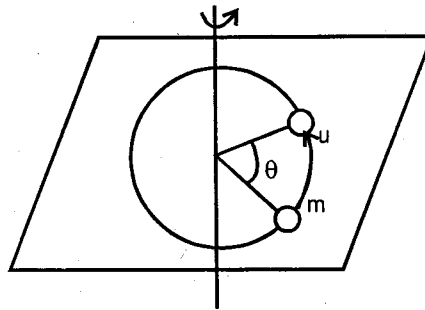


Fig : 1. 8

Using equations 1.16 and 1.17, we get the relation between the linear and angular velocities.

$$u = r\omega \quad \text{----- (1.18)}$$

For uniform rotational motion in a circle  $r$ ,  $\omega$  and  $\nu$  are constants. Using rotational constants, we can express K.E as

$$\text{K.E} = \frac{1}{2}mr^2\omega^2 \quad \text{----- (1.19)}$$

The quantity  $mr^2$  is given a specific name, the moment of inertia  $I$ . So  $I$  is defined by

$$I = m r^2 \quad \text{----} \quad (1.20)$$

Using eq.1.20,

$$K.E. = \frac{1}{2} I \omega^2 \quad \text{----} \quad (1.21)$$

On comparing equations 1.14 and 1.21, it is apparent that  $I$  is the rotational analog of mass  $m$ ,  $\omega$  is the rotational analog of velocity  $u$ .

Angular momentum of rotational motion is given by

$$P = m u r \quad \text{----} \quad (1.22)$$

Using eq.1.18 and 1.20 gives

$$P = I \omega \quad \text{----} \quad (1.23)$$

Use eq.1.23 in eq.1.21 to eliminate  $\omega$  and obtain K.E in terms of  $p$

$$K.E. = \frac{p^2}{2I} \quad \text{----} \quad (1.24)$$

Let us now consider the case of rotation of two masses  $m_1$  and  $m_2$  which are connected by rigid rod of length  $r$ . These masses are rotating about an axis through the center of mass (cm) in fig:1.9 with a constant  $\omega$ .

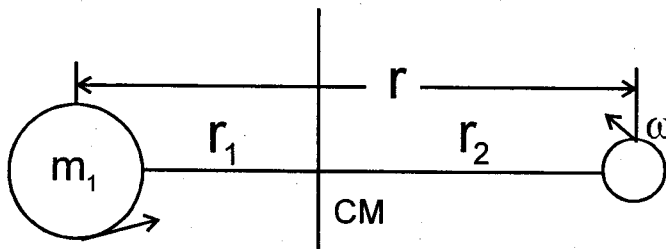


Fig : 1.9

In the fig:  $m_1 > m_2$  and  $r_1 < r_2$  and  $u_2 < u_1$

$$\text{The total K.E} = \frac{1}{2} m_1 u_1^2 + \frac{1}{2} m_2 u_2^2 \quad \text{----} \quad (1.25)$$

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \text{----} \quad (1.26)$$

For the system in fig: 1.9, we can also write

$$m_1 r_1 = m_2 r_2 \quad \text{----} \quad (1.27)$$

$$r = r_1 + r_2 \quad \text{----} \quad (1.28)$$

$$m_1 r_1 = m_2 r_2 \quad \text{i.e.} \quad r_2 = \frac{m_1}{m_2} r_1, \quad r_1 = \frac{m_2}{m_1} r_2$$

$$\text{Since } r = r_1 + r_2, \quad r = \frac{r_1 + m_1}{m_2 r_1}$$

$$r = \frac{m_2 + m_1}{m_1 r_1} \quad \text{or} \quad r_1 = \frac{m_1}{m_2 + m_1} r \quad \text{---- (1.29)}$$

$$\text{similarly} \quad r_2 = \frac{m_2}{m_1 + m_2} r \quad \text{---- (1.30)}$$

using the expressions for  $r_1$  and  $r_2$  of equations 1.29 and 1.30 in eq.1.26 given

$$I = m_1 \left[ \frac{m_2}{m_1 + m_2} r \right]^2 + m_2 \left[ \frac{m_1}{m_1 + m_2} r \right]^2$$

$$= m_1 m_2 \left[ \frac{m_1 + m_2}{(m_1 + m_2)^2} r^2 \right]$$

$$I = \left[ \frac{m_1 m_2}{m_1 + m_2} \right] r^2$$

$$I = \left[ \frac{m_1 m_2}{m_1 + m_2} \right] r^2 \quad \text{----- (1.31)}$$

The expressions containing the masses can be considered to be the mass of a point at the distance  $r$ , from the axis of rotation. This mass is called as reduced mass  $\mu$  so

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Then eq.1.31 can be written as  $I = \mu r^2$  ----- (1.32)

### 1.2.iii) Quantised energy levels of rigid rotator:

If we apply the methods of quantum mechanics to this problem we arrive at the result that only discrete values of energy are possible. These quantised energy levels are determined by a

quantum number which can take on integral values only. The angular momentum  $p$ , of the rigid rotator can only take on values that are integral multiples of

$$\frac{h}{2\pi} \pi \text{ i.e. } p = \sqrt{\frac{j(j+1)h^2}{2\pi^2}} \text{ ----- (1.33)}$$

where  $j$  = rotational quantum number.  $j = 0, 1, 2, 3, 4, \dots$

$J$  serves to restrict the number of possible rotational energy levels. The expression for the energy of quantised levels is

$$E = \frac{h^2}{8\pi^2 I} \times J(J+1) \text{ ----- (1.34)}$$

This is obtained by eq. 1.24 and 1.33. Since  $h, \pi, I$  are constants,  $E$  can have only certain discrete values determined by the value of the integer  $J$ . Thus the rigid rotator have values as shown in fig 1.10

J	E values
5	$\frac{30h^2}{8\pi^2 I}$
4	$\frac{20h^2}{8\pi^2 I}$
3	$\frac{12h^2}{8\pi^2 I}$
2	$\frac{6h^2}{8\pi^2 I}$
1	$\frac{2h^2}{8\pi^2 I}$
0	0

Fig. 1.10

The rotational frequency  $\nu_{rot}$  is given by

$$\nu_{rot} = \left( \frac{h}{4\pi^2 I} \right) \sqrt{J(J+1)} \text{ ----- (1.35)}$$

### 1.2.iv Allowed transitions between rotational energy levels - Rotational spectra.

The emission of light quantum takes place as a result of a transition of the rotator from higher to a lower energy level.

The absorption of light quantum takes place as a result of a transition of the rotator from lower to higher energy level.

From quantum condition

$$\Delta E = h\nu \quad \bar{\nu} = \frac{\Delta E}{hc} = \frac{E^1}{hc} - \frac{E^{11}}{hc} \quad \text{----- (1.36)}$$

where  $E^1$  and  $E^{11}$  are the energies of upper and lower rotational energy levels.

$$\Delta E = E^1 - E^{11} = \frac{h^2}{8\pi^2 I} [J^1(J^1+1) - J^{11}(J^{11}+1)] \quad \text{---- (1.37)}$$

the change in energy correspond to a change in rotational q.no J

$$E^1 (J^1 = 1) - E^{11} (J^{11} = 0) = \frac{(2)h^2}{8\pi^2 I} - \frac{(0)h^2}{8\pi^2 I} = \frac{2h^2}{8\pi^2 I}$$

The wave number  $\bar{\nu}$ , of the spectral line can be obtained from eq.1.36 and 1.37

$$\bar{\nu} = \frac{h}{8\pi^2 c I_0} (J^1(J^1+1)) - \frac{h}{8\pi^2 c I} (J^{11}(J^{11}+1)) = \frac{h}{8\pi^2 c I_0} [J^1(J^1+1) - J^{11}(J^{11}+1)] \quad \text{----- (1.38)}$$

where  $I_0 = \mu r_0^2$  and  $r_0$  is the distance between the centers of the nuclei - intermolecular distance or bond length.

For any given molecule  $I_0$  is constant as h and c.

There fore  $\frac{h}{8\pi^2 c I_0}$  is constant and is known as rotational constant  $B_0$ , so

$$B_0 = \frac{h}{8\pi^2 c I_0} \quad \text{---- (1.39)}$$

Using eq 1.39 and 1.38 can be written as

$$\bar{\nu} = B_0 [J^1(J^1+1) - J^{11}(J^{11}+1)] \quad \text{----- (1.40)}$$

## Selection rules for rotational spectra

1. The allowed transition is there if  $\Delta J = \pm 1$ . i.e., if the transition is from  $J'' = 0$  to  $J' = 1$  or  $J' = 1$  to  $J'' = 0$  allowed. Other transitions corresponds to  $\Delta J = \pm 2$  or  $\pm 3$  are forbidden. Allowed transitions are shown by solid line and forbidden by dashed line in fig :1.11

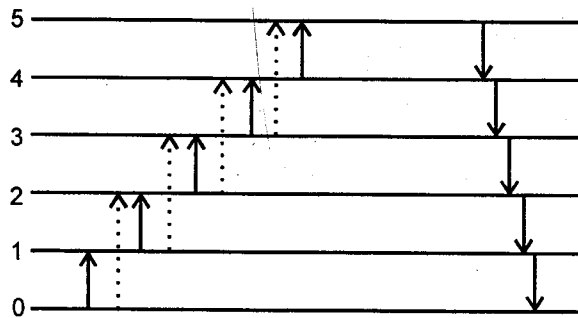


Fig: 1.11

For  $\Delta J = +1$  i.e  $J' > J''$  i.e  $J' = J'' + 1$ .

In equation 1.40 for  $J' = J'' + 1$  is substituted and simplified

$$\begin{aligned} \bar{\nu} &= B_0 \left[ (J''+1)(J''+2) - J''(J''+1) \right] \\ &= B_0 \left[ J''^2 + 2J'' + J'' + 2 - J''^2 - J'' \right] \\ &= 2 B_0 \left[ J'' + 1 \right] \quad \text{----- (1.41)} \end{aligned}$$

where  $J'' = 0, 1, 2, 3, \dots$

The allowed transitions and  $\bar{\nu}$  of the spectral lines obtained are shown in Table 1.3

Table 1.3

Transition	$\bar{\nu}$ from eq.1.41	$\Delta \bar{\nu}$
$J'' = 0 \longrightarrow J' = 1$	$2B_0$	$2B_0$
$J'' = 1 \longrightarrow J' = 2$	$4B_0$	$2B_0$
$J'' = 2 \longrightarrow J' = 3$	$6B_0$	$2B_0$
$J'' = 3 \longrightarrow J' = 4$	$8B_0$	$2B_0$
$J'' = 4 \longrightarrow J' = 5$	$10B_0$	$2B_0$

The spectrum of rigid rotator will consist of a series of equidistant lines with separation of  $2B_0$  i.e.

$$\Delta \bar{\nu} = 2B_0$$

2. Only those molecules possessing permanent dipole moment will give rise to rotational spectra i.e. they are able to change their rotational energy by absorbing or emission of radiant energy in the microwave region.

According to this rule, hetero nuclear diatomic molecules like HI, CO, NO, CN etc. Only give allowed transitions because these are having permanent separation of charge or dipole moment while homo nuclear diatomic molecules like  $H_2$ ,  $Cl_2$ ,  $O_2$  etc. does not give rotation spectra.

**Explanation** - If the permanent dipole moment is there in the molecule, the rotating dipole can interact with the oscillating electric vector, the frequency of which is  $\nu$ . When the frequency of the rotating dipole is not the same as that of the frequency of the wave i.e. when they are in phase, the rotating dipole can interact with the rotation and thereby absorb energy from the radiation.

### Application of microwave spectrum:

The microwave spectra gives equidistant lines and  $\bar{\nu} = 2B_0$  from this we can calculate bond length of the molecule. If we know from spectra  $\Delta \bar{\nu}$ , we can know  $B_0$  there by  $I_0$  and  $r_0$ .

For eg. microwave spectra of HI is found to consist of a series of lines with separation  $\Delta \bar{\nu} = 12.8 \text{ cm}^{-1}$

$$S_0 \quad 2B_0 = 12.8$$

$$B_0 = 6.4$$

$$B_0 = \frac{h}{8\pi^2 c I_0} \quad \text{or} \quad I_0 = \frac{h}{8\pi^2 c B_0}$$

$$\text{Then } I_0 = \frac{6.62 \times 10^{-27}}{8 \times (3.14)^2 \times (3 \times 10^{10}) \times 6.4} = 4.37 \times 10^{-40} \text{ g.cm}^2$$

(Note -  $I_0$  is always obtained in the range  $10^{-40}$ ).

$$I_0 = \mu r^2$$

$$\mu \text{ per molecule} = \frac{m_1 m_2}{m_1 + m_2} \times \frac{1}{N}$$

$$= 1 \times \frac{127}{1+127} \times \frac{1}{6.02 \times 10^{23}} = 1.65 \times 10^{-24} \text{ g.}$$

(Note -  $\mu$  is always obtained in the range  $10^{-24}$  g)

$$r_0 = \frac{\sqrt{4.37 \times 10^{-40}}}{1.65 \times 10^{-24}} = 1.63 \text{ \AA}$$

(Note - Bond length is always obtained in  $\text{\AA}$  or  $10^{-8}$  cm)

Molecular parameters from rotational spectra are given in table 1.4

Table : 1.4

Mol.	$\bar{\Delta\nu}$ $\text{cm}^{-1}$	$B_0$ $\text{cm}^{-1}$	$I_0$ ( $10^{-40}$ $\text{g.cm}^2$ )	$\mu 10^{-24}$ g	$r$ $\text{\AA}$
HF	41.8	20.90	1.34	1.57	0.917
HCL	21.12	10.56	2.65	1.63	1.28
HBr	17.10	8.55	3.51	1.64	1.41
CO	3.86	1.93	14.50	11.40	1.13
NO	3.40	1.70	16.50	12.40	1.15

### 1.2.v) Isotope effect in rotation spectra:

The isotope is there in the molecule, the  $I_0$  value differ from normal molecule. So,  $B_0$  also changes. The spectrum also changes as the  $B_0$  value changes.

**Explanation:** Normal molecule like  $\text{C}^{12}\text{O}^{16}$ , the  $B_0$  expressed as  $B_0^A$  and for isotope  $\text{C}^{13}\text{O}^{16}$ , the  $B_0$  is  $B_0^B$ .

$$B_0^A = \frac{h}{8\pi^2 c I_0^A} \quad B_0^B = \frac{h}{8\pi^2 c I_0^B}$$

$$\text{On dividing} \quad \frac{B_0^A}{B_0^B} = \frac{I_0^B}{I_0^A} \quad \text{----- (1.42)}$$

In  $I_0$  only  $\mu$  is different and  $r_0$  is constant.

So equation 1.42 can be written as

$$\frac{B_0^A}{B_0^B} = \frac{\mu^B}{\mu^A} \quad \text{----- (1.43)}$$

In the above equation  $\mu^B > \mu^A$  and  $B_0^B < B_0^A$ . So the spacing between the rotational lines will be smaller for heavier isotope as shown in fig 1.12.



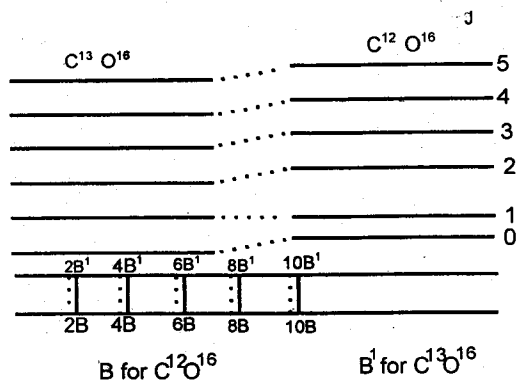


Fig: 1.12

From the values of spectra, if we know  $B$  and  $B^1$ , If we can calculate  $\mu^B$ . If we know the value of  $\mu^B$ , the mass of  $C^{13}$  isotope can be calculated, which was calculated to be  $C^{13} = 13.007$ .

The observation of this decreased separation has led to the evaluation of precise at.wts. Gillium et.al found the first notational absorption  $2B$  for  $C^{12}O^{16}$  at  $3.84235 \text{ cm}^{-1}$  and  $2B^1$  for  $C^{13}O^{16}$  at  $3.67337 \text{ cm}^{-1}$ .

From this values we can calculate

$$B = 1.92118 \text{ cm}^{-1}$$

$$B^1 = 1.83669 \text{ cm}^{-1}$$

$\mu$  for  $C^{12}O^{16}$  calculated is  $= 1.1389 \times 10^{-23} \text{ g}$  then

$$\frac{B}{B^1} = \frac{\mu^B}{\mu}$$

$$\mu^B = \frac{B}{B^1} \times \mu$$

$$= \frac{1.9212 \times 1.389 \times 10^{-23}}{1.8367} = 1.1913 \times 10^{-23} \text{ g}$$

From  $\mu^1$  the mass of  $C^{13}$  can be calculated.

### 1.2.vi) Spectra of non-rigid rotator:

The molecule cannot be strictly rigid when rotating, if we can admit it can perform vibrations along the bond. Hence, a better model for the diatomic molecule, two atoms are connected by weightless spring (rather than weight less rigid bar). Rotation of such a system will give rise to a stretching of the string, owing to the action of centrifugal force.

a stretching of the string, owing to the action of centrifugal force.

The centrifugal stretching causes an increase in the moment of inertia  $I$ . The greater the rotational frequency, the greater is the centrifugal stretching. As rotational q.no.  $J$ , increases the larger will be the value of  $I$ .

The rotational constant  $B = \frac{h}{8\pi^2 c I}$ , we see  $B$  decreases with increasing  $J$  value. This dependence of  $B$  on  $J$  can be shown in eq. 1.44.

$$B = B_0 [1 - b J(J+1)] \text{ ----- (1.44)}$$

Where  $B_0$  = rotational constant for lowest rotational state .

$b$  = correction factor which is very small compared to unity.

Since  $b$  is very small, the second term in eq. 1.44 on the right will not be significant except for large values of  $J$  ( $B = B_0$ ). When  $J$  is large, this term becomes appreciable and  $B < B_0$ .

In equation 1.44, using energy expression

$$E = \frac{h^2}{8\pi^2 I \times J(J+1)} \text{ for } B_0 \text{ for the non-rigid rotator}$$

$$E = [ B_0 J(J+1) - b B_0 J^2 (J+1)^2 ] h c \text{ ----- (1.45)}$$

The quantity  $b B_0$  is given by the symbol  $D$ .  $D$  is known as the centrifugal constant. Then

$$E = [ B_0 J(J+1) - D J^2 (J+1)^2 ] h c \text{ ----- (1.46)}$$

Where  $D$  is

$$D = \frac{4B_0^3}{v_{osc}^2} \text{ i.w. } \frac{10^3}{(10^3)^2 \sim 10^{-3}} \text{ cm}^{-1}$$

The value  $D$  is always much less than that of  $B_0$ . The effect of  $D$  on the energy levels is to decrease in  $E$  will become greater for higher rotational energy .i.e as  $J$  increases. So, the wave number of spectral lines is given by

$$\bar{\nu} = \frac{\Delta E}{hc} = 2B_0 (J^{11}+1) - 4D(J^{11}+1)^3 \text{ ----- (1.47)}$$

using the selection rule  $\Delta J = \pm 1$  i.e.,  $J^1 = J^{11} + 1$

The spectra for rigid rotator and non-rigid rotator is shown in fig 1.13 for comparison

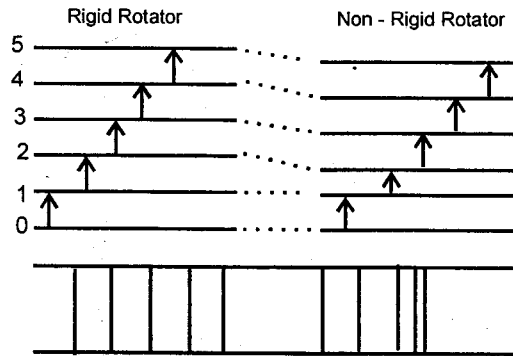


Fig : 1.13

The spectra of rigid rotator have equidistant lines but the spectra of non-rigid rotator, the lines are not equidistant and the spacing between lines decreases as  $J''$  value increases due to centrifugal constant. For example observed values for HCl is  $2B_0 = 20.79$  and  $D = 0.0016$ . we can calculate the  $\bar{\nu}$  for different  $J''$  values.

$$\bar{\nu} = 20.79(J'' + 1) - 0.0016 (J''+1)^3$$

$$\begin{aligned} \text{For } J'' = 1, \quad \bar{\nu} &= 20.79 (1 + 1) - 0.0016 (1+1)^3 \\ &= 41.58 - 0.0128 = 41.5678 \text{ cm}^{-1} \end{aligned}$$

$$\begin{aligned} \text{For } J'' = 3, \quad \bar{\nu} &= 20.79(3 + 1) - 0.0016 (3+1)^3 \\ &= 83.16 - 0.1024 = 83.0576 \text{ cm}^{-1} \end{aligned}$$

$$\begin{aligned} \text{For } J'' = 5, \quad \bar{\nu} &= 20.79 (5 + 1) - 0.0016 (5+1)^3 \\ &= 124.74 - 0.3456 = 124.3944 \text{ cm}^{-1} \end{aligned}$$

### 1.2.vii) Linear polyatomic molecules:

So we have discussed the diatomic molecule. Let us see now Linear polyatomic molecule like OCS, HC = CCl, HCN etc. All atoms lie in a straight line as shown in fig 1.14.

Three moment of inertia along three axes  $I_a$  along y - axis,  $I_b$  along Z - axis and  $I_c$  along X - axis.  $I_a = 0$  since rotation about the molecular axis does not change in energy and  $I_b = I_c$ .

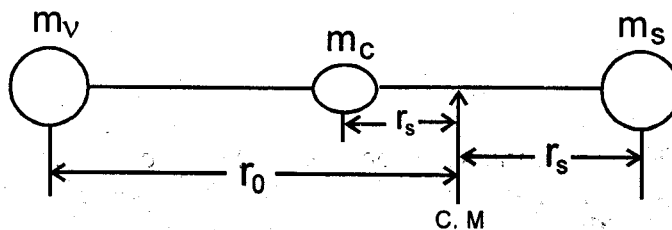


Fig : 1.14 The molecule of carbon oxysulphide OCS.

This gives particularly simple spectra in microwave region. The energy levels are given by the formula

$$E_J = B J (J + 1) - D J^2 (J+1)^2 + \dots \text{ cm}^{-1} \text{ ----- (1.48)}$$

The spectrum will show the same  $2B$  separation modified by the distortion constant. The whole of the discussion on diatomic molecule applies equal to linear molecules. The three points are to be noted for these are -

1. Since  $I$  for end-over-end rotation of a poly atomic linear mol. is considerably greater than that of diatomic molecule, the  $B$  value will be much smaller, and the spectral lines much closely spaced. For eg.  $B$  is  $10 \text{ cm}^{-1}$  for di atomic,  $1 \text{ cm}^{-1}$  for tri - atomic and even smaller for larger mols.
2. The mol. which possess  $m$  exhibit rotational spectrum. For eg.  $\text{OCS}$  active and  $\text{OCO}$  will not, even  $\text{O}^{16}\text{C}^{18}\text{O}$  inactive since there is no change in  $r$ .
3. The linear poly atomic mols. containing  $N$  atoms has altogether  $N - 1$  individual  $r$  to be determined. Thus in  $\text{OCS}$  - for  $\text{CO}$   $r_{\text{co}}$  and  $\text{CS}$   $r_{\text{cs}}$ . There is only one  $I$  for end over end rotation of  $\text{OCS}$  and this value can be determined from the spectrum.

The Microwave spectrum for carbon oxysulphide is given in the table 1. 5

Table 1.5

$J \longrightarrow J+1$	$\bar{\nu}_{\text{obs}} (\text{cm}^{-1})$	$\Delta \bar{\nu}_{(2B)}$	$B(\text{cm}^{-1})$
1 $\longrightarrow$ 0	0.4055	0.4055	0.2027
1 $\longrightarrow$ 2	0.8149	0.4054	0.2027
2 $\longrightarrow$ 3	1.2163	0.4054	0.2027
3 $\longrightarrow$ 4	1.6217	0.4054	0.2027

Take the value of  $B = 0.2027 \text{ cm}^{-1}$ , We can calculate  $I_B$  as

$$I_B = \frac{h}{8\pi^2 BC} = 137.95 \times 10^{-47} \text{ g.cm}^2$$

$$\text{Then } I = m_o r_o^2 + m_c r_c^2 + m_s r_s^2 \text{ ----- (1.49)}$$

$$\text{And } r_o = r_{\text{co}} + r_c \quad r_s = r_{\text{cs}} - r_c \text{ ----- (1.50)}$$

Where  $r_o$  and  $r_s$  are bond length. It is these we wish to determine. This can be done by studying a molecule with different atomic masses but the same bond lengths i.e., an isotopically substituted molecule since this will have a different moment of inertia.

### 1.2.viii) Model questions :

1. What is a rigid rotator model .Derive an expression for the moment of inertia of a diatomic molecule.
2. What are the selection rules of rotational spectra ? Derive expression  $\bar{\nu} = 2 B_0 [J^{11} + 1]$ .
3. Calculate the bond length for CO molecule, if the separation of lines in microwave spectra is  $3.86 \text{ cm}^{-1}$ .
4. What is the isotope effect on the rotator spectra ?
5. Write notes on non-rigid rotator model.
6. Discuss the rotational spectra of linear polyatomic molecules.

### Recommended Books:

- |              |   |
|--------------|---|
| A.J. Sonessa | Introduction to molecular spectroscopy. |
| B.K.Sharma   | Spectroscopy                            |
| C.N.Banwell  | Fundamentals of molecular spectroscopy. |

# Basic Principles Of NMR Spectroscopy

## Objectives

Nuclear magnetism

Nuclei in magnetic field

Resonance condition

Relaxation

Chemical shift

Integration

Spin - Spin coupling

NMR spectrometers.

### 1.3.i) Nuclear Magnetism :

Nucleus consists of protons and neutrons. Protons which are consistent of atomic nuclei, are charged particles. If we consider that a proton is spinning about an axis, it has an associated magnetic field. The proton is said to possess the properties of spin, which gives rise to a magnetic moment. Curiously the other component of atomic nuclei, the neutron also possess spin and has magnetic moment. This appears contradictory that a neutron has no charge and a neutron can decay to produce a proton and an electron both of which are charged. We assume that although the neutron is chargeless (overall) there is an uneven distribution of charge within it, so that spinning neutron can still generate a magnetic field.

A nucleus is made up of protons and neutrons, both of which possess magnetic properties, but not all nuclei are magnetic. This is because neutrons and protons in a nucleus can pair-up in certain complex ways that determine whether the nucleus as a whole retains the properties of spinned magnetic moment.

Spin magnetic moment,  $\gamma$

**Category 1 :** All nuclei with odd mass number (non-zero spin) are magnetic.

**Category 2 :** All nuclei with even mass number and odd number of protons and neutrons are magnetic.

**Category 3:** All nuclei with even mass number and even number of protons and neutrons are non-magnetic.

For eg.  $^1\text{H}$  (1 p) and  $^2\text{H}$  (1 p + 1 n), similarly  $^{13}\text{C}$ ,  $^{14}\text{N}$ ,  $^{15}\text{N}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$  are magnetic.  $^{12}\text{C}$  and  $^{16}\text{O}$  are non-magnetic.

Nuclear spin quantum number,  $I$ .

The spin is a fixed quantity for a particular nucleus, dependent on the amount of non-pairing nucleons. This degree of spin defined by nuclear spin quantum number which is given the symbol  $I$ . Values of  $I$  increase from zero in half integral values i.e. 0,  $1/2$ ,  $1$ ,  $3/2$ ,  $2$ ,  $5/2$ , ....

1.  $I$  values of category 1 have half integral value for eg.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$
2.  $I$  values of category 2 have integral values for eg.  $^2\text{D}$ ,  $^{14}\text{N}$
3.  $I$  values of category 3 have zero for eg.  $^{12}\text{C}$ ,  $^{16}\text{O}$ .

### 1.3.ii) Nuclei in a magnetic field:

A magnetic nucleus is placed in a magnetic field, it will interact with that field. The magnetic moment of the nucleus can only have certain allowed values in the direction of applied magnetic field. This means that the nucleus can take one of several energies i.e. the nucleus can reside in one of several energy levels is  $M_I$ .  $M_I$  can take values  $I, I-1, I-2, \dots, -I$ . So far any value of  $I$ , the  $M_I$  values are  $2I + 1$ . For eg. if  $I = 1/2$ ,  $M_I$  can take two values  $+1/2$  and  $-1/2$ .

Thus under the application of an external magnetic field the nuclear energy level with  $I = 1/2$  split in to two levels. This is as shown in fig 1.15

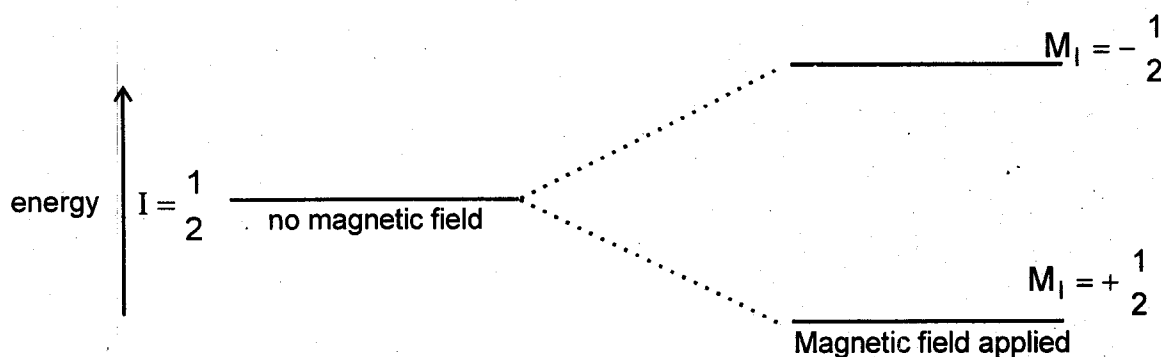


Fig : 1. 15

These two different energies can be thought of as different alignments of the nuclear spin with the external magnetic field.  $M_I = +\frac{1}{2}$  lower energy and the spin of the nucleus parallel to the

field (represented by  $\uparrow$ ) and  $M_I = -\frac{1}{2}$  has higher energy and the spin is antiparallel to the field (represented by  $\downarrow$ ).  $^1\text{H}$  and  $^{13}\text{C}$  are the simplest and most studied and have only two energy levels. The energy of the levels varies directly with the magnetic flux density  $B_0$  of the applied magnetic field (fig.1.16).

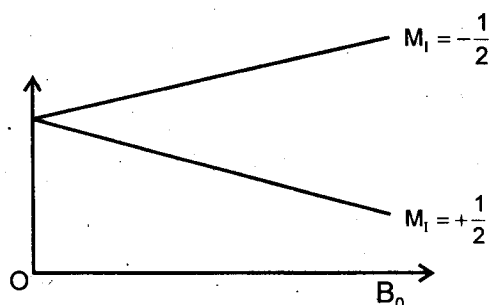


Fig: 1.16 The variation energy with magnetic field.

### 1.3.iii) The resonance condition:

Nuclear magnetic resonance (NMR) spectroscopy is concerned with inducing transitions between these levels by irradiating the sample with electro magnetic radiation of a suitable frequency.

**Selection Rules :** The nuclear transition can only occur between adjacent energy levels.  $\Delta M_I = \pm 1$  (formally).

All these are only two energy levels for  $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ , there is only one allowed transition.

We mean that a nucleus aligned with the field ( $\uparrow$ ) can change its orientation so that it becomes aligned against the field ( $\downarrow$ ) and vice-versa.

The difference in energy  $\Delta E$  between any two adjacent levels is

$$\Delta E = \frac{\gamma_N h B_0}{2\pi} \quad \text{--- (1.51)}$$

where  $\gamma_N$  = Gyrometric ratio with units  $\text{S}^{-1}\text{T}^{-1}$  ( constant for particular Nucleus)

$B_0$  = Strength of the applied magnetic field.

The energy of one quantum is

$$E = h \nu \quad \text{--- (1.52)}$$



If we combine 1.51 and 1.52. We can frequency to separation of energy levels .

$$h\nu = \frac{\gamma_N h B_0}{2\pi}$$

$$\nu = \frac{\gamma_N h B_0}{2\pi} \text{ ----- (1.53)}$$

The equation (1.53) is called the resonance condition and tells us the condition necessary for transition between energy levels. Transition occurs when the frequency of incident radiation satisfies the relationship in equation (1.53)

Magnetic resonance spectrum of the proton in chloroform is shown in fig 1.17

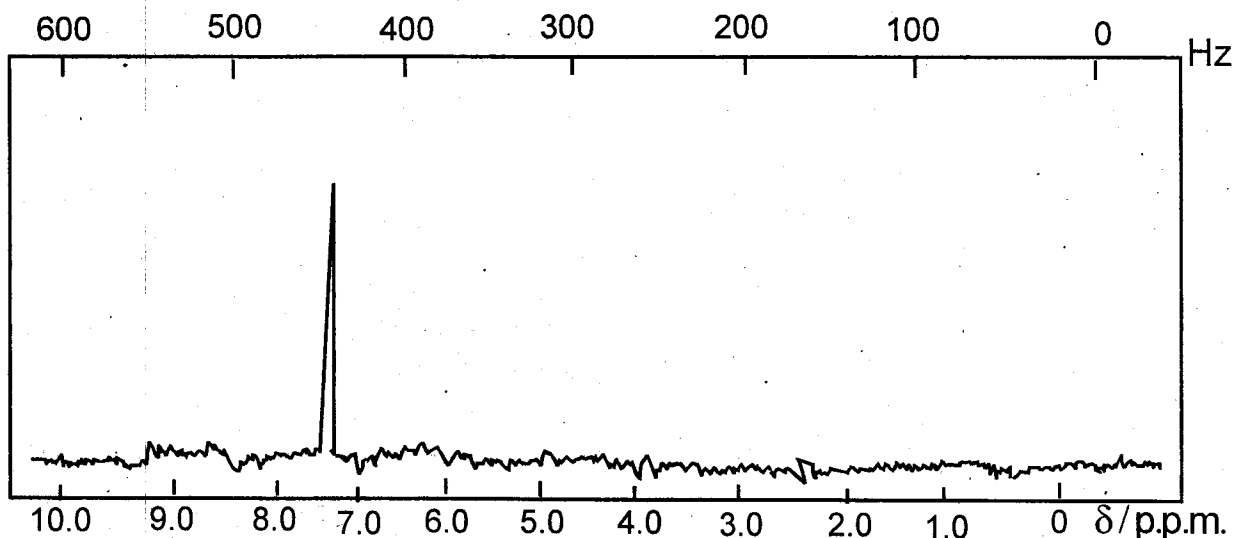


Fig: 1.17 . The p.m.r. Spectrum of chloroform.

It is a single line, corresponds to transition between the two energy levels of the proton. The frequency of applied radiation necessary to induce transition is

$$\nu = \frac{(2.675 \times 10^8 \text{ S}^{-1} \text{ T}^{-1})(1.41 \text{ T})}{2 \times 3.14 \approx 60 \times 10^6 \text{ S}^{-1}} \text{ or } 60 \text{ MHz}$$

where T is telsa

A compound can have a NMR spectrum for each magnetic nucleus present. This is because  $\gamma_N$  is different for each nucleus. Therefore, from equation 1.53 the resonance frequency for each nucleus is different.

The magnetic properties of various nuclei are given in table 1.6

TABLE 1.6

Nucleus	I	$\mu$ magneton	$\gamma_N \text{ S}^{-1} \text{ T}^{-1}$	$\nu_0$
$^1\text{H}$	$\frac{1}{2}$	2.793	$2.675 \times 10^8$	60.00
$^2\text{D}$	1	0.8574	$4.106 \times 10^7$	9.21
$^{13}\text{C}$	$\frac{1}{2}$	0.7022	$6.726 \times 10^7$	15.08
$^{14}\text{N}$	1	0.4036	$1.933 \times 10^7$	4.33
$^{19}\text{F}$	$\frac{1}{2}$	2.627	$2.517 \times 10^8$	56.44
$^{31}\text{P}$	$\frac{1}{2}$	1.1305	$1.083 \times 10^8$	24.29

#### 1.3.iv) Relaxation and the population of energy levels:

The n.m.r. spectroscopy is a form of absorption spectroscopy i.e the transition are observed by monitoring the absorption of incident radiation.

If the energy is absorbed in n.m.r, there must be more nuclei in the lower energy level. We can calculate the relative numbers of nuclei in each level by use of Boltzmann distribution law.

$$\frac{N_1}{N_2} = \exp\left(\frac{-\Delta E}{kT}\right) \text{ ---- (1.54)}$$

Where  $N_2$  = number of nuclei in upper energy level

$N_1$  = number of nuclei in lower energy level.

$k$  = Boltzman constant

$T$  = temperature in Kelvin.

For hydrogen nuclei in a 1.4T magnetic field at 300K,  $\Delta E = 4 \times 10^{-26}$  J given

$\frac{N_2}{N_1} = 0.9999904$ . This means for every million nuclei in the upper energy state there are only about one million and 10 in lower state.

The n.m.r. signal size i.e intensity is directly proportional to the difference in population between the two energy levels.

a) **Saturation:** The number of nuclei being excited from lower  $\uparrow$  to the higher energy level  $\downarrow$  is proportional to  $N_1$ .

The number of nuclei passing from upper level  $\downarrow$  to the lower level  $\uparrow$  is proportional to  $N_2$ .

Therefore more nuclei are being excited than deexcited and as soon as radiation starts to fall on the nuclei, we increase the population of the upper level.

For hydrogen nuclei in a magnetic field 1.4T at 300K, we can see five more excitations than deexcitations of nuclei in each million to equalize the population. At this point, even though there are still transitions occurring in both directions, the intensity of absorption will fall to zero, the signal will no longer be visible. This is called saturation.

b) **Relaxation:** In Relaxation processes, nuclei lose magnetic energy to their surroundings without emitting radio frequency radiation. Relaxation must be fast enough to replenish the excess of nuclei in the ground state that we need for the detection of n.m.r transition.

c) **Spin-lattice relaxation:** The major mechanism for restoring the Boltzmann distribution is spin-lattice relaxation. In spin-lattice relaxation, the higher energy nucleus can rapidly lose energy by transforming  $\Delta E$  to a near by nucleus, either in the same molecule or in a solvent molecule. The word lattice implies that the resonating nucleus may be surrounded by a whole array of such neighbouring atoms. It reestablish the Boltzmann distribution and can effect line-width of resonances.

d) **Spin-spin relaxation:** It does not lead to re-establishment of the Boltzmann distribution but does effect line width. In this process nuclei can exchange spins. One nucleus goes up as the other goes down. The result of this is that the lifetime of a nucleus in a particular energy level is reduced.

The important points of the above discussion are

1. An n.m.r. spectrum can only arise when a magnetic nuclei are placed in a magnetic field.
2. Only transitions between adjacent energy levels are allowed.
3. Transitions are stimulated by radiation of suitable frequency.
4. The resonance condition is  $\nu = \frac{\gamma_n B_0}{2\pi}$
5. For a given nucleus the resonance frequency is directly proportional to the strength of the applied field. ( $\gamma_n$  is a constant).
6. The intensity of absorption is dependent on the population difference.
7. For hydrogen the lower level is more populated but only to the extent of 10 nuclei in 2 million.
8. Relaxation process are important in re-establishing equilibrium population.
9. Spin-lattice relaxation plays the major part in attaining the Boltzmann distribution.
10. Too fast or too slow relaxation broadens and then destroys the n.m.r. signal.

### 1.3.v) The chemical shift:

The difference in position of resonance are called chemical shifts. The chemical shifts arise from the secondary magnetic field produced by the circulation of electrons in the molecule.

Electron circulate under the influence of a magnetic field and in so doing, generate their own magnetic field called secondary or induced magnetic field, opposing the applied magnetic field.

These electronic currents either reduce or enhance the field to which a given proton responds.

The chemical shifts are regarded as arising largely from two sources -

**1.The electro negativity of near neighbours :** The electron moving near a proton, being, charged create their own magnetic field, which opposes the applied field. Thus in order to obtain the resonance condition, the applied field of the magnet must be greater than the effective field at the nucleus.

The difference depends on the electro negativity of the neighbours, which act to near by shielding from around the proton.

**Explanation :** Let us consider the simplest example is that the isolated atom. The applied field  $B_0$ . The induced electronic currents then induce a magnetic field parallel (proportional) to  $B_0$ . The induced field due to electron must oppose  $B_0$ . The nucleus sees a diminished field,  $B_0(1 - \sigma)$ , where  $\sigma$  is the shielding constant. If we substitute  $B_0(1 - \sigma)$  for  $B_0$  in the resonance condition, we get new resonance condition, which applies to atoms and molecules.

$$\nu = \frac{\gamma_N B_0 (1 - \sigma)}{2\pi} \quad \text{---- (1.55)}$$

The original resonance condition i.e eq.1.53 holds only for bare nuclei with no associated electrons. The value of  $\sigma$ , although very small, is different for atoms in different environments. The aldehydic carbon atom in ethanol is in a quite different electronic environment from the methyl carbon atom. Hence two signals in fig: 1.18

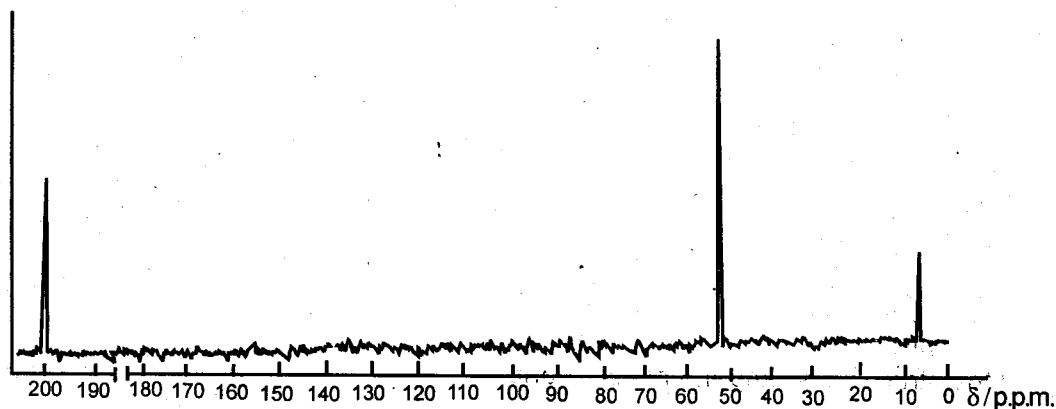


Fig:1.18 The carbon -13 nmr spectrum of ethanol,  $\text{CH}_3\text{CHO}$ . The peak at 0 p.p.m. is due to an internal standard.

Since  $\sigma$  is dependent on number of electrons surrounding the nucleus, the range of chemical shift is greater for atoms with large number of electrons.

2. The molecular magnetic anisotropy arises from the circulation of electrons through the molecule, such as about  $\pi$ -bond. The electronic motion creates a field which may act with or against the applied field, depending primarily on molecular geometry. It causes aromatic protons to resonate at much lower field than ethylenic protons.

In n.m.r spectroscopy, the resonance frequency is a function of applied field (eq. 1.55)

A reference compound is normally added to every sample before its n.m.r spectrum is recorded. We then measure the difference in frequency of our absorption from that of reference compound. In order to obtain a parameter that is independent of the field, the chemical shift parameter  $\delta$  is introduced and is defined by

$$\delta = \frac{\nu(\text{sample}) - \nu(\text{reference})}{\nu(\text{reference}) \times 10^6} \text{ p.p.m.}$$

$\delta$  is quoted in parts per million and the reference is tetra methyl silane TMS and has  $\delta = 0$  p.p.m.

TMS is convenient to use because it gives one sharp signal well away from the majority of both carbon and proton resonances. It is also volatile (b.p.  $27^\circ \text{C}$ ) and therefore easy to remove from a sample, and extremely unreactive and soluble in most organic solvents.

**Problem :** An applied field of 1.41T and spectrometer frequency of 15.09 MHz, the difference in resonance frequency between the TMS carbon and the methyl carbon in ethanol is 470 Hz. What is the chemical shift in ethanol?

Apply equation 1.56

$$\delta(\text{CH}_3) = \frac{470}{15.07} \times 10^6 \times 10^6 = 31.2 \text{ p.p.m.}$$

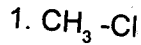
(15.09 MHz means  $15.09 \times 10^6$  Hz) some others use the  $\tau$  (tau scale) where  $\tau = 10 - \delta$ .

The important points about chemical shift

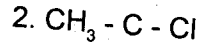
1. The chemical shift or portion of the line in nmr spectrum gives information as molecular environment of the nuclei from which it arises.
2. The chemical shifts of nuclei in different molecules are similar if the molecular environments are similar.
3. The intensity of lines gives directly the relative number of magnetically active nuclei undergoing different chemical shifts.
4. The chemical shift is used for the identification of fundamental groups and as aid in determining the structural arrangements of groups.
5. A deshielded proton would give the resonance signal up field and a shielded proton would absorb down field. These shifts in the position of NMR signals arise from the shielding or deshielding of electrons are generally called chemical shifts.

6. As the distance of proton from electromagnetic atom increases, the deshielding effect due to it decreases.

For eg.



$$\delta = 3.0$$



$$\delta = 1.5$$

In eg 2, the distance of electronegative atom increases and hence  $\text{CH}_3$  proton in 2 experience less shielding in comparison to  $\text{CH}_3$  in 1. This is evident from their  $\delta$  values.

7. In n.m.r. various terms are used to describe the selective chemical shifts of nuclei. These are depicted in fig.1.19

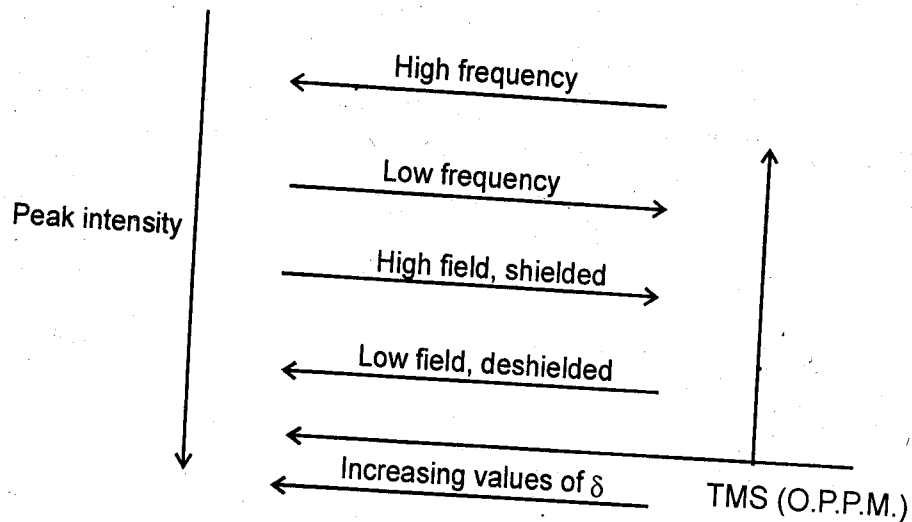


Fig : 1.19

### 1.3.vi) Integration:

In a spectrum with more than one peak (resonance) the intensity ratio of these peaks is directly proportional to the relative numbers of nuclei causing the peaks. Infact, the area under a peak is directly proportional to the number of nuclei causing that peak. The spectrum of chloromethyl ether,  $\text{CH}_2\text{ClOCH}_3$ , consists of two lines, one due to methyl proton and the other due to methylene proton. Above each peak there is stepped line. The steps in this line are a measure of the area of the peak below the steps. This is called integration trace. Chemically equivalent nuclei ( $\text{CH}_2$  proton) are also magnetically equivalent. In the p.m.r spectrum (proton magnetic resonance), the chemical shifts tells us how many sets of equivalent nuclei are there in sample and the integration tells us the ratio of the number of nuclei in each set.

### 1.3.vii) Spin-Spin coupling:

The approach through spin-spin coupling is through two coupled nuclei. The spectra as shown in fig 1.20 are the proton coupled c.m.r (carbon) and p.m.r spectrum of the same compound  $^{13}\text{CHCl}_3$ . (isotopically enriched starting material contains  $^{13}\text{C} > 99$  percent)

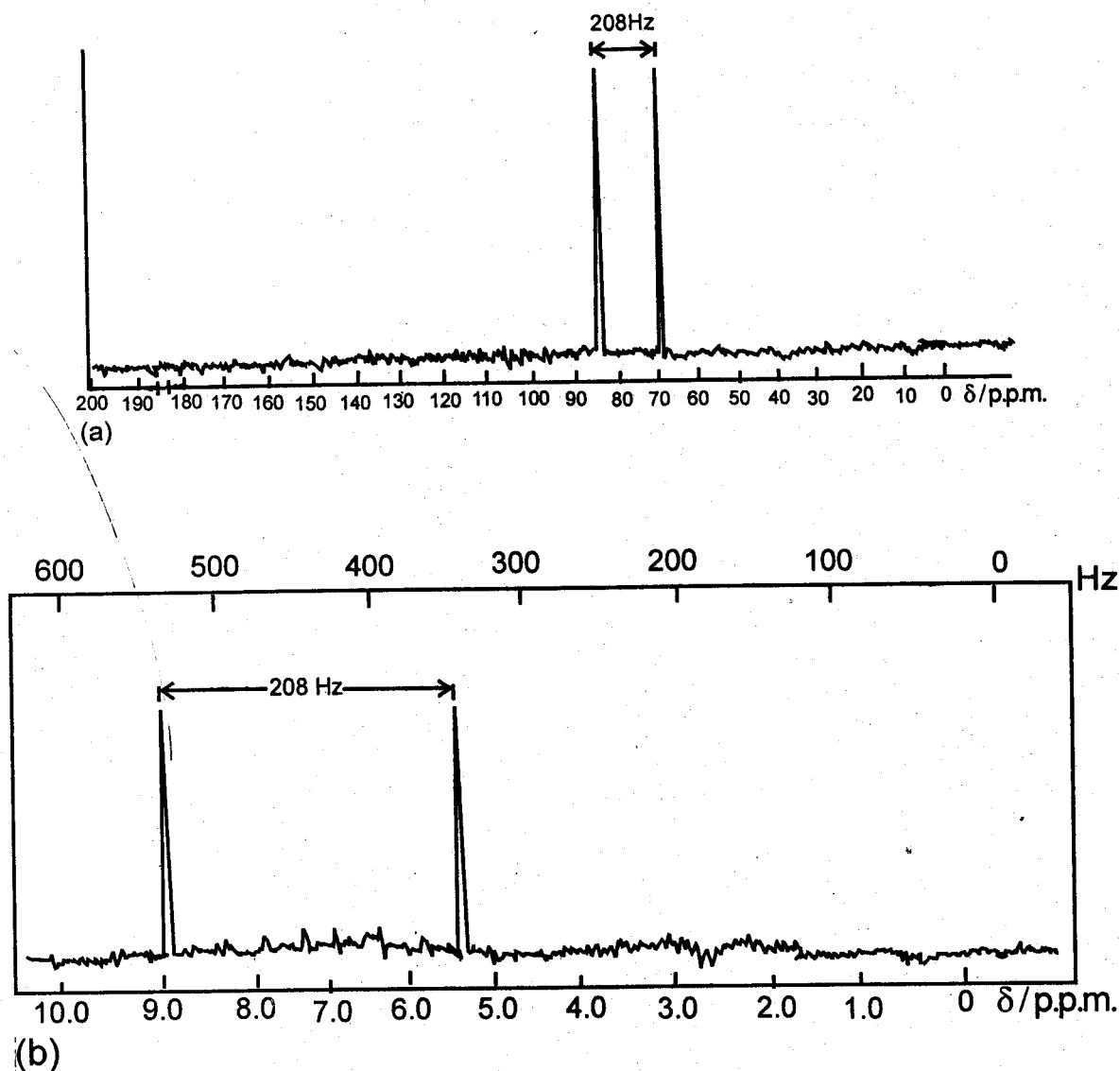


Fig: 1.20 The p.m.r spectrum of  $^{13}\text{CHCl}_3$

Chloroform has only one carbon and hydrogen atom. Therefore in the absence of any other effect, we expect one resonance in the c.m.r and p.m.r spectra. The spectra in the fig. 1.20 both consist of two lines and spacing between two proton lines and two carbon lines identical. This separation of one resonance line into more than one line is called spin-spin splitting.

**Explanation :** Looking at the carbon atom in chloroform we can see that its magnetic environment will depend on whether the adjacent proton has its magnetic field aligned with or against the applied field. So carbon atom can experience one of two different fields, one greater than the applied field. When it is enhanced by the proton field and lesser field when the protons field is aligned against the magnetic field. This is the reasonable model for understanding the origin of spin-spin coupling. The same argument can be used for the proton splitting in chloroform to account for two resonance lines in  $^{13}\text{CHCl}_3$  (doublets)

**Hetero nuclear coupling :** The coupling between carbon and proton is called hetero nuclear coupling. eg. in  $^{13}\text{CHCl}_3$ .

**Coupling constant J :** The separation between peaks is called as coupling constant ( symbol J / Hz).

For any two nuclei A and B coupled together

$$J_{AB} = J_{BA} \quad \text{--- (1.56)}$$

Where  $J_{AB}$  is the splitting of the B nucleus signal by nucleus A.

J only depends on the nature of the coupled nuclei and the number and nature of the bonds between them.

**Homo nuclear coupling :** The coupling between nuclei of same isotopic type is called homo nuclear coupling. In the p.m.r. spectrum of ethanal, the methyl proton signal has been split in to a doublet and the aldehydic proton signal in to a quartet i.e. coupling to one neighboring proton gives a doublet and coupling to three neighbouring proton gives a quartet.

**n+1 rule:** This rule states that n equivalent nuclei will couple to another different nucleus to produce n+1 lines. The intensity of these n+1 lines are related to the probability of the various states. These can be discovered by-

1. Drawing out the possible alternatives and counting the number of equivalent combinations. This gets difficult and long drawn -out for large n.
2. Drawing family tree. This also takes longer as n increases.
3. Solving binomial expansion  $(a+b)^n$  and until the co-efficients. For eg.  $n = 2$ ,  $(a+b)^2 = a^2 + 2ab + b^2$ , in which the co-efficient in the expansions are 1,2,1.
4. Using Pascal's triangle, which is reproduced below .

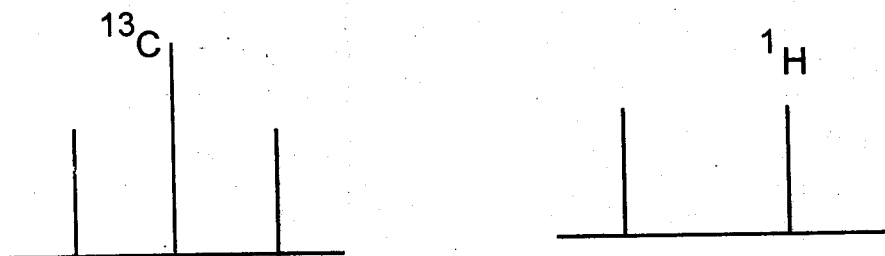
			1			
		1	2	1		
	1	3	3	1		
	1	6	10	6	1	
	1	10	20	15	6	1 etc



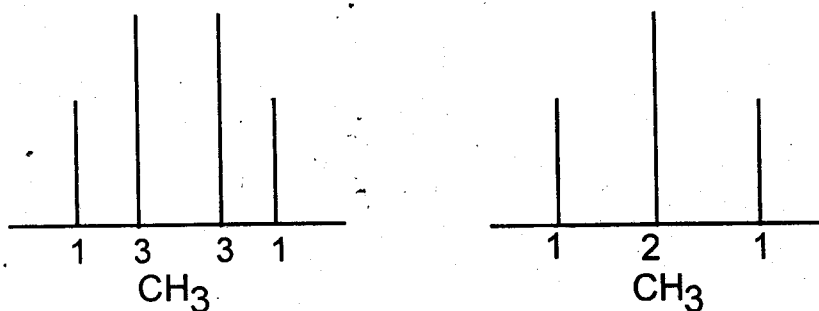
out side lines have low intensity compared with inner lines. It consists inverted triangles with lower number being the sum of the upper two. For eg.

$$\begin{array}{cccc} 1 & 2 & 1 & 0 \\ & 3 & & 1 \end{array} \quad \text{or} \quad \begin{array}{cc} 6 & 4 \\ & 10 \end{array}$$

**Problem :** Using the n+1 rule and Pascal's triangle predict coupling patterns in  $^{13}\text{C}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CH}_2\text{I}$   
 $\text{CH}_2\text{Cl}_2$  - hetero nuclear coupling between one carbon and two equivalent protons. The n+1 rule predicts that carbon resonance should be triplet and the proton resonance a doublet. Pascal's triangle gives intensity of 1:2:1 and 1: 1 respectively.



**$\text{CH}_3\text{CH}_2\text{I}$  :** The methylene proton resonance is split in to a 1 : 3 : 3 : 1 quartet by methyl protons .The methyl proton resonance is split by methylene proton in to a triplet 1 : 2 : 1



1. Magnetic nuclei coupled through one, two, three or four bonds can interact .The interaction is called spin-spin coupling.
2. The result of this interaction is that number of lines due to a nucleus or set of equivalent nuclei increases.
3. If n equivalent nuclei couple with a second nucleus or set of equivalent nuclei to produce n+1 signals for the later.
4. The intensity ratio of the n+1 signals is given by Pascal's triangle.
5. The integration of a multiple signal gives the ratio of the number of nuclei giving rise to resonance, where as the number of peaks tells us the number of nuclei coupled to that set.
6. In any set  $J_{AB} = J_{BA}$  ( J is coupling constant).

### 1.3.viii) n.m.r spectrometers :

The intensity of absorption in n.m.r spectroscopy is proportional to the difference in the population of upper and lower energy levels and that this difference is very small. Sophisticated instrumentation is needed to detect the absorption and structure determination. There are two basic procedures used to record n.m.r spectra -

Continuous wave spectroscopy (CW)

Pulsed Fourier -transform spectroscopy (PFT)

The basic requirements for the methods are

1. A homogeneous magnetic field to remove the degeneracy.
2. A radio -frequency oscillator to induce transitions between magnetic spin states.
3. A method for detecting the energy absorbed.

### 1.3.ix) Model questions :

1. Determine the nuclear spin q.no. I for  $^{13}\text{C}$ ,  $^{14}\text{N}$ ,  $^{19}\text{F}$ ,  $^{16}\text{O}$
2. Derive expression of frequency relation to separation of energy levels.
3. What is the population for hydrogen nuclei?
4. What is relaxation and explain different types of relaxation
5. What is chemical shift? Explain in a detailed manner.
6. Give an account on spin-spin coupling.
7. What is the reference solvent in n.m.r spectra? why it is only used?

### Reference Books :

- |              |   |
|--------------|---|
| A.J. Sonessa | Introduction to molecular spectroscopy. |
| B.K.Sharma   | Spectroscopy                            |
| C.N.Banwell  | Fundamentals of molecular spectroscopy. |

## Lesson - IV Basic Principles Of ESR Spectroscopy

### Objectives

Introduction  
Theory - g - factor  
properties  
Hyper fine structure  
ENDOR and ELDOR  
Summary.

#### 1.4.i) Introduction :

Electron spin resonance ( e.s.r ) or electron paramagnetic resonance ( e.p.r ) is a branch of absorption spectrometer in which radiation of microwave frequency induce transition between magnetic energy levels of electron with unpaired spins. The technique was invented by Zurlskii in 1944, modified by Stevas, Owen and Mc Garvey.

The principle is analogous to NMR. The difference is

1.  $\Delta E$  for ESR  $>$   $\Delta E$  for NMR
2. Absorption occurs in microwave for ESR and in radio wave for NMR.
3. It is useful for unstable free radicals and in concentration up to  $10^{-12}$   $\mu$  provided the life time is  $>$   $10^{-6}$  sec.

Substances with unpaired electrons may either arise naturally or be produced artificially for eg.  $\text{NO}^+$ ,  $\text{O}_2^+$ ,  $\text{NO}_2$ , the ions of transition metals and their complexes, for eg.  $\text{Fe}^{3+}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$  etc. These substances are stable and easily studied by e.s.r short lived radicals at room temperature, may also be studied if they are produced at a low temperature, either in the solid state or trapped in a solid matrix of a host material such as solid inert gas. This is called matrix isolation and increases the lifetime of a trapped radical. The requirement for this is an unpaired electron.

When unpaired electron exists in a substance their spins are aligned at random in the absence of a field. When placed in magnetic field, however, they will each have a preferred direction and, since the spin quantum number is  $\frac{1}{2}$ . Each can be thought of as a spinning either clockwise or anti clock wise about the field direction, E.S.R.

Spectroscopy essentially measures the energy required to reverse the spin of an unpaired electron.

### 1.4.ii) Theory of electron spin resonance:

The spin of nucleus is given by the symbol  $I$  called the spin quantum number.

Angular momentum of a nucleus is

$$I = \sqrt{\frac{I(I+1)h^2}{4\pi^2}} = \sqrt{I(I+1)} \text{ units} \quad \text{----- (1.57)}$$

$$\text{Where } I = 0, \frac{1}{2}, 1, \frac{3}{2}$$

The spin quantum number of electrons and angular momentum of electrons include in eq. 1.57. If we label spin quantum number  $I$  (instead of  $S$ ) and  $I$  can be  $\frac{1}{2}$  only an electron, then equation 1.57 represents the angular momentum of electron. The eq. 1.57 can also be written as

$$I = \frac{Ih}{2\pi} = I \text{ units} \quad \text{----- (1.58)}$$

Along Z-direction

$I_z = I, I-1, \dots, \frac{1}{2}, -\frac{1}{2}, \dots, -I$  (for  $I$  half integral) gives  $2I+1$  components. The components are generally degenerate. The degeneracy was lifted and  $2I+1$  have different energy levels if an external magnetic field is applied.

The spinning behaves as a tiny bar magnet placed along the spin axis. The size of the dipole for a point charge is

$$\mu = \frac{q}{m} \cdot I = q \sqrt{\frac{I(I+1)}{2m}} \frac{h}{2\pi} = \frac{qh}{4\pi m} \sqrt{I(I+1)} \text{ Am}^2 \quad \text{--- (1.59)}$$

where  $q$  = charge                       $m$  = mass

$\text{Am}^2$  ( is fundamental S.I units ) = ampere square meter

$T$  (in S.I units ) = Telsa i.e  $\text{Kg S}^{-2} \text{A}^{-1}$

$1T = 10,000 \text{ gauss}$

The conversion is

$$\text{Am}^2 = (\text{kg s}^{-2} \text{T}^{-1}) \text{ m}^2 = \text{J T}^{-1} \text{ (joules per telsa )}$$

Finally

$$\mu = q h / 4 \pi m \sqrt{I(I+1)} \text{ J T}^{-1} \text{ ----- (1.60)}$$

for electrons the equation 1.60 can be written as

$$\mu = g \beta \sqrt{I(I+1)} \text{ J T}^{-1} \text{ ----- (1.61)}$$

$$\text{where } \beta = \frac{q h}{4 \pi m} = \text{Bhor magneton (+ve constant)}$$

$$= 9.273 \times 10^{-24} \text{ J T}^{-1}$$

$g = \text{Landé splitting factor}$  and its value depends on quantum state of electrons and may be calculated from  $L, S,$  and  $J$  q.no.

In the applied magnetic field (produced by a horse shoe magnet), we see that  $I_z = -1$ , represent a dipole opposed to a magnetic field (i.e of high energy) while  $I_z = +1$  is in the same direction. (i.e of low energy) and  $I_z = 0$  has no dipole. Two energy levels are allowed to an electron

in magnetic field, the lower  $I_z = -\frac{1}{2}$  and higher  $I_z = +\frac{1}{2}$ . The extent of interaction between a magnetic dipole a field of strength  $B_z$  (in telsa) applied along Z- axis is equal to

$$\text{Interaction} = \mu_z B_z \text{ ----- (1.62)}$$

The separation between neighbouring energy levels (where  $I_z$  differs by units) is

$$\Delta E = |g \beta B_z| \text{ J ----- (1.63)}$$

where  $B_z$  is telsa .

$$\frac{\Delta E}{h} = |g \beta B_z| \text{ h Hz ----- (1.64)}$$

where modulus sign indicates +ve differences only considered.

$$\text{For electrons } \beta = 9.273 \times 10^{-24} \times \frac{0.34}{6.63 \times 10^{-34}} = 9500 \times 10^6 \text{ Hz}$$

Electron spin spectra fall at a considerably higher frequency which is on the long wave length edge of the micro wave region ( for nuclear spin is  $100 \times 10^6 \text{ Hz}$ , radio wave region )

If a sample containing unpaired electrons is in thermodynamic equilibrium in a magnetic field. There will be population difference between the two energy levels given by Boltzmann law.

$$\frac{n_1}{n_2} = \exp \frac{-\Delta E}{KT} = \exp \frac{-g\beta B_0}{KT} \text{ ----- (1.65)}$$

Where  $n_1$  and  $n_2$  are populations in upper and lower levels respectively, leading to an excess population in lower level. Electrons in the lower energy level will absorb radiation energy, and get excited to the higher level. Those electrons which are in the higher level, will emit radiation quanta of the same frequency  $\nu$  and return to the lower level. As a result, there will be a net

absorption of energy due to the larger population in the lower level.

**Relaxation :** by which electrons that have been excited to higher energy level can loose energy to their surroundings (lattice) and return to the lower level. Other wise there is continuous absorption of energy until both energy levels were equally populated .

Saturation depends on the intensity of the microwave radiation as well as up on the time required for a mol. in the upper level to fall back to the lower level. This condition of saturation is avoided in ESR measurements by working with a low power level of radiation to induce the electron resonance transition.

Energy levels for unpaired electrons in a magnetic field and ESR spectroscopy are shown in figs 1.21 and 1.22.

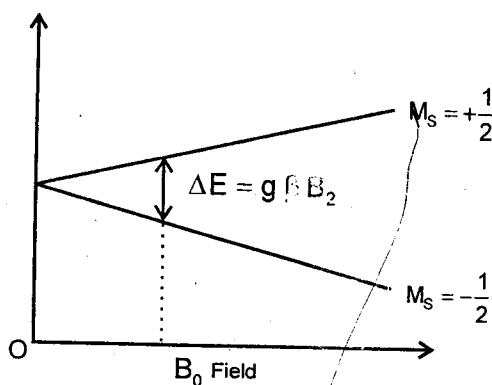


Fig : 1.21 Energy levels for an unpaired electron in a magnetic field

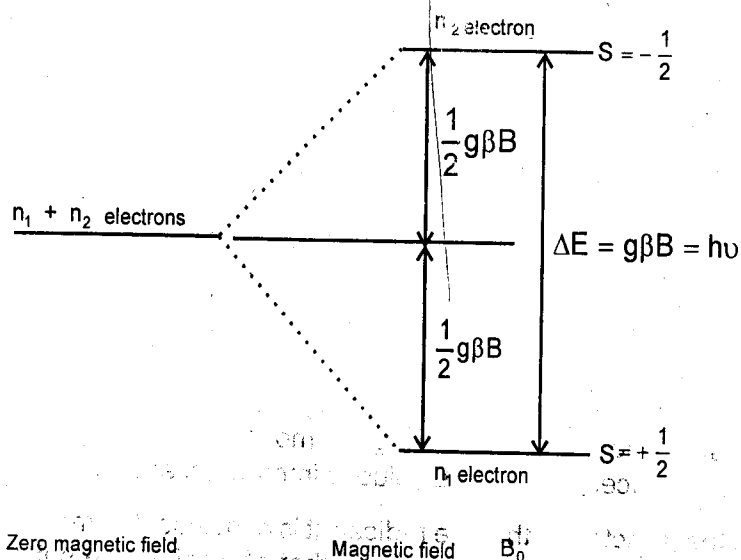


Fig : 1.22 Energy levels in ESR spectroscopy

### 1.4.iii) The g - factor - the position of ESR absorption :

We know that spin energy levels of an electron are separated in an applied magnetic field  $B_z$  is given by

$$\frac{\Delta E}{h} = \frac{g\beta B_z}{h H_z} \quad \text{----- (1.64)}$$

Where  $g$  is the lande splitting factor. Resonance absorption will occur at

$$\nu = \frac{\Delta E}{h} \text{ Hz} \quad \text{---- (1.66)}$$

The position of absorption changes directly with applied field (eq 1.64) since e.s.r spectroscopy operate at different fields, it is convenient to refer to the absorption in terms of the observed  $g$  value. Resonance equation 1.64.

$$g = \frac{\Delta E}{\beta B_z} = \frac{h\nu}{\beta B_z} \quad \text{---- (1.67)}$$

If resonance was observed at 9500 MHz in a field of 0.34 T, it would be reported as the resonance at a  $g$  value of 2.0023. This is very precise  $g$  factor for a free electron.

The  $g$  factor is a dimension less constant and the exact value of  $g$  factor reflects the chemical environment, particularly when heteroatoms are involved because orbital angular momentum of the electron can have an effect on the value of transition  $\Delta M_s = \pm 1$ .

In many organic free radicals  $g$  - value of odd/electrons is close to that of free electron, however in metal ion  $g$  - values are often greatly differ. For eg. The  $g$  values of the ionic crystals lies between 0.2 and 0.8

The reason is the unpaired electron is quantibruated by or belongs to a particular atom in the lattice, usually a transition metal ion due to coupling of orbital angular momentum and spin angular momentum. Many ionic crystals show a  $g$ - factor close to the free electron. This may be.

1. The ion contributes the electron may exist in an S- state ( $L=0$ ) For eg.  $\text{Fe}^{3+}$  - 5 unpaired electrons i.e  $S = \frac{5}{2}$ ,  $2S+1 = 6$  has  $L=0$ . Thus  $J = L + S$  and term symbol  ${}^6S_{5/2}$ , since  $J = S$ ,  $g = 2$ .
2. The electron field set up by all the ions in a crystal may be strong to uncouple the electrons orbital angular momentum and spin angular momentum .So on application of a field, electron spin vector processes. Thus  $L$  value is immaterial and the  $g$ -factor reverts to 2.

To measure the  $g$ -factor for the free radicals it is convenient to measure the field separation between to the center of unknown spectrum and that of a reference substance whose  $g$ - value accurately known. The known may be sample of finely powdered diphenylpicrylhydrazyl (DPPH). Which is completely in free radical state. Two signals may be observed simultaneously with a field separation of  $\Delta H$ . The  $g$ - factor for unknown is given by

$$g = g_{\text{stan}} \left( 1 - \frac{\Delta H}{H} \right) \quad \text{--- (1.68)}$$

Where  $H$  is the resonance frequency,  $\Delta H$  is +ve if unknown has its center at a higher field.

#### 1.4.iv) Properties of ESR spectral lines:

The properties depends on -

**a) Intensity :** Intensity is directly proportional to the concentration of free radical or paramagnetic material present. Conc. up to  $10^{-13}$  mol of free radical can be detected.

**b) Width :** Width depends on relaxation time of the spin state under study. For spin - spin interaction efficient time is  $10^{-6}$  to  $10^{-8}$ s . For spin - lattice interaction efficient time at room temperature is  $10^{-6}$  s but becomes less to reduced temperature, often becomes several minutes at liquid  $N_2$ . The wider e.s.r lines have advantages and disadvantages .

**c) Position :** position of e.s.r absorption depends on the g-factor, which was discussed in 1.4.iii.

**d) Multiplet structure :** The fine structure of e.s.r absorptions (electron nucleus coupling) In e/s.r spectroscopy it is necessary to distinguish between two kinds of multiplet structures.

**Fine structure :** It occurs in crystals containing more than one unpaired electron spin .

**Hyper fine structure :** A smaller effect. When an unpaired electron can get close to a nucleus with non -zero spin.

Electron nucleus coupling constants are very much bigger than those for nucleus - nucleus interaction, because

1. an electron can approach a nucleus more closely than can another nucleus
2. the electron magnetic dipole is some 1000 times larger than that of a nucleus .

For H - atoms two equal lines separated by 0.05 T,  $\nu = 1400$  MHz which is greater than 2 KHz (nucleus - nucleus ). For more organic molecules  $10^{-4}$  to  $10^{-3}$ T, because the unpaired electron does not combined to one nucleus.

The magnitude of coupling is given by

$$A = RP$$

Where  $A$  = coupling constant

$P$  = the electron density

$R$  = intrinsic coupling

For H  $P = 1$ ,  $A = 0.05$  T  $R = 0.05$  T



### 1.4.v) Hyper fine structure:

The splitting of energy levels of the spin states of electron in the vicinity of a spinning nucleus give rise to a number of peaks in the ESR spectrum more than expected is called hyper fine splitting. Total spin of nucleus -vector sum of p (spin due to proton) +n (spin due to neutron) each

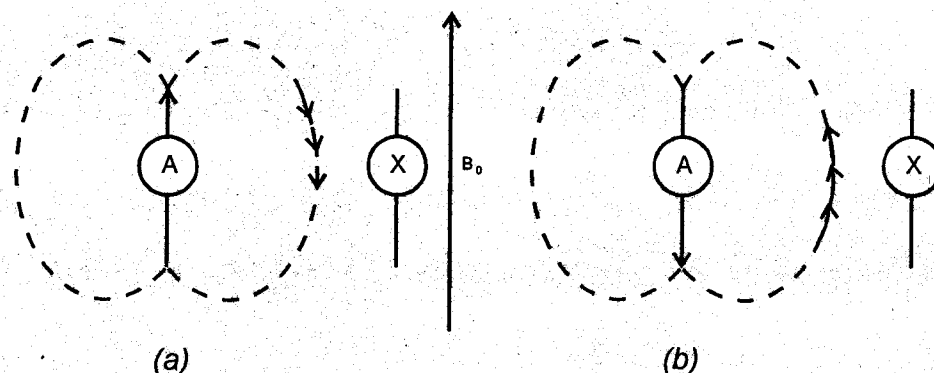
of magnitude  $\frac{1}{2}$ .

The rules are -

1. nuclei with p and n even, (charged mass even ) spin=0 eg.  $^4\text{He}$   $^{12}\text{C}$   $^{16}\text{O}$  etc
2. nuclei with p and n odd (odd integer charge and even mass) eg.  $^2\text{H}$ ,  $^{14}\text{N}$  (spin = 1)  $^{10}\text{B}$  (I = 3).
3. nuclei with half-integral spin

eg.  $^1\text{H}$ ,  $^{15}\text{N}$  (spin =  $\frac{1}{2}$ )  $^{17}\text{O}$  (spin =  $\frac{5}{2}$ )

The spin of nucleus given by a symbol I. Nucleus is in the same field or in opposed in the vicinity of unpaired electron with spin is shown in figure 1.23



In (a) The spin of A decreases the net magnetic field at X.

While in (b) The field at X is increased.

Fig: 1.23 The direct coupling of nuclear spins

This coupling causes the electron spin states to further split into different states depending on the value of I. Each electron spin energy state is split to  $2I + 1$  components.

For eg. a) Hydrogen atom

$$S = \frac{1}{2} \quad m_s = \pm \frac{1}{2}$$

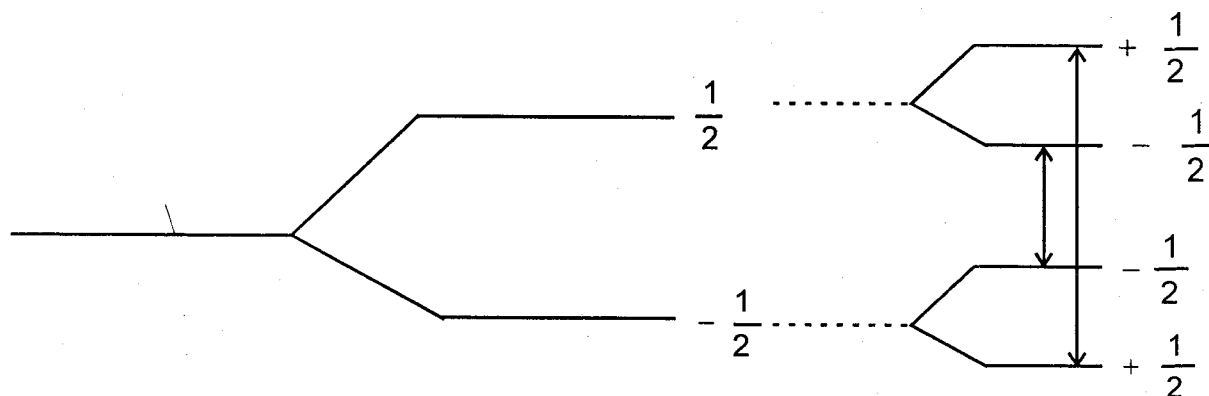


Fig : 1.24

The spins of  $A_{qx}$  if paired they will be in low energy i.e  $\uparrow\downarrow$  or  $\downarrow\uparrow$

$A_{qx}$  if unpaired they will be in high energy i.e  $\uparrow\uparrow$  or  $\downarrow\downarrow$

$$\text{So } m_s = \pm \frac{1}{2} \quad m_l = -\frac{1}{2} \quad m_s = -\frac{1}{2} \quad m_l = +\frac{1}{2} \text{ low energy}$$

$$m_s = +\frac{1}{2} \quad m_l = +\frac{1}{2} \quad m_s = -\frac{1}{2} \quad m_l = +\frac{1}{2} \text{ high energy}$$

The selection rule is  $\Delta m_s = \pm 1$  and  $\Delta m_l = 0$ .

One proton in nucleus interacted with electron, so spins of electron and proton results in splitting of 4 spin states and hence two transitions. The two transitions shown in fig 1.24 giving two peaks with equal intensity.

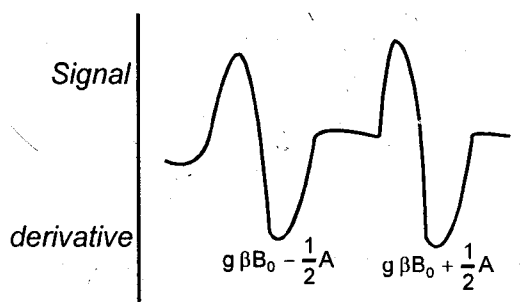


Fig 1.25 ESR spectrum of hydrogen atom

$$\text{Energy levels } E = g\beta B_0 m_s + A m_s m_l \text{ ----- (1.70)}$$

Where  $A$  = hyperfine coupling constant

$\Delta m_l = 0 \quad \Delta m_s = \pm 1$ . So energy transitions

$$1. \quad \left( \frac{1}{2}g\beta B_0 - \frac{1}{4}A \right) - \left( -\frac{1}{2}g\beta B_0 + \frac{1}{4}A \right)$$

$$= g\beta B_0 - \frac{1}{2}A$$

$$2. \quad = g\beta B_0 + \frac{1}{2}A$$

The magnitude of splitting depends on

1. The ratio of nuclear magnetic moment to nuclear spin
2. electron spin density in the intermediate vicinity of nucleus
3. an anisotropy effect.

### b) For Deuterium $H^2$

$$m_s = \pm \frac{1}{2} \quad I = 1 \quad m_1 = 1, 0, -1 \quad (2I + 1)$$

Three transitions are possible which are shown in fig 1.26

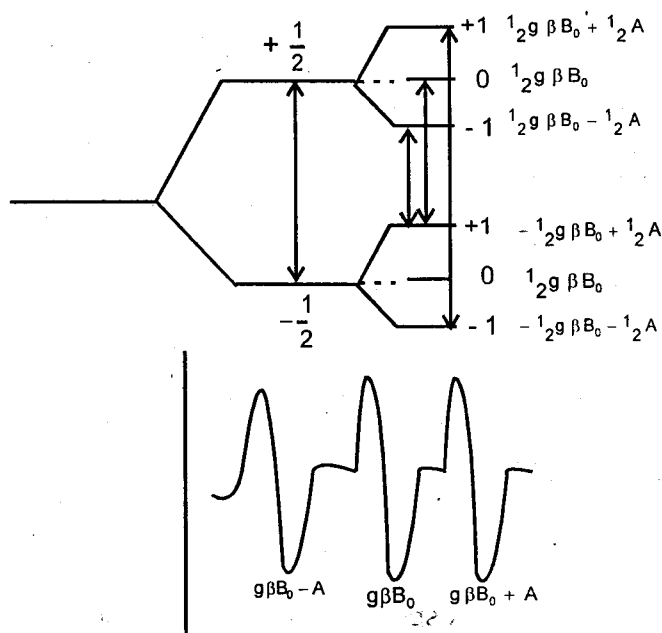


Fig: 1.26 ESR spectrum of  $H^2$  (Deuterium)

c) **Methyl radical  $\text{CH}_3$**  : Simple electrons surrounded by three protons are delocalized on the nuclei having  $I = \frac{1}{2}$

$$M_s = \pm \frac{1}{2}, m_1 = \pm \frac{3}{2} \pm \frac{1}{2}$$

The system has  $\pm \frac{1}{2}$  has three times more probable than  $\pm \frac{3}{2}$

System and the observed relative intensity for corresponding transition in the ratio 1 : 3 : 3 : 1

In general the total number of peaks expected for an electron delocalized are for  $n$  equivalent protons is given by  $2n + 1$  i.e.  $2nI + 1$  and the relative intensities of the peaks are given by the coefficients of binomial expansion.

$$(1+x)^m = 1 + mx + m(m-1) \times \frac{x^2}{1 \times 2} + m(m-1)(m-2) \times \frac{x^3}{1 \times 2 \times 3} + m(m-1)(m-2)(m-3) \times \frac{x^4}{1 \times 2 \times 3 \times 4} \dots (1.71)$$

$$(1+x^4) = 1 + 4X + 6X^2 + 4X^3 + X^4 = 1 : 4 : 6 : 4 : 1 \dots (1.72)$$

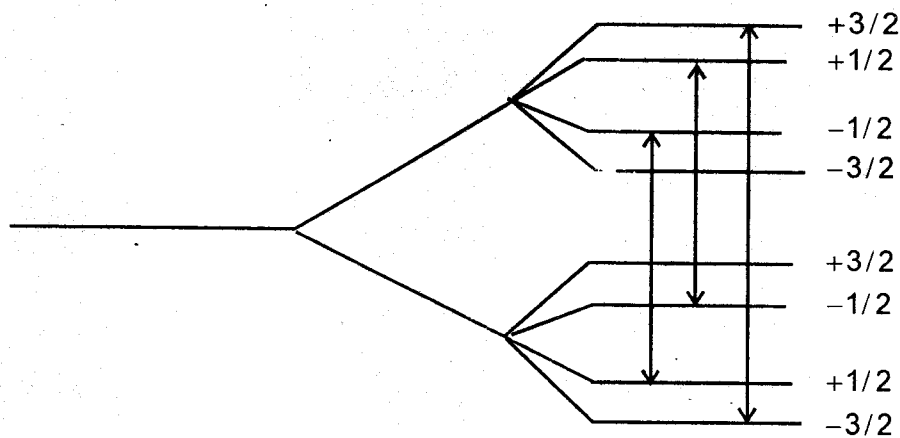


Fig: 1.27 Hyperfine splitting in  $\text{CH}_3$  radical

Fig 1.28 shows the e.s.r spectrum of the methyl radical. This is the derivative spectrum, the actual center of the each peak should be measured at the point where the slope is zero i.e. where the down word - sloping line crosses the X-axis. However, the height of the maximum of each point above the x - axis is good approximation to the intensity of normal non-derivative.

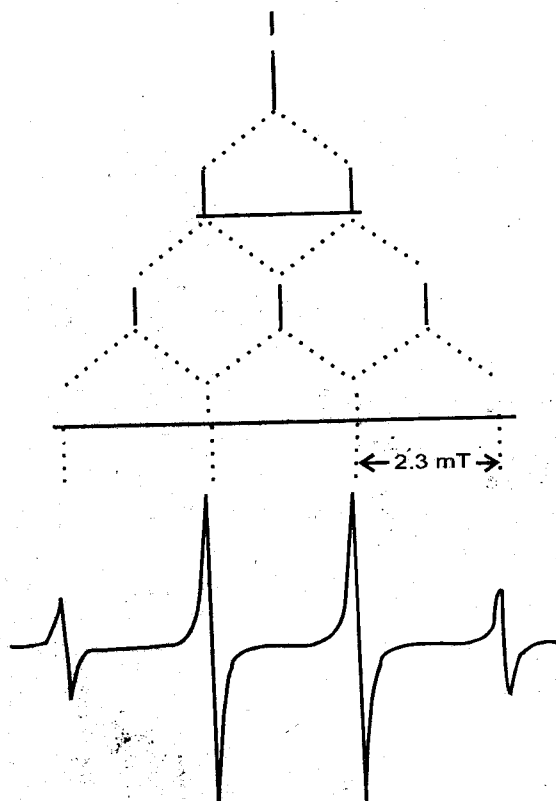


Fig : 1.28 e.s.r spectrum of the benzene radical and the family tree of couplings which produce it .

Fig . 1.28 shows the e.s.r spectrum a methyl radical and the family tree of couplings which produce it line in the spectrum, and it is clear that the fig.1.27 arises from a 1:3:3:1 quartet. Normally, we would expect the electron to spend an equal amount of time on each hydrogen, and so to couple equally to all three; this would result in the electron resonance being split in to a 1:3:3:1 quartet ,as shown by the family tree. The separation between the lines coupling is found to be about 2.3 mT (milli telsa). So we can use equation 1.69 to calculate

$$P = \frac{A}{R} = \frac{0.0023}{0.05} = 0.046$$

Then we have electron density at each hydrogen to be 0.046 or 4.6 % and so we know that the electron spends nearly 5% of its time at each hydrogen atom and the remaining  $100 - 3 \times 4.6 = 86\%$  on the carbon .

d) Benzene radical,  $C_6H_6$ . The e.s.r spectrum is shown in fig:1.29

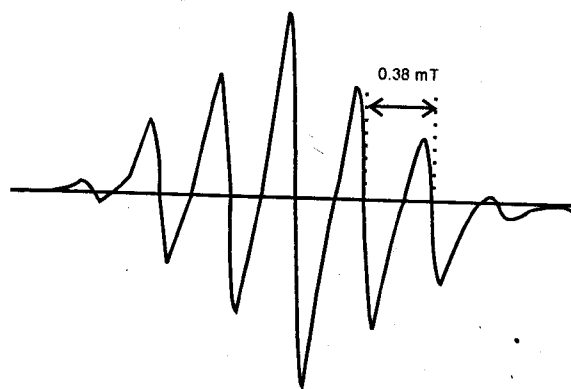


Fig 1.29 the e.s.r spectrum of benzene radical .

Here septet of lines indicating equal coupling to all six hydrogens. The coupling constant is

$$0.38 \text{ mT} \cdot P = \frac{0.38 \times 10^{-3}}{0.05 \approx 7.6 \times 10^{-3}}$$

There are six hydrogens with their electron density, making a total of  $6 \times 7.6 \times 10^{-3} = 0.046$  or nearly 5% in total. Clearly the remaining 95% of the electron time is spent equally on the six carbon atoms, making nearly 16% on each.

**d) Naphthalene radical :** The electron couple to more than one set of nuclei ,the pattern becomes more complicated, but can be rationalized by using family tree. The fig .1.30 shows e.s.r spectrum of the naphthalene radical.

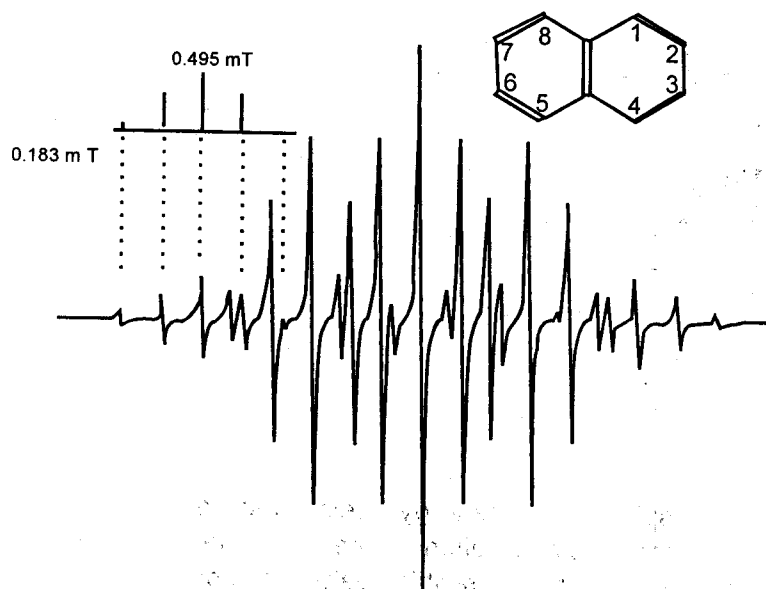


Fig : 1.30 The e.s.r spectrum of the naphthalene radical .

The molecule is symmetrical, there are only two different types of H<sub>2</sub>, 1, 4, 5, 8 are one and 2, 3, 6, 7 another set. The electron couples with later group, A = 1.83 x 10<sup>-4</sup> T. And since there are four hydrogens, the pattern will be 1 : 4 : 6 : 4 : 1 pentet. One such pentet on left side. The other group of 4 hydrogens (A = 4.95 x 10<sup>-4</sup> T), This pentet will itself be split in to a 1 : 4 : 6 : 4 : 1 pentet.

#### 1.4.vi) ENDOR and ELDOR:

**ENDOR** : It is electron nuclear double resonance. The technique was invented by Feher to improve the effective resolution of an e.s.r spectrum. Here sample is irradiated simultaneously with a microwave frequency suitable for electron resonance and radio frequency suitable for nuclear resonance. The radio frequency is swept while noticing e.s.r spectrum under condition of microwave saturation.

**ELDOR** : It is electron double resonance. The sample is irradiated simultaneously two microwave frequencies. One of them is used to observe an e.s.r signal at some point of the spectrum, while the other is swept through other parts of the spectrum to display the e.s.r signal as a function of the difference of the two microwaves frequencies. The technique is useful for separating overlapping multi-radical spectra and for studying various relaxation phenomena including spin and chemical exchange.

#### 1.4.vii) Summary:

1. Electron spin resonance (e.s.r) or electron paramagnetic resonance (e.p.r) is a technique in absorption spectroscopy, which is mainly used for detecting paramagnetism.
2. ESR is based on splitting of magnetic energy levels caused by the action of magnetic field on an unpaired electron contained in an ion, molecule or atom.
3. The Para magnetism is due to magnetic moment of unpaired electron or odd electron, this technique is applicable to transition metal ions, complexes, free radicals, biradicals, molecules with triplet state electrons and conduction electrons in metals.
4. The free electron behaves as a spinning, charged particle with a resulting magnetic moment opposite in sign to the proton and most other nuclei.
5. Spin number of electron is  $\frac{1}{2}$  and has two magnetic energy levels.
6. The magnetic moment of electron is about 1000 times greater than that of proton and thus the frequency of absorption in a given magnetic field is much larger.
7. The magnitude of magnetic moment of free electron is  $9.2732 \times 10^{-21}$  erg. gauss<sup>-1</sup> ESR spectroscopy is based on transition between energy levels produced by the action of a magnetic field.
8. In a magnetic field, splitting of the energy levels of the electron occurs and this splitting can be observed by microwave absorption. More over, the electron spin can couple with the spin of nuclei in the species to give splitting pattern analogous to those observed for nuclear spin-spin coupling.

9. The resonance frequency of an electron depends up on the magnetic fields at the electron and the effect of magnetic moment of nuclei on the ESR spectrum is known as hyperfine interaction.
10. When an electron interacts with  $n$  equivalent nuclei, its resonance peak is split into  $(2nI + 1)$  peaks where  $I$  is the spin quantum number of nuclei.
11. The magnitude of splitting, usually given in gauss is called hyperfine coupling constant.

#### 1.4.viii) Model questions :

1. Give an account on the theory of ESR.
2. Derive an equation for separation between neighbour energy levels.
3. Write equation for population difference between two energy levels.
4. what is  $g$ -factor Derive expression and explain.
5. Discuss about hyperfine structure esr spectra.
6. Explain the hyperfine structure of methyl radical.
7. Why H atom gives two peaks and  $^2\text{D}$  gives three peaks in ESR spectra ? Explain?
8. What do you mean by ENDOR and ELDOR.
9. The  $p$ -benzosemi quinine radical ion  $[\text{OC}_6\text{H}_4]$  exhibits a hyperfine spectrum of five lines with relative intensities  $1 : 4 : 6 : 4 : 1$  explain.

**Ans:** This radical ion contains four equivalent protons and so it exhibits five lines according to  $(n + 1) = (4 + 1) = 5$  rule. There will be no splitting from carbon and oxygen because  $^{12}\text{C}$  and  $^{16}\text{O}$  isotopes have no nuclear spin.

10. Calculate the ESR frequency in a magnetic field of 25000 gauss of  $g = 2$  and  $\beta = 9.273 \times 10^{-24} \text{ JT}^{-1}$ .

**Ans :**  $h\nu = g\beta B_0$  or  $\nu = \frac{g\beta B_0}{h}$

Here  $B_0$  is 25000 gauss = 2.5 Telsa  $1\text{T} = 10000 \text{ gauss}$ .

$$\nu = \frac{2 \times 9.273 \times 10^{-24} \times 2.5}{6.626 \times 10^{-34}} = 7000\text{MHz} \quad (h \text{ is in Joules}).$$

#### Recommended Books :

A.J. Sonessa

B.K.Sharma

C.N.Banwell

Introduction to molecular spectroscopy  
Spectroscopy,

Fundamentals of molecular spectroscopy



## UNIT - II

### Lesson I

# Vibrational spectra of diatomic molecules.

## Objectives

- Simple harmonic oscillator
- Quantisation of vibrational energy
- Requirement for I.R.
- Selection rules
- Isotope effect
- Anharmonic oscillator
- Overtone
- Hot bands.

### 2.1.i) Vibrational Motion - Simple Harmonic Oscillator:

The molecules perform vibrational motions, consider the simple case of the vibrational motion of single mass attached to weight less spring Fig.2.1

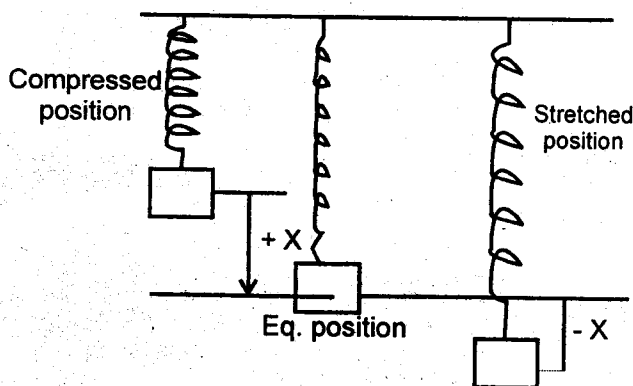


Fig : 2.1

The motion of this mass on a spring held by a rigid support can be analysed using the chemical law known as Hooke's Law.

It is experimentally observed that when the mass is displaced from its equilibrium position by some externally applied force, a restoring force arises in the spring in the direction opposite to

that of displacement and acts to bring mass back to its original position.

**Hooke's Law :** It states that the restoring force  $F$  is directly proportional to, but in opposite direction to, the displacement  $X$  from its equilibrium position. i.e.

$$F \propto (-X) \text{ or}$$

$$F = K X \text{ ---- (2.1)}$$

The proportionality constant is a +ve quantity and -ve arises because  $F$  acts in a direction opposite to  $X$ .

**Force constant :** The proportionality constant  $K$ , is known as the force constant of the spring. From the fig:2.1, it is apparent that for a given displacement of the spring, a larger value of  $K$  will result in a larger value of the restoring force. The  $K$ , is the measure of the stiffness of the spring. A large value of  $K$  means a stronger and less flexible spring and a small value of  $K$  means a weaker, more flexible spring.

**Equation of motion :** It gives the variation of the displacement  $x$  with the variation in time  $t$ .

$$X = f(t) \text{ ---- (2.2)}$$

Where  $f(t)$  is some function of  $t$ .

This can be obtained directly by equating the restoring force in eq.2.1 to  $ma$

$$F = m a \text{ ---- (2.3)}$$

Where  $a$  = acceleration (second direction of displacement)

$m$  = mass

(Newton's second law of motion)

For a mass, -ve (downward) displacement  $-X_{\max}$  (stretched position). The mass will return through its equilibrium position and then continue upward to a max +ve displacement  $+X_{\max}$  (compressed position) equal in magnitude to -ve  $X_{\max}$ . If there are no frictional losses, the particle will continue to oscillate between the extremes.

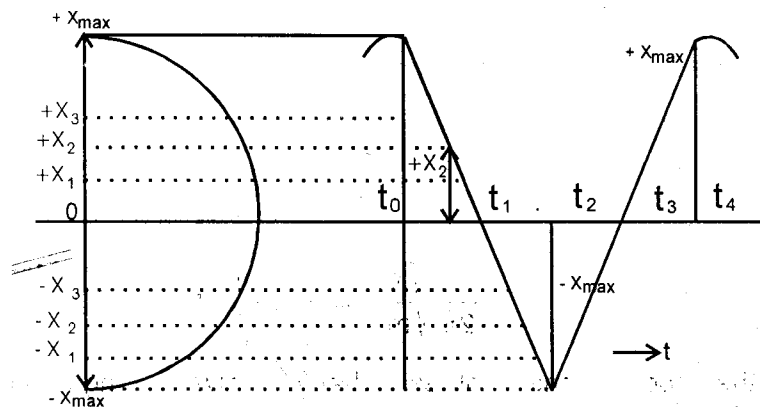


Fig : 2.2 simple harmonic motion of vibrational motion of mass on a weightless spring

Now let us transpose the points to a circle of radius  $X_{\max}$  with its center at  $X = 0$ . It is apparent that the vertical displacement can be considered as the motion of a point about the circumference of the circle. Hence, vibrational motion of mass on a spring is equivalent to the circular motion of a point. A complete revolution about the circle corresponds to a complete cycle of the vibrational motion, i.e. from  $-X_{\max}$  through  $X_{\max}$  to  $-X_{\max}$ . This periodic motion is known as simple harmonic motion, which is analogous to wave motion.

Let us transpose the points from the circumference of the circle to co-ordinate axis in which the displacements are plotted as ordinate and the time is plotted as abscissa (Fig:2.2). The displacement is  $+X_{\max}$  at  $t = 0$  i.e., we arbitrarily begin the motion in the compressed position, the displacement goes through the equilibrium position ( $X = 0$ ) at some later time ( $t = t_1$ ) and finally completes cycle at  $t = t_4$ . The similarity between the graph  $X$  vs  $t$  in this case and  $E$  vs  $t$  in electric vector indicates that the function  $f(t)$  in  $X = f(t)$  is exactly the same as in the latter case i.e.,  $f(t) = \cos 2\pi vt$ . Then

$$X = X_{\max} \cos 2\pi vt \quad \text{----- (2.4)}$$

+ sign on the  $X$  arises for compression .

- sign on the  $X$  arises for stretching.

The sign follows from cosine term.

Since we are dealing with circular motion, angular velocity

$$\omega = 2\pi v \quad \text{---- (2.5)}$$

As mentioned above

$$F = m a = -K X \quad \text{---- (2.6)}$$

where  $a = \frac{\partial^2 x}{\partial t^2}$  and differentiating eq.2.5 twice with respect to time gives

$$\begin{aligned} a &= 4\pi^2 v^2 X_{\max} \cos 2\pi vt \\ &= -4\pi^2 v^2 X \quad \text{---- (2.7)} \end{aligned}$$

Using this for  $a$  in eq. (2.6) and solving for give  $K$  give

$$K = 4\pi^2 v^2 m \quad \text{---- (2.8)}$$

Solving for  $v$  gives

$$v = \frac{1}{2\pi} \sqrt{\frac{K}{m}} \quad \text{---- (2.9)}$$

Eq.2.9 yield the important chemical result that for a given spring and mass, there is only one frequency possible i.e., vibrational frequency.

Let us now consider a system of consisting of two masses  $m_1$  and  $m_2$  connected by a spring

This model later is used for representing the diatomic molecule, Fig: 2.3

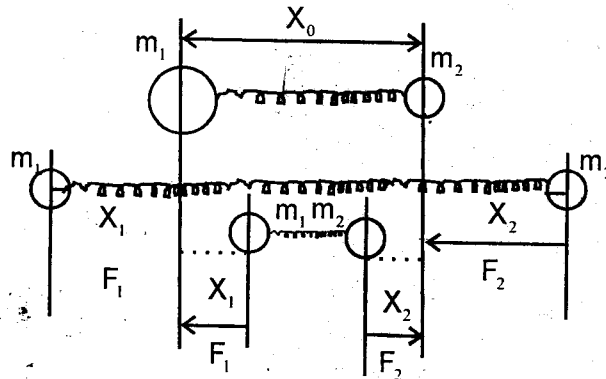


Fig : 2.3

Let the  $m_2$  be moved an amount  $X_2$  to the right (+ve  $X$ ) and  $m_1$  to  $X_1$  to the right (-ve  $X$ )

This will give net extension

$$X_{\text{net}} = X_2 + (-X_1) = (X_2 - X_1) \quad \text{--- (2.10)}$$

This stretching will give rise to a restoring force i.e.,

Proportional to  $X_{\text{net}}$  and is given by

$$F = -K (X_2 - X_1) \quad \text{--- (2.11)}$$

This restoring force acts to move  $m_1$  in toward right and  $m_2$  in toward the left. Applying  $F=ma$ ,

$$F \text{ (acts on } m_2) = -F \text{ (acts on } m_1) \quad \text{--- (2.12)}$$

But each is equal to  $-K (X_2 - X_1)$ , we get

$$-(X_2 - X_1) = m_2 a_2 \quad \text{--- (2.13a)}$$

$$(X_2 - X_1) = m_1 a_1 \quad \text{--- (2.13b)}$$

using a form equation 2.7 in 2.13a and 2.13b

$$KX_1 = (K - 4\pi^2 v^2 m_2) X_2 \quad \text{--- (2.14a)}$$

$$KX_2 = (K - 4\pi^2 v^2 m_1) X_1 \quad \text{--- (2.14b)}$$

Elimination  $X_1$  and  $X_2$  by dividing equation 2.14a and 2.14b

$$KX_1 + (4\pi^2 v^2 m_2 - K) X_2 = 0$$

$$KX_2 + (4\pi^2 v^2 m_2)X_1 = 0$$

$$\begin{vmatrix} K & (4\pi^2 v^2 m_2 - K) \\ 4\pi^2 v^2 m_1 - K & K \end{vmatrix} = 0$$

cross multiplication

$$K^2 - (4\pi^2 v^2 m_1 - K)(4\pi^2 v^2 m_2 - K) = 0$$

$$K^2 - [16\pi^4 v^4 m_1 m_2 - 4\pi^2 v^2 m_1 K - 4\pi^2 v^2 m_2 K + K^2] = 0$$

$$16\pi^4 v^4 m_1 m_2 - 4\pi^2 v^2 K(m_1 + m_2) = 0$$

$$4\pi^2 v^2 m_1 m_2 = K(m_1 + m_2)$$

$$\frac{4\pi^2 v^2}{K} = \frac{m_1 + m_2}{m_1 m_2}$$

$$K = 4\pi^2 v^2 \frac{m_1 m_2}{m_1 + m_2} \quad \text{--- (2.15)}$$

Finally we write the oscillation frequency,  $v_{\text{osc}}$  is

$$v_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \quad \text{--- (2.16)}$$

$$E = \frac{h}{2\pi} \sqrt{\frac{K}{\mu}} \quad \text{--- (2.17)}$$

### Energy Expression

Potential energy (P.E) varies as the square of the displacement  $X$ . Since  $X$  is max at end points of the vibration and zero at the equilibrium position.

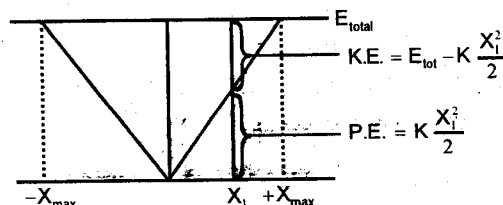


Fig: 2.4 potential energy diagram for simple harmonic oscillator.

When the masses are given a displacement equal in magnitude to  $X_{\max}$ , the energy of the system is all P.E, equal in magnitude to  $\frac{KX^2}{2}$ . If the masses are then released, the restoring force acts to set the masses into motion back toward their equilibrium position. This motion gives Kinetic Energy (K.E). So

$$E_{\text{tot}} = \text{P.E} + \text{K.E} \quad \text{--- (2.18)}$$

$$= \frac{1}{2}KX^2 + \frac{1}{2}\mu u^2 \quad \text{--- (2.19)}$$

For any one values of  $E_{\text{tot}}$  the particle will be restricted to move between the end points  $X_{\max}$  to  $+X_{\max}$ . This continuous variation in  $E_{\text{tot}}$  will give rise to very large no. of energy levels (horizontal lines on the parabola in Fig:2.4.

## 2.1.ii) Quantisation Of Vibrational Spectra For The Harmonic Oscillator:

The wave mechanical treatment of the system yields the result that the energy can take on the values given by

$$E = \frac{h}{2\pi} \sqrt{\frac{K}{\mu}} \left( V + \frac{1}{2} \right) \quad \text{--- (2.20)}$$

$$= h\nu_{\text{osc}} \left( V + \frac{1}{2} \right) \quad \text{--- (2.21)}$$

$$\text{Since } \nu_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$$

where  $V$  = vibrational quantum number

$$= 0, 1, 2, 3, 4, \dots$$

These are the only values of the energy that are allowed by the theory. The  $V$  is an integer substituting the value of  $V$  i.e.

$$V=0 \quad -E = \frac{1}{2} h\nu_{\text{osc}}$$

$$V=1 \quad -E = \frac{3}{2} h\nu_{\text{osc}}$$

$$V=2 \quad -E = \frac{5}{2} h\nu_{\text{osc}}$$

**Zero point energy** : The theory tells us that even in the lowest vibrational level, the molecule still possesses some vibrational motion. This situation corresponds to the case the systems of mol-

olecules are brought near the absolute temperature ( $0^{\circ}\text{K}$ ). In this state, there is no rotational motion and translational motion but the molecule still possesses some vibrational motion due to zero point energy.

$$E = h\nu_{\text{osc}} \left( V + \frac{1}{2} \right)$$

if  $V = 0$ . We will get

$$E_{\text{zeropoint}} = h\nu_{\text{osc}} \left( 0 + \frac{1}{2} \right) = \frac{1}{2} h\nu_{\text{osc}}$$

### Allowed transition levels and vibrational spectra

**Selection rules :** For the vibrational spectra the selection rules are :

- 1) The change in quantum numbers  $\Delta V = \pm 1$ .

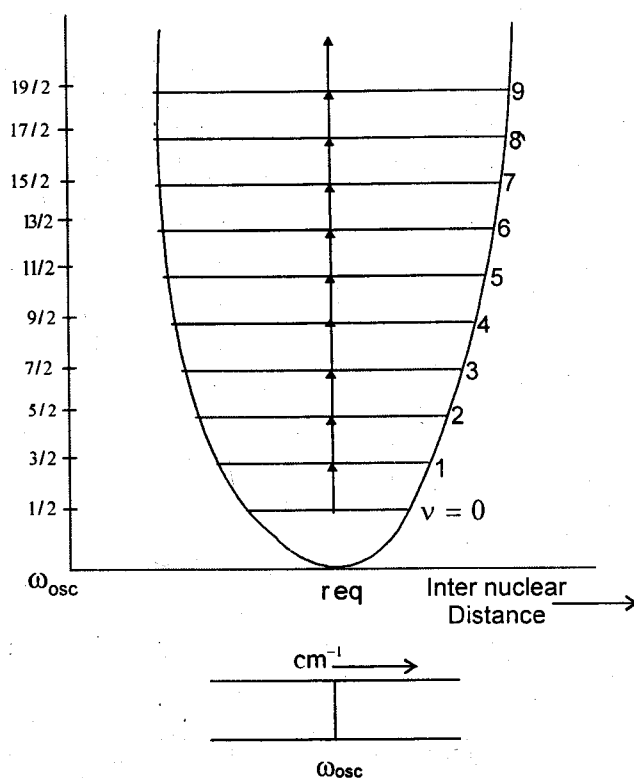


Fig .2.5 : Allowed energy levels of simple harmonic oscillator

$$\text{i.e. } V^i - V^{ii} = \pm 1 \quad \text{or } V^i = V^{ii} + 1.$$

Spacing between energy levels is equal and  $\Delta E = h\nu_{\text{osc}}$  i.e.

$$\nu = \nu_{\text{osc}} \quad \text{--- (2.22)}$$

since  $\Delta E = h\nu$  Each allowed transition give rise to the same spectral frequency as the

chemical frequency of the oscillator. Hence only one spectral line will arise according to the simple harmonic oscillator approximation of a diatomic molecule. This predicted spectral lines will correspond to the fundamental band observed under low resolution.

- 2) The permanent dipole is required for obtaining vibrational spectra. The requirement for a vibration to be infrared active is that the vibrational motion of the nuclei must give rise to change in the dipole moment of the molecule. When the bond stretches and compresses during the vibration in diatomic molecule, the increased or decreased bond distance increases or decreases the magnitude of the already present dipole moment. Homonuclear diatomic molecules like  $N_2$ ,  $Cl_2$  and  $H_2$  are not infrared active.

### Calculations :

$$1) \text{ Fundamental frequency } \nu = \overline{\nu c} = 2886 \times 3 \times 10^{10} \\ = 8.66 \times 10^{13} \text{ Hz.}$$

$$\text{Rotational frequency } \nu_{\text{rot}} = 8.95 \times 10^{11} \text{ Hz}$$

We can see that  $\nu_{\text{osc}}$  is one hundred times larger than  $\nu_{\text{rot}}$ . So vibrational transitions occur at higher frequency regions.

$$2) \text{ Calculation of force constant } K = 4\pi^2 \nu^2 \mu \\ = 4(3.14)^2 (8.66 \times 10^{13})^2 (1.63 \times 10^{-24}) = 4.8 \times 10^5 \text{ dyne.cm}^{-1}$$

For other hydrogen halides etc. the force constant values are given in table 2.1

**Table 2.1**

Molecule	Fundamental bond $\nu$ Hz	Force constant $K \times 10^5$ dyne.cm <sup>-1</sup>
HF	2907	9.7
HBr	2559	4.1
HI	2230	3.2
CO	2143	118.4

From the table it is clear that CO is having high force constant value i.e the bond is more stiff (strong) because there is a triple bond where hydrogen halides have low values and the bonds are more flexible because there is a simple bond.

- 3) Calculation of maximum displacement.

$$E = \frac{1}{2} K X^2 + \frac{1}{2} \mu u^2$$

Where X is max.



$$E = \frac{1}{2} K X^2 \text{ and equating this to quantised energy}$$

$$E = h\nu_{\text{osc}} \left( V + \frac{1}{2} \right)$$

$$\frac{1}{2} K X_{\text{max}}^2 = h\nu_{\text{osc}} \left( V + \frac{1}{2} \right)$$

For lower energy level  $V = 0$

$$X_{\text{max}} = \pm \sqrt{\frac{6.62 \times 10^{-17} \times 8.66 \times 10^{13}}{4.8 \times 10^5}}$$

$$= \pm 1.1 \times 10^{-9} \text{ cm} = \pm 0.11 \text{ \AA}$$

For lower energy level  $V=0$

$$X_{\text{max}} = \pm \sqrt{\frac{h\nu_{\text{osc}}}{K}}$$

Where + ve and - ve signs corresponds to compression and stretching. So

$$X_{\text{max}} = \pm \sqrt{\frac{6.62 \times 10^{-27} \times 8.66 \times 10^{13}}{4.8 \times 10^5}}$$

$$= \pm 1.1 \times 10^{-9} \text{ cm} = \pm 0.11 \text{ \AA}$$

Comparing this with the equilibrium internuclear distances of  $1.127 \text{ \AA}$ , the bond can stretch or compresses by 10% of normal bond length.

Maximum vibrational Q.No to which bond can stretch -

Dissociation of energy of HCl =  $110 \text{ k cal. mol}^{-1}$

D.E for 1 mole =  $7.4 \times 10^{-12}$

$$\text{Equate } 7.4 \times 10^{-12} = \frac{1}{2} K X_{\text{max}}^2$$

$$X_{\text{max}} = 0.6 \text{ \AA}$$

$$\text{From } \frac{1}{2} K X_{\text{max}}^2 = \frac{1}{2} h\nu_{\text{osc}} \left( V + \frac{1}{2} \right) = V = 13.$$

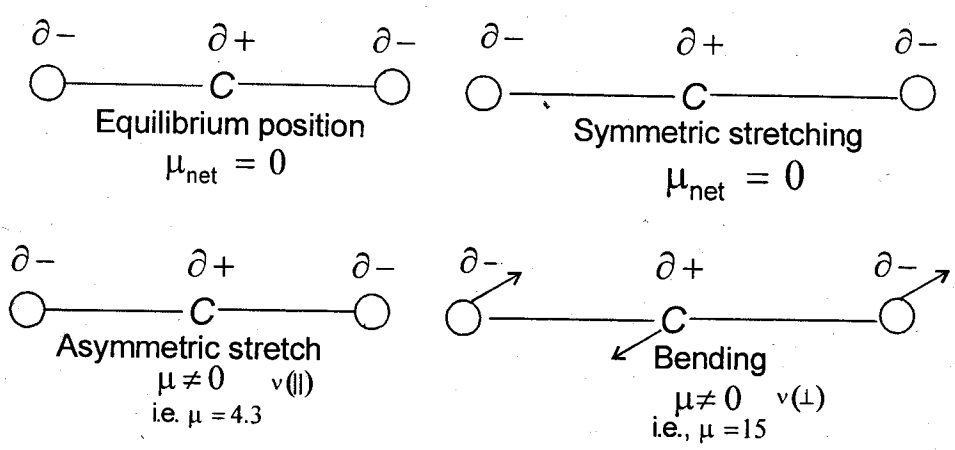
Enough energy is absorbed in to the vibrational degrees of freedom of HCl to raise it to the

13th vibrational level, the amplitude of vibration will be of such an extent that the molecule will dissociate. This result indicates that the simple harmonic oscillator model of a diatomic molecule is at best only a rough approximation to real molecules. It predicts only the occurrence fundamental bond.

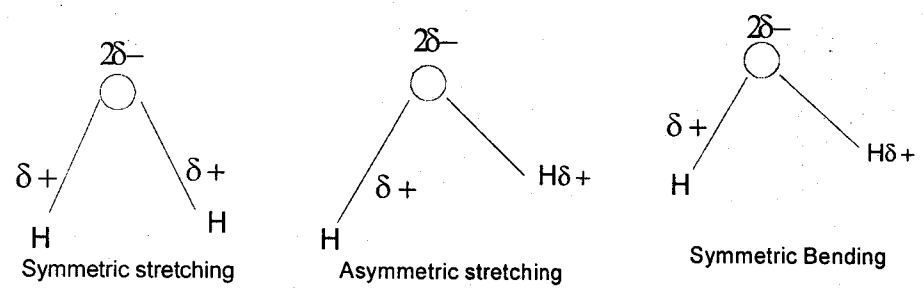
### 2.1.iii) Requirement for infrared activity in polynuclear molecules

#### Poly Nucleated Molecules

The requirement for bond vibration will give rise to a change in dipole moment does not imply that the molecule as a whole must have a permanent dipole moment. CO<sub>2</sub> is a typical example of a molecule that does not possess a permanent dipole but which is infrared active.



The vibrational motion of asymmetric stretch and bending motion are infrared active. A non-linear triatomic molecule such as H<sub>2</sub>O or SO<sub>2</sub> will have all three vibration IR active.



The dipole moment change along the line of symmetry axis in symmetric stretching and bending symbol, parallel || and across the axis symbol perpendicular ⊥. Stretching ν<sub>osc</sub> > ν<sub>bend</sub>.

### 2.1.iv) Isotope effect in vibrational spectra :

Let us now consider the effect of different isotopic molecules on the fundamental bond wave numbers. Eq.2.16 shows that  $\nu_{osc}$  depends on the value of  $K$  and  $\mu$ .  $K$  depends on the nature of the bond and therefore on the electronic arrangement in the mol. Isotopic mols, have essentially identical electronic arrangement but differ only in the mass of elements. Hence  $K$ , be identical for isotopic mols. and differ in  $\mu$ . Let A and B are, two isotopic molecules and using eq.2.16, we obtain

$$\nu_{osc}^A = \frac{1}{2\pi} \sqrt{\frac{K}{\mu^A}} \quad \text{---- (2.23a)}$$

$$\nu_{osc}^B = \frac{1}{2\pi} \sqrt{\frac{K}{\mu^B}} \quad \text{---- (2.23b)}$$

Dividing eq.2.23a by 2.23b gives

$$\frac{\nu_{osc}^A}{\nu_{osc}^B} = \sqrt{\frac{\mu^B}{\mu^A}} \quad \text{---- (2.24)}$$

If A contains the heavier isotope, then  $\mu^A > \mu^B$

For eg.  $H^1Cl^{35}$  and  $H^2Cl^{35}$  (DCl)

$\mu$  for  $H^1Cl^{35} = 1.63 \times 10^{-24}g$

$H^2Cl^{35} = 3.14 \times 10^{-24}g$

$\nu_{osc}$  for  $H^1Cl^{35} = 2886$

$$\text{Then } \nu_{osc} \text{ for } H^2Cl^{35} = 2886 \sqrt{\frac{1.63 \times 10^{-24}}{3.14 \times 10^{-24}}} = 2078 \text{ cm}^{-1}$$

Experimentally the  $\nu_{osc}$  for  $H^2Cl^{35}$  observed at  $2094 \text{ cm}^{-1}$ . This is an excellent agreement.

The fundamental  $\bar{\nu}$  for an isotopic molecules are summarized in table 2.2

Table : 2.2

Molecule	$\mu$ (g)	Fundamental bond $\bar{\nu}$ ( $\text{cm}^{-1}$ )
$H^1F^{19}$	$1.59 \times 10^{-24}$	2907
$H^2F^{19}$	$3.01 \times 10^{-24}$	2110
$C^{12}O^{16}$	$11.4 \times 10^{-24}$	2143
$C^{12}O^{18}$	$12 \times 10^{-24}$	2092

So the isotope effect is, the fundamental bond decreases for heavier isotopic molecules, which is clear from the table.

### 2.1.v) Anharmonic oscillator :

The restoring forces and the potential that arises from vibrations according to Hooke's law increases indefinitely with increasing displacement. This cannot be the case for real molecule, since increased separation will eventually lead to bond rupture and dissociation. Dissociation corresponds to the case where the attractive force between the atoms is zero and consequently P.E is constant. Vibrational motion of this type is said to be anharmonic and the system is called anharmonic oscillator. The real molecules do not obey exactly the laws of simple harmonic motion, real bonds, although elastic are not so homogeneous to obey Hooke's law. If the bond between atom is stretched for instance, there comes a point at which it will break. The molecule dissociate in to atoms. Then although for small compression and extensions the bond may be taken as perfectly elastic, for larger amplitudes say greater than 10% of the bond length- a much more complicated behavior must be assumed. Fig.2.6 show diagrammatically the shape of energy curve for a typical diatomic molecule, together with (dashed) ideal simple harmonic parabola.

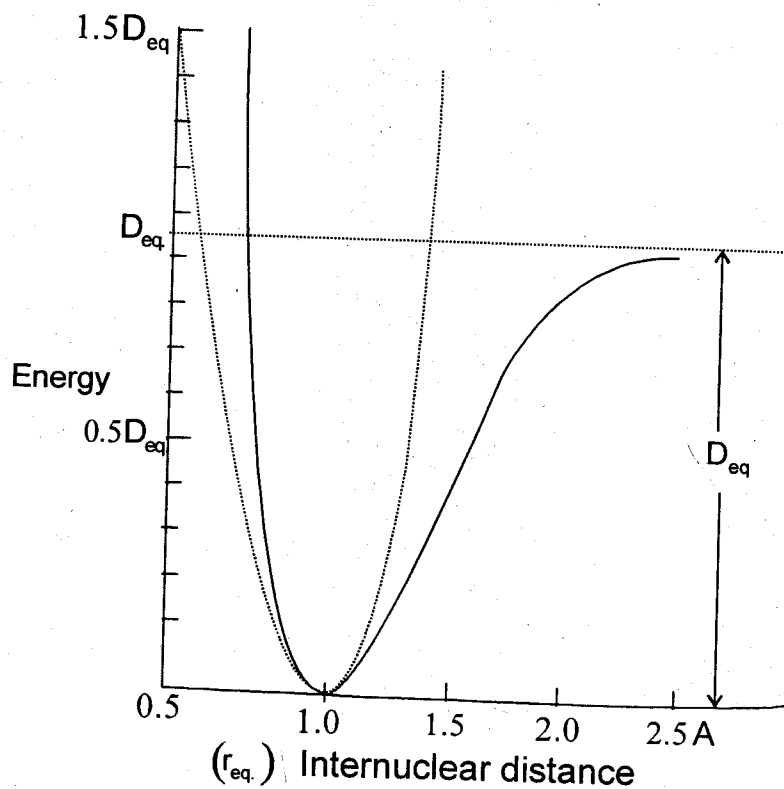


Fig 2.6 The Morse curve : the energy of a diatomic molecule under going anharmonic extensions and compressions.

A purely empirical expression which fits this curve to a good approximation was derived by P.M. Morse and is called the Morse function.

$$E = D_{eq} [ 1 - \exp \{ a ( r_{eq} - r ) \} ]^2 \quad \text{--- (2.25)}$$

where  $a$  is constant for a particular molecule and  $D_{eq}$  is the dissociation energy.

The minimum of the curve occurs at  $r_{eq}$ , the equilibrium bond length. As one goes larger in the nuclear separations, the anharmonic curve diverges significantly from the harmonic curve. At very larger  $r$ , the curve symbolically approaches the constant P.E value corresponds to dissociation.

The energy expression for the anharmonic oscillator

$$E = h\nu_{osc} \left( V + \frac{1}{2} \right) - h\nu_{osc} X_e \left( V + \frac{1}{2} \right)^2 \quad \text{--- (2.26)}$$

Where  $X_e$  = anharmonicity constant ( + ve )

Anharmonicity constant is a measure of the dissociation from harmonic motion in the molecule. The second term in 2.26 is the correction term on the harmonic term. The magnitude of  $X_e$  is very much smaller than  $\nu_{osc}$ , and will contribute significantly for large values of  $V$ . The energy level diagram consists of equally spaced levels for low values of  $V$  but as  $V$  increases and the second term in the eq.2.26 becomes important and the separation between levels will decrease. For larger  $V$ , the resulting larger amplitude will lead eventually to dissociation of molecule. The P.E curve for anharmonic oscillator is shown in Fig: 2.7.

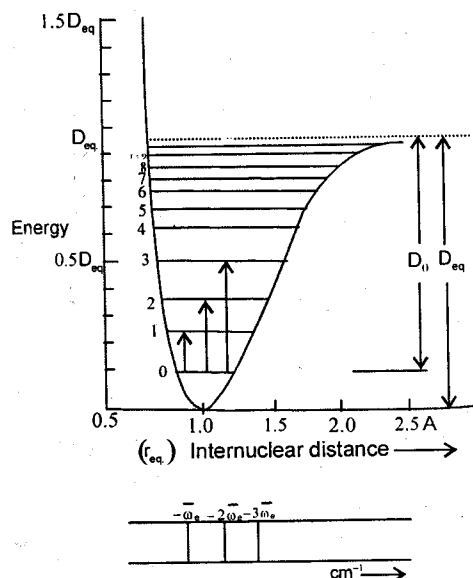


Fig: 2.7 The vibrational energy levels and some transition between them for a diatomic mol. undergoing anharmonic oscillator.

The dissociation energy can be obtained from the P.E curve (Fig: 2.7). The energy differ-

ence between lowest energy level ( $V = 0$ ) and the constant P.E asymptote (the case of infinite separation and therefore disassociation)

**Selection rules :** The selection rules are  $\Delta V = \pm 1$ ,  $\Delta V = \pm 2$ ,  $\Delta V = \pm 3$  not only the  $\Delta V = \pm 1$  but also others  $\Delta V = \pm 2$ ,  $\Delta V = \pm 3$  etc are predicted with decreasing intensity.

The possible transitions from ground vibrational state ( $V=0$ ) are

- 1)  $V=0 \longrightarrow V = 1$  Fundamental band
- 2)  $V=0 \longrightarrow V = 2$  First overtone
- 3)  $V=0 \longrightarrow V = 3$  Second overtone etc.

Thus for transitions  $V'' = 0$  to  $V' = V$  ( $1, 2, 3, \dots$ )

$$\bar{\nu} = \frac{\Delta E}{hc} = E(V' = V) - (V'' = 0) \quad \text{--- (2.27)}$$

$$\bar{\nu} = \left[ \bar{\nu}_{\text{osc}} \left( V + \frac{1}{2} \right) - \bar{\nu}_{\text{osc}} X_e \left( V + \frac{1}{2} \right)^2 \right] - \left[ \bar{\nu}_{\text{osc}} \left( 0 + \frac{1}{2} \right) - \bar{\nu}_{\text{osc}} X_e \left( 0 + \frac{1}{2} \right)^2 \right] \quad \text{--- (2.28)}$$

$$= \bar{\nu}_{\text{osc}} V - \bar{\nu}_{\text{osc}} X_e V - \bar{\nu}_{\text{osc}} X_e V^2 \quad \text{--- (2.27)}$$

Factoring out the  $\bar{\nu}_{\text{osc}} V$  and rearranging gives

$$\bar{\nu} = [1 - (1+V) X_e] \bar{\nu}_{\text{osc}} V \quad V=1, 2, 3 \quad \text{--- (2.28)}$$

We rewrite

$$\bar{\nu} = \bar{\nu}_e [1 - 2 X_e] \text{ for fundamental band}$$

$$\bar{\nu} = 2 \bar{\nu}_e [1 - 3 X_e] \text{ for first overtone (two times)}$$

$$\bar{\nu} = 3 \bar{\nu}_e [1 - 4 X_e] \text{ for second overtone (three times)}$$

where  $\nu_e$  is the hypothetical equilibrium oscillation frequency.

$$\text{For eq. } \bar{\nu}_{\text{osc}} = 2.99 \times 10^3 \quad X_e = 0.0174 \text{ for HCl}$$

Then Fundamental band =  $2886 \text{ cm}^{-1}$  considerable intensity

First overtone =  $5668 \text{ cm}^{-1}$  small intensity

Second overtone =  $8347 \text{ cm}^{-1}$  with normally negligible intensity.

The selection rules are same as for the harmonic oscillator, with the additional possibility of

large jumps. Further, the spacing between the vibrational levels is of order  $10^3 \text{ cm}^{-1}$  and at room temperature, we use the Boltzmann distribution

$$\frac{N_{v-1}}{N_{v-0}} = \exp \left\{ \frac{6.63 \times 10^{-34} \times 3 \times 10^{10} \times 10^3}{1.38 \times 10^{-23} \times 300} \right\}$$

$$= \exp(-4.8) = 0.008$$

In other words, the population of  $V = 1$  state is nearly 0.01 or some 1% of the ground state population. Thus to a good approximation, we may ignore all transitions originally at  $V = 1$  or more and restrict the above three transitions (shown in Fig: 2.7). Molecular data determined by IR spectra are given in table 2.3

Table 2.3  
Molecular Data

Molecule	vibration $\text{cm}^{-1}$	Anharmonic constant $X_e$	Force constant $10^5 \text{ dyne.cm}^{-1}$	Internuclear distance $r_{eq} (\text{Å})$
HF	4138.5	0.0218	9.66	0.927
HBr	2649.7	0.0171	4.12	1.414
HI	2309.5	0.0172	3.14	1.609
NO	1904.0	0.0073	159.50	1.151

**Hot bands :** The transitions from  $V = 1$  state to higher states occur if the temp. is raised or if the vibration has a particularly low frequency, the population of the  $V = 1$  state may become appreciable. Thus at say 600 K ( $\approx 300^\circ\text{C}$ )  $N_{v=1} / N_{v=0}$  becomes  $\exp(-2.4)$  or about 0.09 and transitions from  $V=1$  to  $V=2$  will be some 10% the intensity of those from  $V = 0$  to  $V = 1$ . A similar increase in the excited state population would arise if the vibrational frequency were  $500 \text{ cm}^{-1}$  instead of  $1000 \text{ cm}^{-1}$ . The  $\bar{\nu}$  is

$$\bar{\nu} = \bar{\nu}_e (1 - 4 X_e) \text{ cm}^{-1} \quad \text{--- (2.31)}$$

These weak absorptions are usually called hot bands since a high temperature is one condition for their occurrence.

### 2.1.vi) Model Questions:

1. Derive an expression for the force constant of the simple harmonic oscillator.
2. What is zero point energy? What is its importance?
3. Write the selection rules for infrared activity. Why some vibrations of  $\text{CO}_2$  are IR active and some not explain?

4. Calculate  $X_{\max}$  for  $V = 1$  state.
5. What is the isotope effect on vibrational spectra? Explain
6. What do you mean by anharmonic oscillator? Whether real molecule is a model of anharmonic oscillator or not.
7. Explain overtones and derive expressions for the first and second overtones. why the intensity decreases for the overtones than fundamental band.
8. What are the differences between fundamental band, overtone bands and hot bands.
9. The given force constant for HBr molecule is  $4.1 \times 10^5$  dyne.cm<sup>-1</sup>. Calculate frequency and energy for HBr molecule.

### Recommended Books:

- |              |   |
|--------------|---|
| A.J. Sonessa | Introduction to molecular spectroscopy. |
| B.K.Sharma   | Spectroscopy,                           |
| C.N.Banwell  | Fundamentals of molecular spectroscopy. |



## Lesson II Simultaneous Vibrational-Rotational Spectra of diatomic molecules - IR spectra.

### Objectives:

Introduction -

Born-oppenheimer approximation

Break down of the Born Oppenheimer approximation

### 2.2.1) Introduction:

Simple harmonic oscillator approach shows that only a single frequency  $\nu_{osc}$ , would be expected in any IR band. But the band under high resolution for HCl consists of two branches. The appearance of these branches can be interpreted by assuming that the diatomic molecule rotates at the same time as it is performing vibrational motion. The energy for the vibrational motion is sufficient for the molecule to perform rotational motion.

### 2.2.ii) Born-Oppenheimer approximation:

Typical diatomic molecule has rotational energy separation of  $1 - 10 \text{ cm}^{-1}$ , the vibrational energy separations were nearly  $3600 \text{ cm}^{-1}$ . Since the energies of two motions so different, we may, as a first approximation, consider that a diatomic molecule can execute rotations and vibrations quite independently. This, which will call the Born-oppenheimer approximation, is tant amount to assuming that the combined rotational - vibrational energy is simply the sum of separate energies.

The total energy  $E_{vr}$  as the sum of the energies of the simple harmonic oscillator and the rigid rotator i.e

$$E_{vr} = h\nu_{osc} \left( V + \frac{1}{2} \right) + B_0 hc J(J+1) \quad \text{--- (2.32)}$$

Let us construct an energy level diagram.

1. Let  $V=0$  and  $J=0$  if we substituting in eq.2.32, we will get  $E_{vr} = \frac{1}{2} h\nu_{osc}$  which corresponds to lowest energy level or ground state of the oscillator.
2. Let  $V=0$  and  $J=1$ , this gives

$$E_{vr} = \frac{1}{2} h \nu_{osc} + 2B_0 hc$$

3. Continuing this process using  $V = 0, J = 2, 3, 4, 5, \dots$ , we obtain a series of rotational levels in the ground vibrational state. The energy levels are shown in Fig 2.8.
4. Using the same procedure for  $V = 1$  and  $J = 0, 1, 2, 3, 4, \dots$  we obtain the series of rotational levels in the next highest vibrational state.
5. To obtain the spectral lines predicted by this energy level diagram (Fig 2.8) we must consider the allowed transitions.
6. Selection rule  $\Delta V = \pm 1$  and  $\Delta J = \pm 1$
7. Simultaneous change in vibrational and rotational energies corresponding to a transition from a rotational level  $J^{11}$  in the lower vibrational state  $V^{11}$  to a rotational level  $J^1$  in the upper vibrational state  $V^1$

$$\Delta E_{vr} = E_{vr}^1 - E_{vr}^{11} \quad \text{--- (2.33)}$$

$$= h \nu_{osc} (V^1 - V^{11}) + B_0 hc [J^1 (J^1 + 1) - J^{11} (J^{11} + 1)] \quad \text{--- (2.34)}$$

Considering the fundamental band transition  $V^{11} = 0 \longrightarrow V^1 = 1$ , ignoring for a moment the changes in rotational quantum number, we get

$$\Delta E_{vr} = h \nu_{osc} + B_0 hc [J^1 (J^1 + 1) - J^{11} (J^{11} + 1)] \quad \text{--- (2.35)}$$

Now consider the allowed transitions of  $J$ , which is governed by  $\Delta J = J^1 - J^{11} = \pm 1$ . This gives rise to

a)  $J^1 = J^{11} + 1$

$$\Delta E_{vr} = h \nu_{osc} + 2B_0 hc (J^{11} + 1) \quad \text{where } J^{11} = 0, 1, 2, 3, \dots \quad \text{--- (2.36)}$$

b)  $J^1 = J^{11} - 1$

$$\Delta E_{vr} = h \nu_{osc} - 2B_0 hc J^{11} \quad \text{where } J^{11} = 1, 2, 3, \dots \quad \text{--- (2.37)}$$

8) PQR branch lines

The wave numbers for transitions are -

$$\bar{\nu}(R) = \frac{\Delta E_{vr}}{hc} = \bar{\nu}_{osc} + 2B_0 (J^{11} + 1) \quad \text{--- (2.38)}$$

$$\bar{\nu}(P) = \frac{\Delta E_{vr}}{hc} = \bar{\nu}_{osc} - 2B_0 J^{11} \quad \text{--- (2.39)}$$

Hence, the simultaneous vibrational-rotational transitions gives rise to two series of lines,

one series rises from eq.2.38 and these lines lie on the high  $\bar{\nu}$  side of  $\bar{\nu}_{\text{osc}}$ . These are known as the +ve or R branch of fundamental band. The second series rises from eq.2.39 and the lines lie on the low  $\bar{\nu}$  side of  $\bar{\nu}_{\text{osc}}$ . These lines constitute the -ve or P branch of the band. The lines in both cases are equally spaced i.e.  $\Delta\bar{\nu} = 2B_0$ ,

Q - branch or Q - band - if  $\Delta J=0$ , the Q branch lines occur. In the case of vibrational transitions,  $\Delta J=0$  is not accompanied by any significant rotational changes. The moment of inertia in the final state must, however, be different from that in the initial state. This indicates that there must be some small changes in rotational energy of these molecules. These changes give rise to a series of very closely spaced lines, known as Q branch or Q band. This band is usually observed in polyatomic molecules.

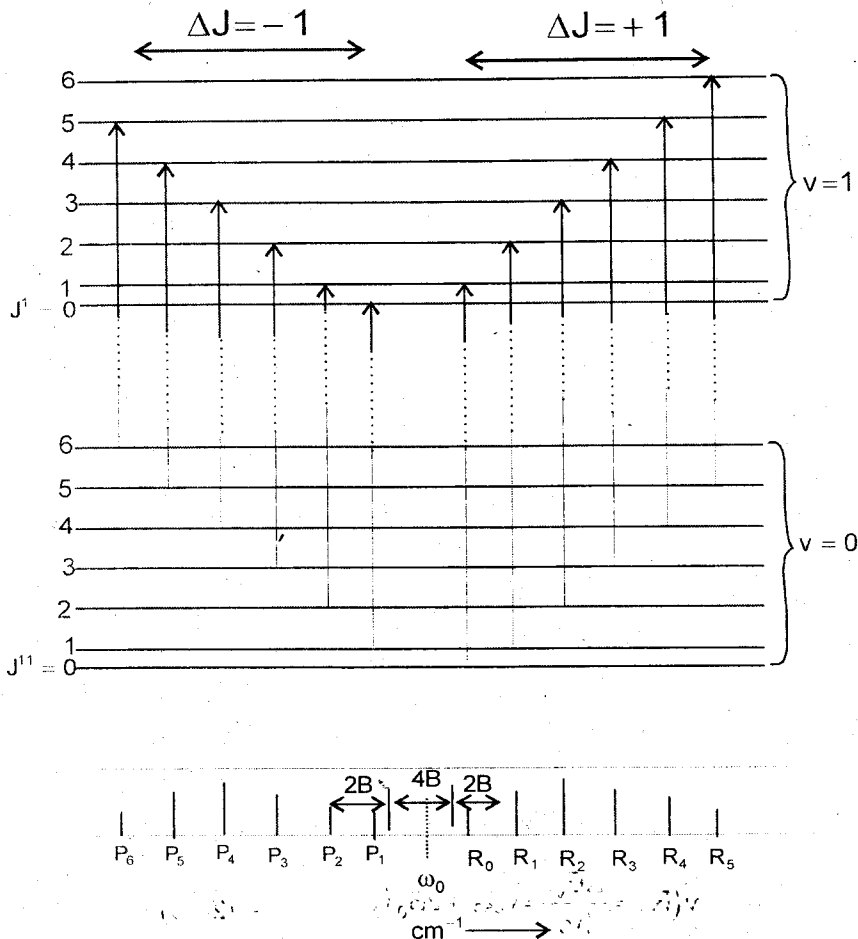


Fig: 2.8 some transitions between the rotational - vibrational energy levels of a diatomic molecule, together with the spectrum arising from them.

### 2.2.iii) Breakdown of the Born-oppenheimer Approximation:

Let us consider that there is interaction between vibrational and rotational motion. A more realistic model would take in to account the anharmonic nature of the vibration. Let us designate  $B_e$  - rotational constant at equilibrium bond length re.  $B_v$  rotational constant in vibrational state.

$$B_v = B_e - \alpha \left( V + \frac{1}{2} \right) \quad \text{--- (2.40)}$$

where  $\alpha$  = +ve constant and is small when compared to  $B_e$ .

Thus  $B_v$  will arise for each vibrational state. In effect, the expression for  $E_{vr}$  must now be written using the energy expressions for the anharmonic oscillator and the non-rigid rotator, where  $B_0$  must be changed to  $B_v$

$$E_{vr} = h\nu_{osc} \left( V + \frac{1}{2} \right) - h\nu_{osc} X_e \left( V + \frac{1}{2} \right)^2 + B_v hc J(J+1) - D_v hc J^2 (J+1)^2 \quad \text{--- (2.41)}$$

If we consider simultaneous transitions of J and V for the particular case  $V=0 \longrightarrow V=1$ , We get the wave numbers of the resulting lines.

$$\bar{\nu} = \bar{\nu}_0 + B_v^1 J^1 (J^1 + 1) - B_v^{11} J^{11} (J^{11} + 1) \quad \text{--- (2.42)}$$

Where  $\bar{\nu}_0$  = wave number of pure vibrational transition i.e., the transition for which  $j^1 = j^{11} = 0$ .

$B_v^1$  and  $B_v^{11}$  = Rotational constants in the upper and lower vibrational states.

Using the transition  $\Delta J = +1$  we obtain  $\bar{\nu}(R)$

$$\bar{\nu}(R) = \bar{\nu}_0 + (B_v^1 + B_v^{11})(J^{11} + 1) + (B_v^1 - B_v^{11})(J^{11} + 1)^2 \quad \text{--- (2.43)}$$

where  $J^{11} = 0, 1, 2, 3, \dots$  using the transition  $\Delta J = -1$ , we obtain  $\bar{\nu}(P)$

$$\bar{\nu}(P) = \bar{\nu}_0 - (B_v^1 + B_v^{11})(J^1 + 1) + (B_v^1 - B_v^{11})(J^1 + 1)^2 \quad \text{--- (2.43) where } J^1 = 0, 1, 2, 3, \dots$$

The  $\bar{\nu}(P)$  and  $\bar{\nu}(R)$  to represent the wave numbers of the P and R branch lines respectively. These two equations can be combined into the expression

$$\nu_{P,R} = \nu_0 + (B_v^1 + B_v^{11})m + (B_v^1 - B_v^{11})m^2 \text{ cm}^{-1} \quad \text{--- (2.44) where } m = \pm 1, \pm 2, \dots$$

+m = refer to R branch

-m = refer to P branch

If we ignore the vibration and rotation interaction,  $B_v^1 = B_v^{11} = 0$ . If interaction is there,  $B_v^1 < B_v^{11}$ , the last term of equation 2.44 is always -ve, irrespective of the sign of m, and the effect on

spectrum of a diatomic molecule is to crowd the rotational lines more closely together with increasing  $m$  on the R branch side, while the P branch lines become more widely spread as  $-m$  increases. Normally  $B_V^1$  and  $B_V^{11}$  differ only slightly and the effect is marked only for high  $m$  values. The spectrum predicted from eq.2.42 and 2.43 is shown in Fig:2.9

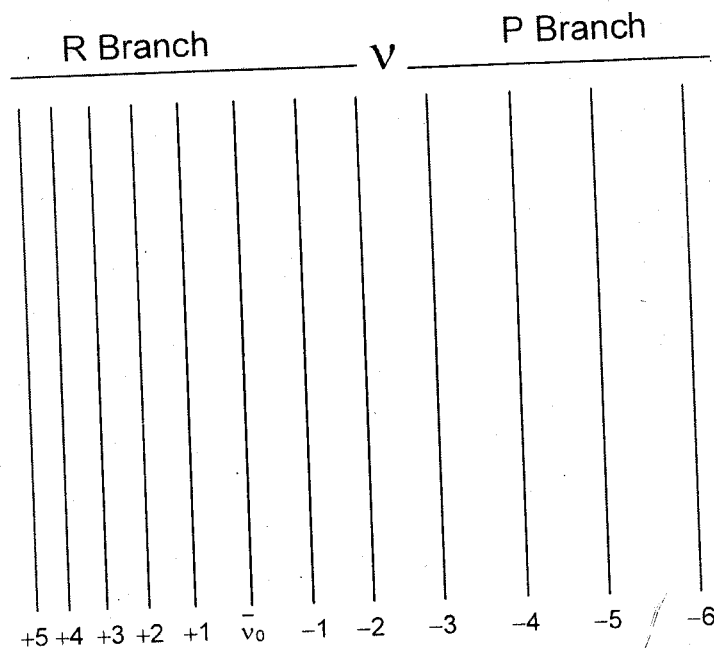


Fig: 2.9

The spectrum carbon monoxide is shown in Fig: 2.10

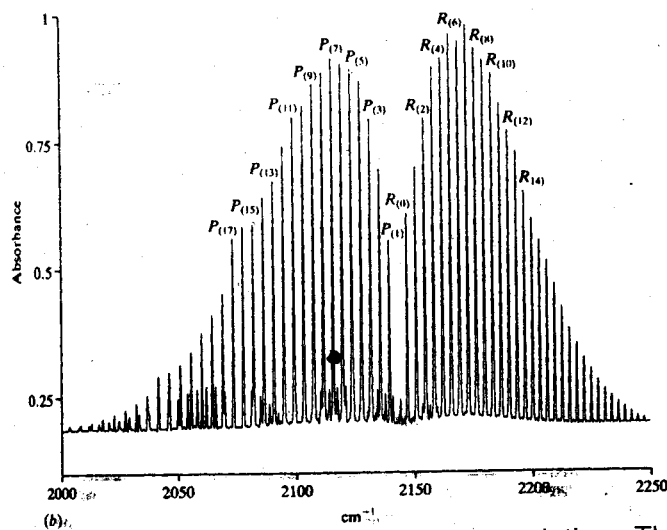


Fig:2.10 The fundamental band under high resolution. The lines are labeled according to their  $J''$  values.

The part of IR spectrum results are given in table 2.4

Table 2.4

Line	$\bar{\nu}$	$\Delta\bar{\nu}$	Line	$\bar{\nu}$	$\Delta\bar{\nu}$
P(1)	2139.43		R(0)	2147.08	
		3.88			3.78
P(2)	2135.55		R(1)	2150.86	
		3.92			3.73
P(3)	2131.63		R(2)	2154.59	
		3.95			3.72
P(4)	2127.68		R(3)	2158.31	
		3.98			3.66
P(5)	2123.70		R(4)	2161.97	

**Problem:** For CO molecule  $B_v^1 = 1.898 \text{ cm}^{-1}$ ,  $B_v^{11} = 1.915 \text{ cm}^{-1}$ ,  $\bar{\nu}_0 = 2143.28$ .

$$\begin{aligned}\bar{\nu} &= 2143.28 + (1.898 + 1.915)m + (1.898 - 1.915) m^2 \text{ cm}^{-1} \\ &= 2143.28 + 3.813 m - 0.0175 m^2 \text{ cm}^{-1}.\end{aligned}$$

From this, the calculate  $\bar{\nu}$  of some lines in the spectrum of CO are given in table 2.5

Table 2.5

m	$J^{11}$	$\bar{\nu}_{\text{obs}}$	$\bar{\nu}_{\text{cal}}$
30	29	2241.64	2241.91
25	24	2227.63	2227.65
20	19	2212.62	2212.54
15	14	2196.66	2196.53
10	9	2179.77	2179.66
5	4	2161.97	2161.90
0	-	Band center	2143.28
-5	5	2123.70	2123.78
-10	10	2103.27	62103.40
-15	15	2082.01	2082.15

-20	20	2059.91	2060.02
-25	25	2037.03	2037.02
-30	30	2013.35	2013.14

By using eq.2.40, we have

$$a = 0.018 \quad B_e = 1.924 \text{ cm}^{-1}$$

Further we can calculate the eq. Bond length  $r_{eq}$  and the bond length is the  $V = 0$  and  $V = 1$

states by calculating  $I$  from  $I = \frac{h}{8\pi^2 c B}$  and using  $I = \mu r^2$  as

$$r_{eq} = 1.13 \text{ \AA} \quad r^1 (V = 1) = 1.113 \text{ \AA} \quad r^{11} (V = 0) = 1.136 \text{ \AA}$$

#### 2.2.iv) Model questions:

1. What are PQR branches? Derive equations for PQR branches of diatomic molecule when the Born-oppenheimer approximation considered.
2. Draw the energy levels and spectrum of diatomic vibrating rotator when there is no interaction between vibrational and rotational motion.
3. Write the selection rules for the vibration rotator.
4. Discuss above the nature of spectrum when there is break down of Born-Oppenheimer approximation.
5. The given values of HCl fundamental  $\bar{\nu} = 2886 \text{ cm}^{-1}$ ,  $B_V^1 = 10.137$  and  $B_V^{11} = 10.440$ .  $\alpha = 0.3019$ . Calculate  $\bar{\nu}$  for  $m = 5, 10, 20, m = -15, -25, -30$ . Also calculate  $r_{eq}$  and  $r$  in  $V = 0$  and  $r$  in  $V = 1$ .

Ans:  $B_e = B_V^{11} = -\left(\frac{\alpha}{2}\right)$ . The remaining same as calculated for CO molecule under problem.

6.  $\Delta \nu$  is increased in which branch. What is the reason for increase in  $\Delta \bar{\nu}$  in that branch.

#### Recommended Books :

- |              |   |
|--------------|---|
| A.J. Sonessa | Introduction to molecular spectroscopy. |
| B.K.Sharma   | Spectroscopy.                           |
| C.N.Barwell  | Fundamentals of molecular spectroscopy. |

## Lesson III      Vibrational Electronic spectra of diatomic molecules.

### Objectives:

- Introduction
- Electronic energy
- Analysis of energy changes
- Vibrational structure of electronic spectra
- Classification of bands
- Intensity of vibrational electronic spectra
- Frank Condon principle.

### 2.3.i) Introduction:

In previous lesson of this unit, we learned that a great deal of information concerning the size of molecule can be obtained from the study of the fine structure of vibrational bands. We also learned, the requirement that the vibration must produce a change in dipole moment in order for it to be able to absorb I.R i.e. only in the case of heteronuclear molecules. Of course, this requirement precludes the determination of the molecular parameters of homonuclear diatomic molecules by this I.R method. It is possible, then, to obtain these parameters for such molecules for the analysis of fine structure of the bands occurring in the ultraviolet region of the spectrum. These bands arise from transition between different electronic energy levels in the molecule.

### 2.3.ii) Electronic energy:

The total energy of the molecule consists of the sum of the Kinetic and potential energies of all the electrons and nuclei. The exact calculation of these electronic energies for a given electronic state is difficult even for simple molecules like HCl or CO. This energy we can obtain from spectral studies in the visible and ultraviolet, the magnitude of change of electronic energy between two different states of the molecule. The molecule is performing vibrational and rotational motion in each of the electronic states. In the IR spectra the vibrational rotational levels in one lowest or ground electronic state. Thus the transition between ground electronic state to excited electronic state gives electronic spectra. Electronic transitions require a large energy then do vibrational or rotational transitions. Thus, if we take  $350\text{m}\mu$  as a typical wavelength for an UV band, then

$$\text{Wave number} = 28,540 \text{ cm}^{-1}$$

$$\text{Energy for transition} = 5.8 \times 10^{-10} \text{ erg (for IR energy is } 10^{-13} \text{ erg)}$$



The spacing between electronic energy levels are greater than those for vibrational levels. The vibrational motion in each electronic state is characterized by a potential energy curve of the type is shown in Fig 2.11. The potential energy curves are shown schematically in Fig 2.11 for the ground and for the next highest in energy electronic state (the first excited state). The vibrational levels in each electronic state are indicated in the usual manner by horizontal lines, the Q.no's  $V^0$  and  $V^1$  designate the vibrational energy levels of the upper and lower electronic states respectively.

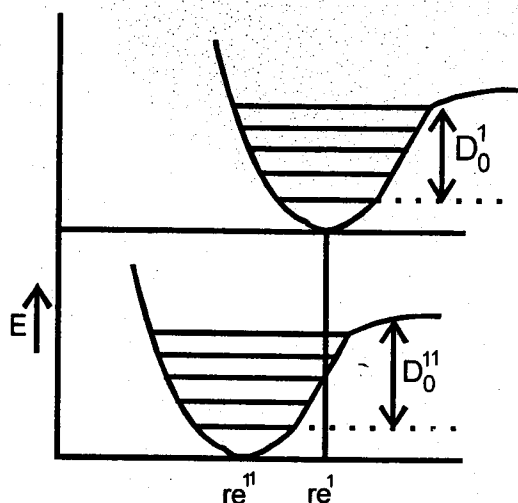


Fig:2.11 Potential energy curves for a diatomic molecule in the first excited and ground electronic states.

In the Fig,  $D_0^1$  and  $re^1$  are the dissociation energy and equilibrium internuclear separation in the first excited states and  $D_0^{11}$  and  $re^{11}$  are the corresponding quantities in the ground state. It is clear from the Fig that  $re^1 > re^{11}$ . This would be expected if the energy that leads to promotion to higher electronic levels also increases the vibrational energy. This means that a molecule in the higher state will be easier to dissociate i.e.,  $D_0^1 < D_0^{11}$ . So, the P.E curve in the upper electronic state is broader (larger amplitude) than the curve in lower electronic state.

### 2.3.iii) Analysis of energy changes in electronic spectra:

The total energy of the molecule in a given state consists of contribution from the P.E and K.E of electrons, the P.E and K.E due to vibrational motion and kinetic energy due to rotational motion. To determine the absolute magnitude of this total energy would be an impossible task except possibly for some of the simplest molecules such as  $H_2$  and  $He_2$ . In the analysis of electronic spectra we are interested only in changes in the total energy.

Let us designate

$E_e$  = electronic energy

$E_v$  = vibrational energy

$E_r$  = rotational energy

$E_t$  = total energy, Then

$$E_t = E_e + E_v + E_r \quad \text{--- (2.45)}$$

The  $E_r$  will be assumed to be that of the non-rigid rotator

$$E_r = h c B_v J(J+1) - h c D_v J^2(J+1)^2 \quad \text{--- (2.46)}$$

The  $E_v$  will be assumed to be that of an anharmonic oscillator

$$E_v = h \nu_{\text{osc}} \left( V + \frac{1}{2} \right) - h \nu_{\text{osc}} X_e \left( V + \frac{1}{2} \right)^2 \quad \text{--- (2.47)}$$

The wave numbers of the spectral lines corresponding to transitions between two electronic states is

$$\nu = \frac{\Delta E}{hc} = \frac{(E_e^I - E_e^{II}) + (E_v^I - E_v^{II}) + (E_r^I - E_r^{II})}{hc} \quad \text{--- (2.48)}$$

Where prime and double prime request for upper and ground electronic states.

We can also write

$$\bar{\nu}_e = \frac{\Delta E}{hc} = \frac{E_e^I - E_e^{II}}{hc} \quad \text{--- (2.48a)}$$

$$\bar{\nu}_v = \frac{\Delta E}{hc} = \frac{E_v^I - E_v^{II}}{hc} \quad \text{--- (2.48b)}$$

$$\bar{\nu}_r = \frac{\Delta E}{hc} = \frac{E_r^I - E_r^{II}}{hc} \quad \text{--- (2.48c)}$$

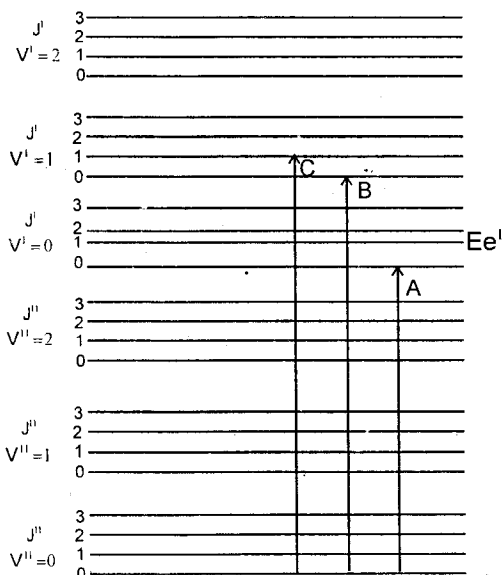


Fig 2.12 Energy level diagram shows the vibrational and rotational energy levels for the lower and upper electronic states.

From the eq. 2.47 and 2.48, we conclude that electronic transitions occur between the rotational levels of the different vibrational levels in the two electronic states. These transitions are represented in Fig. 2.12.

Where  $Ee^1$  and  $Ee^{11}$  are labeled for upper and lower electronic states, the vibrational Q. Nos are labeled as  $V^1$  and  $V^{11}$  and rotational Q. No  $J^1$  and  $J^{11}$  for upper and lower electronic states.

In the Fig there are three transitions separated by vertical lines.

$$A = Ee^{11} \longrightarrow Ee^1 \text{ and } V^1 = V^{11} = 0, J^1 = J^{11} = 0$$

$$\Delta E = Ee^1 - Ee^{11}, \text{ Pure electronic transitions}$$

$$B = Ee^{11} \longrightarrow Ee^1, V^{11} = 0 \text{ to } V^1, \text{ and } J^1 = J^{11} = 0$$

$\Delta E = \Delta Ee + \Delta Ev$  simultaneous change in electronic and vibrational energy levels.

$$C = Ee^{11} \longrightarrow Ee^1, V^{11} = 0 \rightarrow V^1 = 1, \text{ and } J^{11} = 0 \longrightarrow J^1 = 1$$

$\Delta E = \Delta Ee + \Delta Ev + \Delta Er$  simultaneous change in electronic, vibrational and rotational energy levels.

From the Fig 2.12, it is apparent that the change in electronic energy is constant for a given electronic transition i.e.  $\bar{\nu}_e$  is constant. The total energy change therefore is obtained by addition of the change in vibrational and rotational energy, which arise from simultaneous change in vibrational and rotational energies.

The vibrational transition expression is

$$\bar{\nu}_v = \left[ We^1 \left( V^1 + \frac{1}{2} \right) - We^1 Xe^1 \left( V^1 + \frac{1}{2} \right)^2 \right] - \left[ We^{11} \left( V^{11} + \frac{1}{2} \right) - We^{11} Xe^{11} \left( V^{11} + \frac{1}{2} \right)^2 \right] \quad \text{--- (2.49)}$$

$$\text{where } \omega_e = \frac{v_{osc}}{c}$$

$\omega_e^1$  and  $\omega_e^{11}$  are the vibrational frequencies measured in wave numbers of the oscillator in upper and lower electronic state respectively.

$Xe^1$  and  $Xe^{11}$  are anharmonicity constant in the two electronic states.

The rotational transition expression is

$$\bar{\nu}_r = \left[ B_v^1 J^1 (J^1 + 1) - D_v^1 J^{12} (J^1 + 1)^2 \right] - \left[ B_v^{11} J^{11} (J^{11} + 1) - D_v^{11} J^{112} (J^{11} + 1)^2 \right] \quad \text{--- (2.50)}$$

$B_v^1$  and  $D_v^1$  in the upper vibrational state and  $B_v^{11}$  and  $D_v^{11}$  in the lower electronic state.

### 2.3.iv) Vibrational structure of electronic transitions:

Let us consider the transitions between rotation less states corresponds to  $J^1 = J^{11} = 0$  (line B in Fig.2.12)

$$\text{Then } \bar{\nu} = \bar{\nu}_e + \bar{\nu}_v \text{ and } \bar{\nu}_r = 0 \quad \text{--- (2.51)}$$

In eq.2.51  $\bar{\nu}_v$  is only variable, there transitions give rise to vibrational or coarse structure of the electronic transitions. Using the eq.2.49 we obtain the expression

$$\bar{\nu} = \bar{\nu}_e + \left[ \omega e^1 \left( V^1 + \frac{1}{2} \right) - \omega e^1 X e^1 \left( V^1 + \frac{1}{2} \right)^2 \right] - \left[ \omega e^{11} \left( V^{11} + \frac{1}{2} \right) - \omega e^{11} X e^{11} \left( V^{11} + \frac{1}{2} \right)^2 \right] \quad \text{--- (2.52)}$$

Eq.2.52 represents the wave numbers of all possible transitions between the transition levels  $V^1$  and  $V^{11}$  of the upper and lower electronic states. The selection rules that served to restrict the changes in  $V$  for the pure vibrational transitions are not operative in the electronic spectra. So we can expect very large number of spectral lines due to eq.2.52. These lines are actually closed spaced lines, which corresponds to bands obtained under the low resolution.

Consider the eq.2.52 and let us designate  $\bar{\nu}_\infty$ , the wave number of the band corresponds to  $V^{11} = 0 \longrightarrow V^1 = 0$  using these number of values in Eq.2.52. we obtain

$$\bar{\nu}_\infty = \bar{\nu}_e + \left( \frac{1}{2} \omega e^1 - \frac{1}{4} X e^1 \omega e^1 \right) - \left( \frac{1}{2} \omega e^{11} - \frac{1}{4} X e^{11} \omega e^{11} \right) \quad \text{--- (2.53)}$$

Solving eq.2.53 for  $\bar{\nu}_e$  and substituting the result in eq 2.52 give

$$\bar{\nu} = \bar{\nu}_\infty + \left[ (1 - X e^1) \omega e^1 - \omega e^1 X e^1 V^1 \right] V^1 - \left[ (1 - X e^{11}) \omega e^{11} - \omega e^{11} X e^{11} V^{11} \right] V^{11} \quad \text{--- (2.54)}$$

Since  $X e$  and  $\omega e$  are constants, then eq.2.54 can be written as

$$\bar{\nu} = \bar{\nu}_\infty + (a^1 - b^1 V^1) V^1 - (a^{11} - b^{11} V^{11}) V^{11} \quad \text{--- (2.55)}$$

$$\text{where } a = (1 - X e) \omega e \quad \text{--- (2.55a)}$$

$$b = \omega e X e \quad \text{--- (2.55b)}$$

$$a + b = \omega e \quad \text{--- (2.55c)}$$

From the study of the wave number of the observed bands, one can obtain an empirical eq. that fits in to theoretical eq.2.55

For eq for CO molecule, a band system is found that fits the equation is

$$\bar{\nu} \text{ (cm}^{-1}\text{)} = 64746.5 + (1498.36 - 17.251V^1)V^1 - (2156.05 - 13.260V^{11})V^{11}$$

From the values of  $a^1$  and  $b^1$ , we can have

$$\omega e^1 = 1515.61 \text{ cm}^{-1} \text{ (from eq.2.56c)}$$

$$Xe^1 = 0.01137 \text{ (from eq.2.56b)}$$

Finally we can calculate force constant of CO in the upper electronic state  $K^1$  i.e

$$K^1 = 4\pi^2 \nu_{\text{osc}}^2 \mu^2 = 4\pi^2 \omega e^2 c^2 \mu^2$$

By using the value of  $\omega e^1$  in the above, we obtain

$$K^1 = 9.23 \times 10^5 \text{ dyne.cm}^{-1}$$

Similarly we can calculate

$$K^{11} = 19.0 \times 10^5 \text{ dyne.cm}^{-1}$$

$$\omega e^{11} = 2169.31 \text{ cm}^{-1}$$

$$Xe^{11} = 0.00611$$

The larger value of  $Xe$  in upper electronic states indicates that the vibrations in CO are less like a simple harmonic oscillator than they are in ground state. The lower value of the force constant in the upper electronic state means that the band is more flexible, owing to the moment of electronic charge between the atoms in the band during the electronic transition. Both factors indicate the probable transition to be from the normal CO structure to an ionic structure. The ionic double bonded structure is more flexible and has larger band distance than thus the ground state triple bonded structure.

### 2.3.iv) Classification of Bands:

The large number of bands that are possible in electronic transitions can be classified according to vibrational Q.Nos involved in the transition. These bands are classified into two classes - 1) Band progression 2) Band sequence.

**1) Band progression :** In this either  $V^1$  or  $V^{11}$  Q.No has definite value and the other will varies regularly.

For eq  $V^1=0$  and  $V^{11}$  varies i.e  $V^{11} = 0,1,2,3,\dots$

This is named as  $V^{11}=1$  band progression.

These are shown in Fig.2.13.

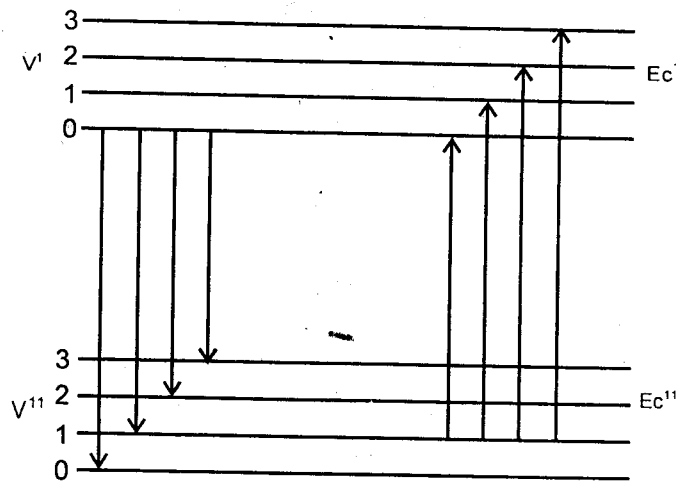


Fig : 2.13 Band Progression.

2) **Band Sequence** : The band sequence can be made according to the value of  $\Delta V$ .

For eg  $V^I - V^{II} = -2$  than we can have the sequence 0 - 2, 1 - 3, 2 - 4, 3 - 5 this  $\Delta V = -2$  sequence.

$$V^I - V^{II} = 0 \text{ i.e., } V^I=0 \text{ to } V^{II}=0, V^I=1 \text{ to } V^{II}=1 \text{ etc.}$$

This is  $\Delta V = 0$  sequence. This band sequence is shown in Fig 2.14

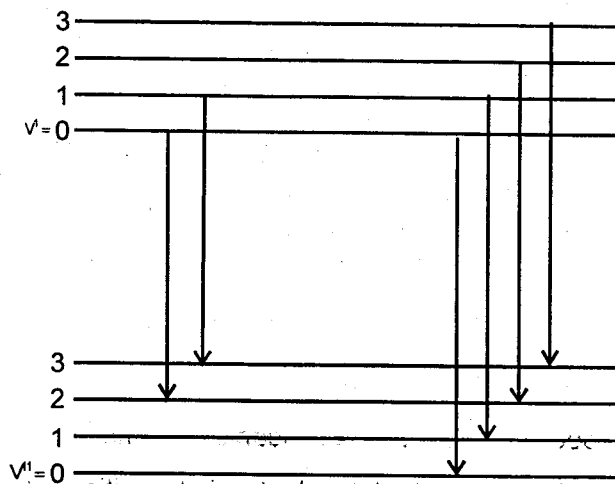


Fig: 2.14 Band Sequence.

### 2.3.v) Intensity of vibrational - Electronic spectra

#### The Franck-Condon Principle:

The quantum mechanics does not impose restrictions on the change in the vibrational quantum number. During an electronic transition, the vibrational lines in the progression are not all observed to be of the same intensity.

For eg in some spectra (0, 0) transition is the strongest, in others the intensity increases to a max at some value of  $V^1$ , while in yet others only a few vibrational lines with high  $V^1$  are seen followed by continuously (Fig: 2.15).

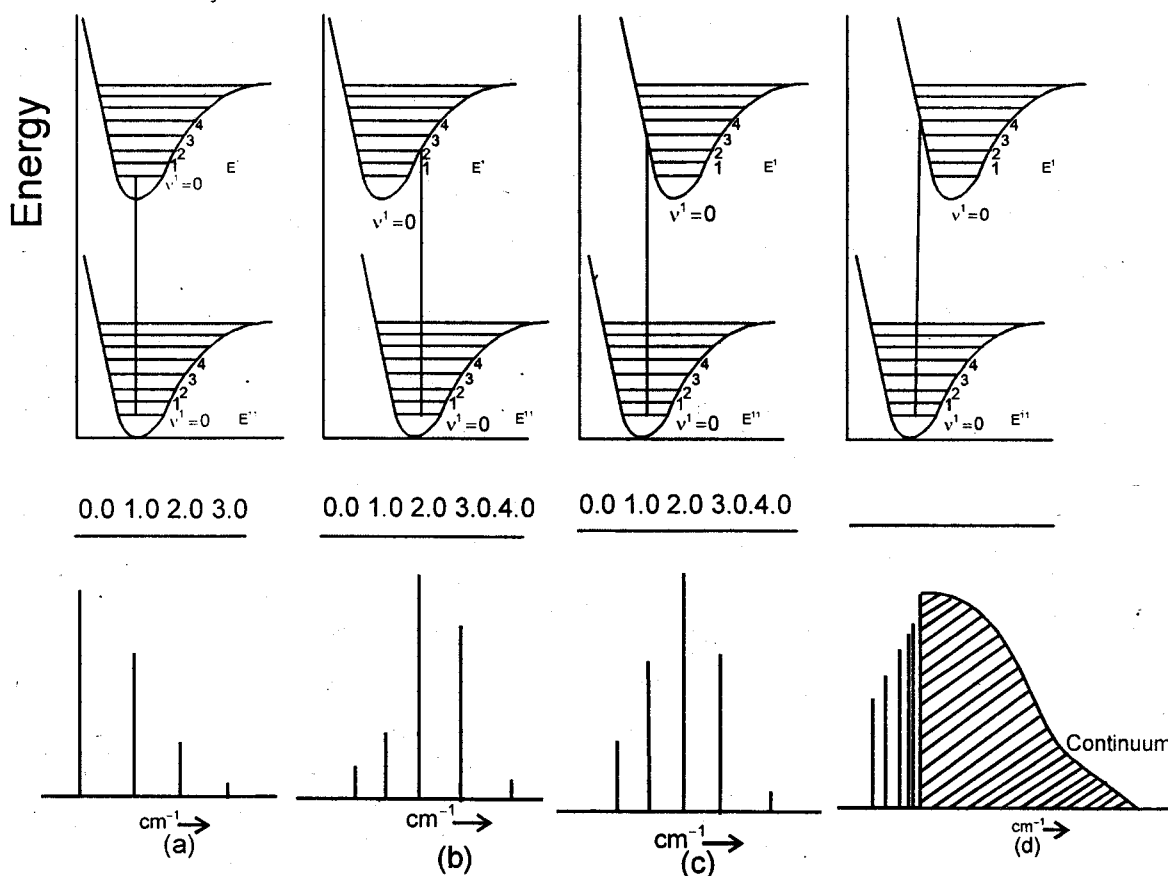


Fig : 2.15 The operation of Franck-Condon principle

All these types of spectrum are readily explicable in terms of the Franck-Condon principle.

Franck-Condon principle states that an electronic transition takes place so rapidly that a vibrational molecule does not change its inter nuclear distance appreciably during the transition.

**Fig 2.15 shows four possibilities.**

- a) Intermolecular distance  $r_e$  is same in the upper and lower electronic states. This principle states that a transition occurs vertically on the diagram. The strongest spectral line is  $V'' = 0$  progression (0, 0). However quantum theory only says that the probability of finding the oscillating atom is greatest at the equilibrium distance in the  $V'' = 0$  state, it allows some, although small, chance of the atom being near the extremities of its vibrational motion. Hence there is a chance of the starting from the ends of the  $V'' = 0$  states and finishing in the  $V' = 1, 2, 3$  etc states i.e (1, 0) (2, 0) etc. lines diminish rapidly in intensity.
- b) The excited electronic state has a slightly smaller inter nuclear separation than the ground state. A vertical transition from the  $V'' = 0$  level will be most likely to occur in to the upper vibrational state  $V' = 2$ , transitions to lower and higher  $V'$  states being less likely.
- c) The excited electronic state has a slightly larger  $r_e$  than the ground state but the resulting transitions and spectrum are similar.
- d) The upper state separation is drawn on considerably greater than that in the lower state. We see firstly, the vibrational level to which a transition takes place has a high  $V'$  value. Further, the transitions can now occur to a state where the excited molecule ( $E_{ex}$ ) has energy in excess of its own dissociation energy ( $D_0$ ). From such states the molecule will dissociate with out any vibrations and since the atoms, which are formed, may take up any value of kinetic energy, the transitions are not quantised and a continuous results.

$$\bar{\nu}_{\text{continuous limit}} = D_0'' + E_{ex} \text{ cm}^{-1} \quad \text{--- (2.56)}$$

Each progression will show two maxima which will coincide only if the equilibrium separations are the same in both states.

### 2.3.vi) Model questions:

1. Give a brief account of vibrational structure of electronic spectra.
2. Discuss about the vibrational coarse structure of electronic spectra.
3. Derive an expression vibrational transition of electronic spectra.
4. Give total energy equation for electronic spectra.
5. How many types of bands are obtained in the coarse structure and explain.
6. Define and explain the Franck-Condon principle.

### Recommended Books:

- |              |   |
|--------------|---|
| A.J. Sonessa | Introduction to molecular spectroscopy. |
| B.K.Sharma   | Spectroscopy.                           |
| C.N.Barwell  | Fundamentals of molecular spectroscopy. |



# Rotational Electronic Spectra of diatomic molecules.

## Objectives

Rotational structure of electronic bands

Formation of band shading and band head in electronic spectra.

### 2.4.i) Rotational structure of electronic bands:

Let us now consider in this lesson, the more realistic case where changes in the rotational state can take place for a given change in the vibrational state of the molecule (line c in Fig 2.12)

For a given vibrational transition, the quantities  $\bar{\nu}_e + \bar{\nu}_v$  is constant. Let us call this a  $\bar{\nu}_0$ , which is known as band origin. Then

$$\bar{\nu} = \bar{\nu}_0 + \bar{\nu}_r \quad \text{--- (2.57)}$$

where  $\bar{\nu}_r$  is variable that depends on the different values of rotational Q Nos. in upper and lower electronic states. All possible transitions between rotational levels, for a constant  $\bar{\nu}_0$ , give rise to single band. The band will consist of a series of lines, each line arises from a given change in J values i.e. for a given rotational transition.

Let us derive the expression

$$\bar{\nu}_r = \frac{\Delta E_r}{hc} = E_r(J^l) - \frac{E_r(J^{ll})}{hc} \quad \text{--- (2.58)}$$

Using eq.2.50 for  $\bar{\nu}_r$  in 2.58, we obtain

$$\bar{\nu}_r = B_v^l J^l (J^l + 1) - D_v^l J^{l2} (J^l + 1)^2 - B_v^{ll} J^{ll} (J^{ll} + 1) - D_v^{ll} J^{ll2} (J^{ll} + 1)^2 \quad \text{--- (2.59)}$$

Where  $B_v^l$  and  $D_v^l$  for the mol. in upper electronic state and  $B_v^{ll}$  and  $D_v^{ll}$  for the mol. in lower electronic state.

Comparing 2.57 and 2.59, we obtain an eq.

$$\bar{\nu} = \bar{\nu}_0 + \left[ B_v^l J^l (J^l + 1) - D_v^l J^{l2} (J^l + 1)^2 - B_v^{ll} J^{ll} (J^{ll} + 1) - D_v^{ll} J^{ll2} (J^{ll} + 1)^2 \right] \quad \text{--- (2.60)}$$

Eq.2.60 gives the wave numbers of all the lines arising from rotational transition for a given vibrational and electronic transition.

**Selection Rules :** The selection rules are similar to those introduced for pure rotational transitions i.e  $\Delta J = \pm 1$  are allowed. However, the fact that the electronic charge distribution in the molecule may also change during an electronic transition leads to the transition where

$\Delta J = 0$  is also allowed in some cases. So we obtain for the selection rules for rotational transitions in electronic spectra.

R branch is obtained when  $\Delta J = + 1$  (+ve)

P branch is obtained when  $\Delta J = - 1$  (-ve)

Q branch is obtained when  $\Delta J = 0$

Substituting

$$J^1 = J^{11} + 1 \text{ in eq. 2.60}$$

- $$\bar{\nu}(R) = \bar{\nu}_0 + 2B_v^1 + (3B_v^1 - B_v^{11})J^{11} + (B_v^1 - B_v^{11})J^{112} \text{ --- (2.61)}$$

(Neglect small correction terms, centrifugal constant, D)

where  $J^{11} = 0, 1, 2, 3, \dots$

$J^1 = J^{11} - 1$  in eq 2.60

$$\bar{\nu}(P) = \bar{\nu}_0 + (B_v^1 + B_v^{11})J^{11} + (B_v^1 - B_v^{11})J^{112} \text{ --- (2.62)}$$

where  $J^1 = J^{11}$

$$\bar{\nu}(Q) = \bar{\nu}_0 + (B_v^1 + B_v^{11})J^{11} + (B_v^1 - B_v^{11})J^{112} \text{ --- (2.63)}$$

where  $J^{11} = 1, 2, 3, \dots$

We obtain simple formula for eq. 2.61 and 2.62 as we got earlier.

$$\bar{\nu} = \bar{\nu}_0 + (B_v^1 + B_v^{11})m + (B_v^1 - B_v^{11})J^{112} \text{ --- (2.64)}$$

Where  $m = \pm 1, \pm 2, \pm 3$

So when  $m = + 1$  R branch and  $m = -1$  P branch. The lowest level of  $J^{11}$  value in R branch is 0 and in the P branch is 1 and as a result, no line appears for the transition  $J^{11} = J^1 = 0$  corresponding to  $\bar{\nu} = \bar{\nu}_0$ , the band origin and a gap appears in the spectrum at this wave number.

When the transitions  $\Delta J = 0$  are allowed, then all the three branches PQR appear. The spectral lines from R branch will overlap the lines of the P and R branch leading to a more complicated band than in the case of only P and R branch.

The eqs. for P and R branches in electronic transitions and vibrational - rotational transitions (IR) are same. The difference lies in the magnitudes of  $B_v^1$  and  $B_v^{11}$  in these two types of transitions. The rotational constants for two electronic states will differ from one another to a much

greater extent than they will for two vibrational states in the same electronic state.

## 2.4.ii) Formation of Band shading and Band Head in electronic spectra:

In electronic transitions, excitation to a higher state can lead to either a increase or decrease in the band length, depending on the nature of the electronic rearrangement in the molecule.

Let us consider two cases in which the rotational constants differ as 1)  $B_v^1 < B_v^{11}$  and

2)  $B_v^1 > B_v^{11}$  The two cases will lead to band-head formation in either the R or the P branch.

**Case-I -  $B_v^1 < B_v^{11}$**

The quantities  $B_v^1 - B_v^{11}$  is -ve (eq.2.64)

$$\text{Let us write } B_v^1 + B_v^{11} = a \quad \text{--- (2.65)}$$

$$B_v^1 - B_v^{11} = a \quad \text{--- (2.66)}$$

The eq.2.64 can be written after introducing eq.2.65 and 2.66 as

$$\bar{\nu} = \bar{\nu}_0 + am - bm^2 \quad \text{--- (2.67)}$$

If we take m as +ve, we will get R branch lines. Since  $b \ll a$ , when m is small  $\bar{\nu}(R) = \bar{\nu}_0 + am$

As m increases, the square term  $-bm^2$ , becomes more important. Since this term is -ve, it will result in a decrease in the separation of lines in the R branch at large m. We find the lines converge more rapidly and causing them to crowd together, thus resulting in the formation of a band head.

At some value of m, the negative square term will only weigh the +ve linear term (am). This results in the lines of the R branch turning back on themselves. Obviously, there must exist some value of m for which  $\bar{\nu}(R)$  has a maximum value. This  $\bar{\nu}(R)$  corresponds to band head. In this case the band head occurs in R branch. The P branch lines are obtained when m is -ve. The linear (am) and square term ( $-bm^2$ ) and the wave number of P branch lines occur between  $\bar{\nu}_0$  and the separation of lines increases to a greatly extent as a m value increases, So the band will shade or degrade or diffuse in the P branch.

A graphical representation of the wave number of the rotational lines as a function of m can be obtained from eq.2.64 and 2.67. The equations represent f-axis parabolas. If we plot m as ordinate and  $\bar{\nu}$  as abscissa, we obtain a parabola known as Fortrat parabola shown schematically in Fig: 2.16 for case - I. The interaction of parabola with the horizontal axis at  $m=0$  and therefore given  $\bar{\nu}_0$ . The spectrum obtained from the points on the Fortrat parabola is shown systematically below the graph.

Case I.  $B_v^1 < B_v^{11}$ 

$$I_v^1 < I_v^{11}$$

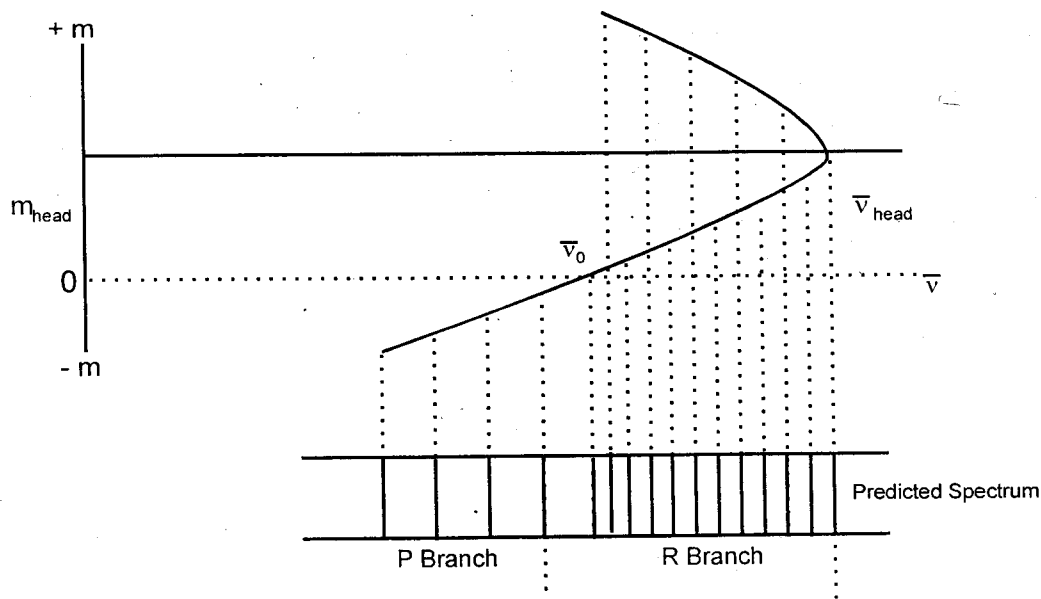


Fig: 2.16 Fortrat Parabola.

There is a band head is formed in electronic spectra where as no band head is formed in IR spectra (vibrational rotational spectra). The reason is -

In IR spectra, the moment of inertia are not very different in the two states involved in transition, So that  $B_v^1 - B_v^{11}$  is very small. Therefore we would have to go to very high  $m$  values to outweigh the  $-bm^2$  over  $am$  and there very high rotational transitions is too low to be observed. Consequently the band head is not detectable in IR spectra.

**Case II:**  $B_v^1 > B_v^{11}$

The quantity  $B_v^1 - B_v^{11}$  is +ve number and therefore we can write eq.2.64 as

$$\bar{\nu} = \bar{\nu}_0 + am + bm^2 \quad \text{--- (2.68)}$$

Again  $a \gg b$  when  $m$  is +ve, there is a continuous increase in the wave number of lines in the R branch. So band shade occur in R branch on the higher wave number side. When  $m$  is +ve, the linear term  $am$  is -ve. As  $m$  gets larger, the lines in the P branch get crowd together until the +ve  $bm^2$  out weigh -ve  $am$  and the lines turn back. So we conclude that in this case, the band head is obtained in P branch and band shade in the R branch. The Fortrat parabola for this case is

shown in Fig.2.17.

Case II  $B_v^1 > B_v^{11}$

$$I_v^1 < I_v^{11}$$

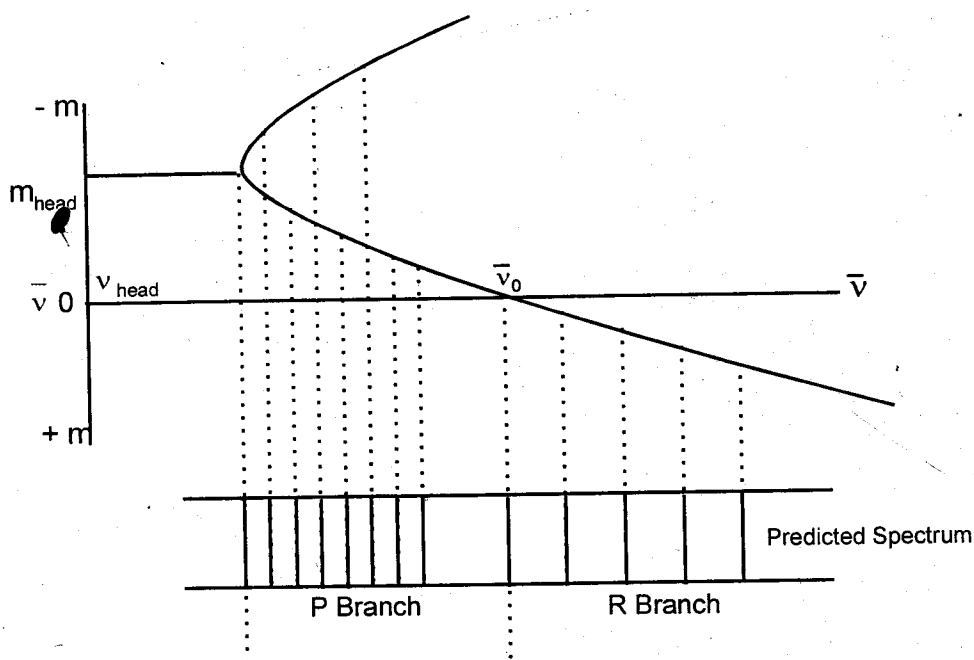


Fig 2.17 Fortrat Parabola

The equations for  $m_{\text{head}}$  and  $\bar{\nu}_{\text{head}}$  are -

$$m_{\text{head}} = \frac{B_v^1 + B_v^{11}}{2(B_v^1 - B_v^{11})} \quad \text{--- (2.69)}$$

It corresponds to value of  $m$  where maximum density of spectral lines occur

$$\bar{\nu}_{\text{head}} = \bar{\nu}_0 - \frac{(B_v^1 + B_v^{11})^2}{4(B_v^1 - B_v^{11})} \quad \text{--- (2.70)}$$

$\bar{\nu}_{\text{head}}$  Corresponds to maximum of the branch is  $\bar{\nu}_{\text{head}}$ .

From eq.2.70, when  $B_v^1 < B_v^{11}$ ,  $\bar{\nu}$  head occurs at a wave number greater than  $\bar{\nu}_0$  and the band shade towards lower  $\bar{\nu}$  end.

### 2.4.iii) Model Questions:

1. Explain the formation of band head and band shade in the rotational fine structure of electronic spectra.
2. Derive equation for PQR branches of electronic spectra.
3. Draw the Fortrat parabolas for  $B_v^1 > B_v^{11}$  case and explain why band head and band shade are formed.
4. What is the reason in IR spectra band head is not formed while in electronic spectra it will occur.
5. Write the expressions for m head and  $\bar{\nu}$  head.

### Recommended Books :

- |              |   |
|--------------|---|
| A.J. Sonessa | Introduction to molecular spectroscopy. |
| B.K.Sharma   | Spectroscopy.                           |
| C.N.Banwell  | Fundamentals of molecular spectroscopy. |

## UNIT - III

# SAMPLING AND TREATMENT OF ANALYTICAL DATA

## SAMPLING :

This unit deals with the importance of sampling, various methods of sampling of gases, liquids and solids, transmission and storage of samples.

The major part of the unit that is with regard to treatment of analytical data deals with understanding the terms like Accuracy, Precision, Errors, Standard deviation, Confidence intervals etc.,

Further treatment includes testing of the significance of the value obtained, rejection of data and control charts. The values will be subjected for regression analysis and method of least squares.

## Theory of Sampling :

Sampling is the process of extracting a small portion from a large quantity of material which is truly a representative of the composition of the whole material. This process is of great importance since, if it is not satisfactorily done, the labour and time spent in making a careful analysis of the sample may be completely wasted. Further it is to be borne in mind that the reputation of the analytical chemist rests ultimately on his ability to produce correct results.

Process of sampling can be divided into 3 major operations.

1. Collection of 'gross' sample.
2. Reduction of gross sample to a proper and convenient size for transportation to the laboratory.
3. Preparation of the sample for analysis.

**Sampling Unit :** The sampling unit may be defined as that portion of the material where there is high probability that it will contain the different sized particles of the material in the proportion in which they occur in the entire bulk of the material.

The sampling unit, if taken under carefully prescribed conditions for each different class, should be a proper representative of the material. In practice several number of sampling units will be selected, depending on the size of the shipment to be sampled and combined into one large sample called the gross sample which is more expedient. (Useful for effecting a desired result, based on what is of use or advantageous rather than what is right or just guided by self-interest).

The character of the material, sizes of the various particles, uniformity of the composition and the prominence of any one or more constituents are the factors that govern the amount of the sampling unit.

## I. Collection of the Gross sample:

The amount of the substance to be included in the gross sample depends more on the size of the individual particles than upon the size of the shipment, since it is simply a multiple of the sampling unit.

**1. From Carload lots :** The top surface is divided into 8 equal areas and from each of these sections, approximately equivalent sampling unit may be achieved as follows :

From a stable bank of the material beginning from the bottom, ten equal positions of the material are taken with a shovel at regular and equal intervals from the bottom to the top of the bank, Combine these sampling units for the gross sample.

## The stable bank may be obtained :

1. By digging down to the bottom of the carload at the centre of each section.
2. As the centre of each section of the carload is reached during the ordinary process of unloading by shovelling or otherwise.

### 2. From Bags, Carts, Trays etc.

- a) From a specified number of containers selective, increments may be taken and are combined to get gross sample.
- b) The entire content of every  $n$  th container is taken and combined to get the gross sample.
- c) If the material is fairly uniform and composed of small particles, the gross sample may be obtained by taking ten equal specified increments uniformly distributed on two right angle diagonals across the surface of the container.

### 3. For powdered samples :

By a specially designed thief or by means of a shovel, dipper etc.

- a) **From large shipments :** On a line length wise through the centre of the holder, several portions will be taken from every  $n$  th feet and collected to get gross sample.

- b) **From cars etc. :**

Several specified portions from each holder with the thief or shovel are taken and are combined to form a gross sample.

- c) **From barrels, bags, etc :**

A combination of each portion collected from every  $n$  th container will form the gross sample.

- d) **From small piles (not more than 6 feet in height) :**

With the aid of a thief one portion vertically at the peak of the pile and one vertically at each of ten points uniformly distributed along the line around the pile, half way between the peak and the edge of the pile are taken and combined to get the gross sample.

### 4. From Wet Material :

The collected portions must be kept in moisture tight container.

When fine solid material which is non uniformly suspended in a liquid several vertical sections of the material may be taken by means of a specially designed thief and combined to get the gross sample.

### 5. From hygroscopic or deliquescent materials :

The sample can be taken by means of a thief or a small scoop (ladle) or a shovel when the material is contained in air tight container, which may be readily opened and closed.

### 6. Sampling of non ferrous metals and alloys :

- a) **In the form of piles, sheets, slabs etc.**

- i) The saw dust obtained sawing completely through the specimen, is mixed thoroughly and quartered down on a clear surface and the required amount of sample is drawn.



- ii) The punchings or drillings so obtained by punching or drilling completely through, if the equipment permits or half way through from the opposite sides, holes are placed along a diagonal line from one corner to the other are combined and carefully melted in a clean graphite crucible which are either granulated by completely pouring into distilled water and thoroughly drying or by casting into thin slabs, which may be sawed completely through in several places and the saw dust so obtained can be combined to get a sample.

## II. Reduction of Gross sample to Laboratory Sample :

Approximately (1000 lbs = 500 kg one lb = 453.6 g ) crushed to about

22.6 mm - 1 mesh ; thoroughly mixed and halved by the long pile and alternate shovel method.

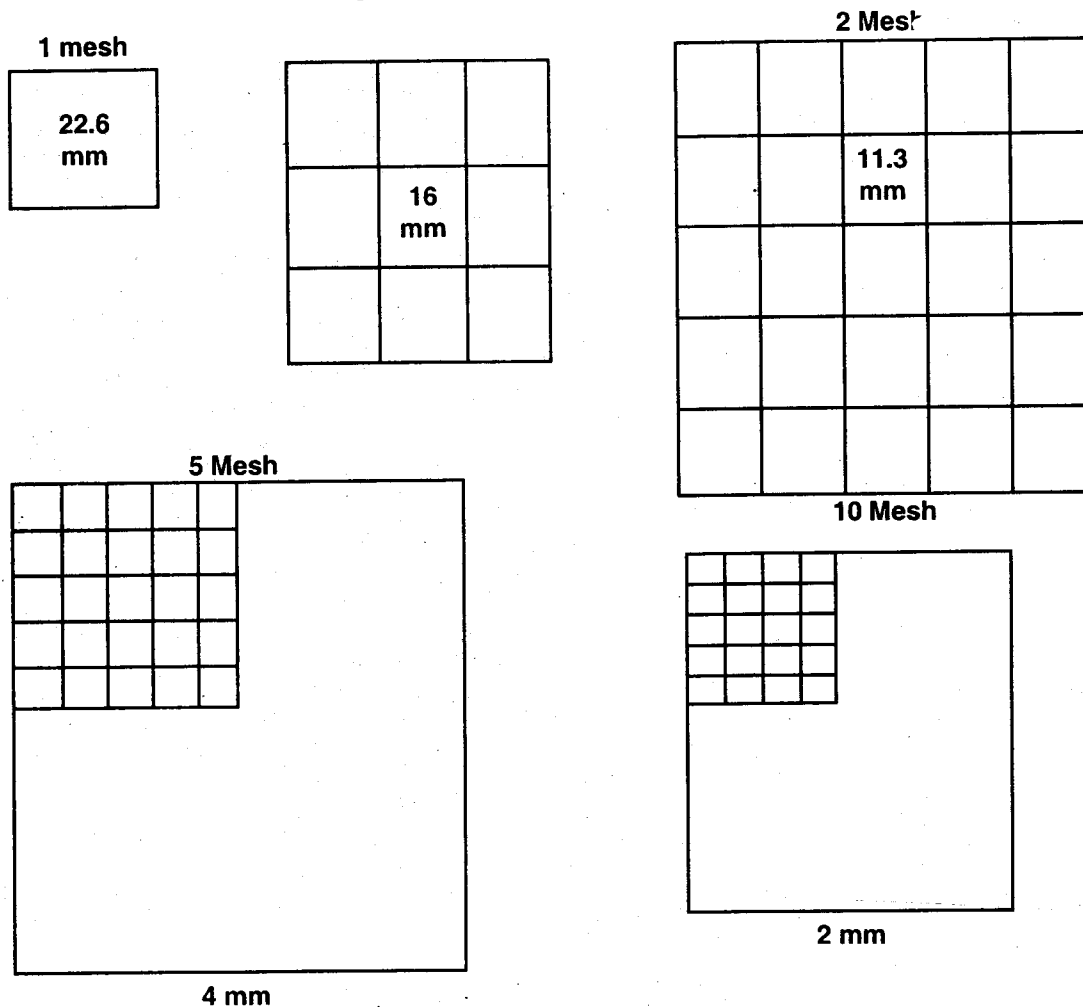


Figure - 3.1 : Sieves with Different Mesh Sizes

Discard

- 1/2 One half crushed to about 16 mm - 1.5 mesh mixed and halved by the LP and AS procedure. (i.e., Long Pile and Alternate Shovel method).
- 1/2 One half crushed to about 11.3 mm - 2 mesh mixed and halved by the LP and AS procedure.
- 1/2 One half crushed to about 4 mm - 5 mesh mixed rolling on canvas, halved by cone and quartering procedure.

1/2 One half crushed to about 2 mm -10 mesh mixed by rolling on canvas; halved by riffing (or sampling machine) or by the cone and quartering procedure.

1/2 One half mixed and riffled down to about 8 lbs.

In the case of moisture sample, the sampling unit must be collected and stored under conditions where by moisture would not be lost or absorbed. The mixing, crushing and halving operations must be done as rapidly as possible.

In the case of the gross samples containing an excessive amount of water which would be lost in operating to reduce to lab sample, the moisture driven off should be accounted for in the calculations and evaluation of the sample.

### III. REDUCTION OF GROSS SAMPLE

#### (LONG PILE AND ALTERNATE SHOVEL METHOD)

1. The entire gross sample is thoroughly mixed after crushing in a suitable manner until all pieces are approximately one inch or less in any dimension by shovelling it into a cone shaped pile depositing each shovelful on the apex of the pile.
2. All the material is shovelled into a pile about the width of the shovel and approximately 10 inches long according to the total amount of material, spreading each shovelful uniformly over the whole length of the pile, beginning alternatively from opposite ends.
3. The long pile is divided into two equal portions by beginning on one side of the pile, at either end, and taking successive shovelfuls advancing each time by the width of the shovel around the pile, combining the first and every alternate shovelful into a neat cone shaped pile as in (1) and discarding the second and every alternative shovel.
4. The above operation is repeated until a portion of about 500 lbs is obtained.
5. The material is crushed until no piece is greater than approximately 3/4 inch (197 mm) in any dimension, and the operation (3) is repeated.
6. The material is crushed until no piece is larger than approximately 1/2 inch (127mm) in any dimension and then the operation (3) is repeated.
7. A portion of about 125 lbs is so obtained which is further reduced by the cone and quartering procedure.

#### REDUCTION OF GROSS SAMPLE::

##### CONE AND QUATERING PROCEDURE

1. The material amounting to about 125 lbs is mixed by crushing to pass a 4 mm-5 mesh sieve and shovelled into a neat cone.
2. The cone is flattened by pressing the apex vertically down with the shovel, so that, when quartered, each quarter will contain the material originally contained there in.
3. The flattened pile is divided into equal quarters by passing a straight edge board vertically twice through centre of the pile at right angles, each time drawing half of the pile a few inches to one side.
4. The top and bottom quarters are discarded and all the fine particles are brushed away from the exposed surface.

5. The remaining quarters are crushed to pass a 2 mm - 10 mesh sieve and thoroughly mixed by shovelling into a neat cone.
6. The operations (3) and (4) are repeated or riffled (cut or graze or robbed) to about 20 pounds.
7. The retained sample is subjected for grinding to pass 0.85 mm - 20 mesh sieve. The material is thoroughly mixed on a clean canvas by raising alternate opposite corners of the canvas, thus the material is rolled from side to side (one side to the other) for one hundred times.
8. The sample is further treated to suit the requirements of the particular material.

## SAMPLING OF LIQUIDS

Generally, a uniform and representative sample of liquid is more feasible. When the liquid is thin, non viscous and does not contain immiscible constituents, a homogenous condition usually exists and a sample from any part of the bulk is sufficiently true representative of the whole. When viscous or immiscible materials are present, a heterogeneous condition exists and care is to be taken to obtain a representative sample. The proper selection of a representative sample of a liquid therefore, involves a consideration of the physical properties of liquids, their chemical activity, the miscibility of all components and the interference of any insoluble materials carried by the liquid.

**The sampling of liquids is divided into 3 classes :**

1. Sampling of liquids in silent or inert state
2. Sampling of liquids in motion
3. Sampling of special liquids

Eg : Immiscible liquids, Volatile liquids, Liquids containing sediments etc.

### 1. Sampling of Liquids in quiescent State

All liquids not in motion may be sampled by obtaining portions at specified points from the top to the bottom of the liquid by means of a suitable sampling apparatus.

#### i) From storage tanks, cars etc.

- a) If the liquid has been thoroughly agitated or is known to be reasonably uniform in composition, several portions are transferred to a container by means of a suitable dipper, the several dippings being taken throughout the mass of liquid.
- b) If the character and condition of the liquid is such as to permit the formation of zones of different composition, samples are obtained by means of a suitable apparatus, where by proper proportions of the liquid are taken at every point from the top to the bottom. These samples are combined to form gross sample after thoroughly mixing. By slowly lowering the sampling bottle into the liquid with the outlet open, a portion of the liquid from every point passes through the inlet into the bottle, unless if outlet is kept closed until the desired depth is reached, the entire sample may be taken at any desired point.



Rubber stopper (or)  
ground glass stopper

Figure - 3.2 - Thief for Collecting sample

## 2) From Drums, Carboys, Barrels etc.

- 1) By means of a thief proportional fractions are taken from each container, and these increments are combined and mixed to get the composite gross sample.

If the contents of the container are such as to preclude thorough mixing or if the material has the tendency to form strata of varying compositions, the open thief should be lowered into the liquid at such a rate as to keep the levels of liquid inside and outside of the thief very nearly equal, in order to include portions at all points from the top to the bottom of the liquids.

## Sampling of Liquids in Motion

### 3) From a pipe of continuous full flow under constant (or) varying head.

- a) By means of a suitable sampling wiper a definite fraction of varying flow can be collected over a required period of time.
- b) With large pipes and large flows, the apparatus consists of 3 pipes 1,2,3 bent at  $90^\circ$  angles with opening facing the flow at different levels are inserted in pipe P and connected to a common pipe A. The flow through A is then sampled by B the opening of which faces the flow at a point half way between the centre and bottom of the pipe A. Pipe B is fitted with a stop cock C where by the amount of the sample flow through B may be regulated.

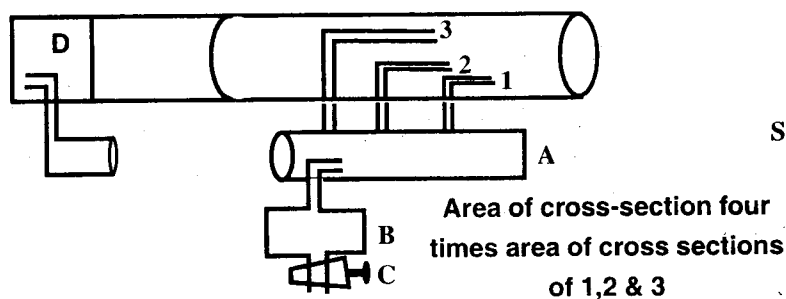


Figure 3.3 -  
Special Design for collecting samples  
of liquids in motion

## Sampling of special liquids :

### 4. Liquids containing insoluble mater in suspension :

- a) When the sediments remains in reasonably uniform suspension during the periods required for taking the sample, the liquid is thoroughly mixed and the sample obtained in one of the ways that are being mentioned earlier.
- b) When the sediment settles rapidly or is impossible of uniform distribution, the liquid is thoroughly mixed and a complete column of the liquid is rapidly taken by a special thief. By repeating this operation several times a fairly representative sample is obtained.

### 5. Liquids composed of immiscible layers :

The layers are separated and portions of each layer are combined in proper ratios of the material is placed in a container of uniform cross section, then proper proportions are taken from each layer after measuring the depth of each layer.

### 6. Volatile liquids :

These are best sampled from a continuous flow while the liquid is being discharged or by means of a siphon from containers. If the liquid is uniform in composition, or can be made so by agitation, a portion may be run to the bottom of the sampling bottle until the bottle overflows through another tube from the top into another bottle to such an extent as to leave a liquid in the first bottle containing the maximum amount of the volatile constituent. The sample bottle now, quickly stoppered and sealed.

## Sampling of Gases :

### Sampling of Gases

Sampling of gases is difficult when it passes through a pipe or conduit from the source of production. Gases travel through straight pipes or conduits in an irregular succession of waves with the maximum velocity being at the centre of the pipe. The temperature of gases will vary through out the cross section of the pipe.

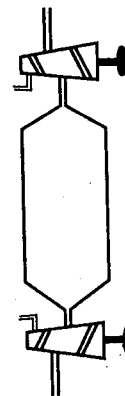
If it is possible to discharge total gas to be sampled into a large holder and provide time for it to thoroughly diffuse, a true representative sample could be obtained by withdrawing a portion of it.

Under varying conditions of velocity, composition and temperature, it is impossible to detect a point of approximately average velocity, temperature or composition from which a representative instantaneous sample can be taken. Hence it is necessary to collect a sample over an extended period, such that there is a high probability for a true sample under same conditions. Useful data regarding composition and gas-flow is obtained by taking frequent "grab" sample.

### Gas samples : Two types

1. Continuous sampling
2. Instantaneous sampling.

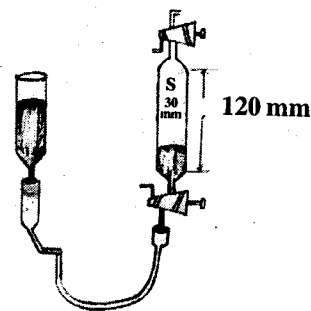
Fig 3.4  
Apparatus for gas sampling



The figure represents very simple pipette for sampling gases. It may be made in any size from 5 ml to 25 ml. The three way capillary stop cocks permit the flushing out of the connecting tubes with the sample itself or with a confining liquid. Into the vertical capillary tube at the upper end mercury is introduced. The vessel is evacuated to about 1 mm pressure and then by means of lower tap the pipette is closed. The air from the lower capillary inlet is displaced and the tap is turned so that the gas flows into the evacuated vessel until the pressure is slightly above that of atmosphere. The gas may then be transferred to the gas analysis apparatus by connecting to a pair of small aspirators filled with mercury by suitable manipulation of the taps.

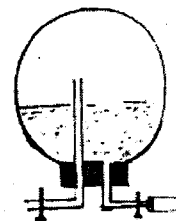
Alternatively the following apparatus may be used where in the gas is collected in 'S' by lowering the reservoir 'R'.

Fig - 3.5. Another model for Gas Sample



A sample of gas holder may also be constructed with the aid of round bottomed flasks as shown in figure fitted with a rubber cork with two holes. The right side tube may be connected to a levelling bulb.

Fig -3.6 Gas Sample Holder



## TREATMENT OF ANALYTICAL DATA

### Introduction :

When a quantity is measured with the greatest exactness that the instrument, method and observer are capable of, it is found that the results of successive determinations differ among themselves to a greater or lesser extent. At the same time we cannot consider that all the values obtained are correct within the reasonable limits of measurements. The average value of a series of measurements is accepted as the most probable value. However it should be noted that the average value may not always be the true value. At times the difference may be too small, but in case of others it may be so large that the result cannot be accepted. The reliability of the result depends upon the magnitude of the difference between the average value and the true value.

### Accuracy and Precision :

**Accuracy :** The accuracy has been described as the degree of agreement between a measured value and the most probable or the true value.

On the other hand the accurate value is one which is true value or exact value. But in scientific experiments we never expect an exact value since the true value is never known except within certain limits.

Hence, we can approach a true value but we cannot attain it.

Thus we can say that the accurate values are one which were obtained by a skilled scientist with all best quality of instruments.

### Precision :

Precision is the reproducibility of a number of similar measurements. It may be defined as the concordance of a series of measurements of the same quantity.

In analytical chemistry the term precision of a value is defined as

“The degree of agreement between the true value and other values obtained under similar experimental conditions”.

On the other hand precision is used to describe the reproducibility of the results, while accuracy has been used to express correctness of a measurement.

However, a high degree of precision does not imply accuracy. Generally the terms accuracy and precision are often used as synonyms in ordinary usage, but in connection with scientific data they must be distinguished carefully.

An accurate result is one that agrees closely with the true value of a measured quantity. The comparison is usually made on the basis of an inverse measure of the accuracy.

viz. the error (the smaller the error, the greater the accuracy). The error is most frequently expressed relative to the size of the measured quantity, for example, in percent or in parts per thousand (ppt).

In view of the nebulous (not clear) nature of the true values, it is clear that accuracy cannot often be ascertained. Precision on the other hand, refers to the agreement among of a group of experimental results, and implies nothing about their relation to the true value.

Precise values may well be inaccurate, since an error causing deviation from the true value may effect all the measurements equally and hence not impair (damage) their precision.

A determinate error which leads to inaccuracy may or may not affect precision, depending upon how nearly constant it remains through out a series of measurements.

On the other hand, accuracy without precision is obviously impossible, but precision does not by any means imply accuracy.

When an individual is able to reproduce two or more measurements with only slight differences in the results, his / her work be regarded as precise. It should be noted that a high degree of precision does not imply accuracy.

### **Expression of Accuracy -Explanation :**

For example, a volume of twenty five milli litres carefully measured in a hundred-milli litre graduated cylinder should not be expressed as 25.0 ml, as cylinder is graduated in a milli litre units and it is not possible to estimate the fraction of such units closer than tenths of milli litres.

On the other hand, the same volume measured in a fifty milli litres burette may be expressed as 25.00 ml, as here the apparatus is graduated directly in tenths of milli litres and the hundredth place is capable of possible estimation. The accuracy of measurement with burette is greater than with the graduated cylinder.

Like wise, a ten gram weight when measured on a side shelf balance may be expressed as 10.00 g but on analytical balance as 10.0000 g.

Thus in each case, the accuracy of measurement is limited by the nature of the instrument used and the skill of the observer in making the observation.

The difference between the numerical values can be expressed as the absolute difference or as the relative difference (generally relative difference will be expressed in parts per thousand i.e. ppt )

For example : 3.042, 3.031 are two numerical values.

The absolute difference of these two values will be 0.011, while the relative difference will be .

$$\frac{0.011}{3.042} \times 1000 = 3.616 \text{ppt}$$

Now, we know that absolute error of a determination is the difference between the observed or measured value and the true or most probable value.

In the case of above example, if 3.042 is regarded as the true value, the absolute error of the value 3.031 is 0.011. The relative error is the absolute error divided by the true or most probable value. Thus the relative error is 3.616 ppt. in the case of value 3.031.

Deviations in parts per thousand (ppt) may be readily computed between any two numbers of similar magnitude by comparison of such difference without regard to the decimal point.

**Ex :** The difference between 6.3 and 6.4 is

one part in about 64 (or)

Ten parts in about 640 (or)

100 parts in about 6400 (or)

$$1 \times \frac{1000}{64} \approx 16(15.625) \text{ ppt but it should be expressed as 16 ppt}$$

## ERRORS::

**Definition :** The deviation from the probable value or true value are named as error. Error in any set of measurements can be broadly divided in two categories.

- I. Determinate (or) Constant errors.
- II. Indeterminate (or) Random Errors.

It is not always possible to distinguish between them.

### 1. Determinate (or) Constant (or) Systematic Errors :

A determinate error is a tangible one. These errors may be discovered, corrected (or) eliminated.

A determinate error may have the same value under variety of conditions and may remain constant from one measurement to the other. These errors occur with definite regularity owing to the faulty methods, technique or defective measuring instruments.

### Examples of sources of Determinate Errors :

- (i) In correct weights,
- (ii) a poorly calibrated burette
- (iii) an impurity in a reagent.
- (iv) an appreciable solubility in precipitate



(v) a side reaction in a titration and

(vi) heating a sample at a very high temperature.

Determinate errors have been classified as methodical, operative and instrumental according to their origin.

**Methodic :** The method of analysis as it reflects the properties of the chemical systems involved.

**Operative :** Inefficiency of the experimenter

**Instrumental :** Failure of measuring devices to perform in accordance with required standards frequently, the source of an error may always be expected in weighing a hygroscopic substance but it may increase if the analyst has poor balancing technique.

**Personal Errors and Errors of Operation :**

These are due to the factors for which the experimenter is responsible.

Example for this type are

- a) Improper technique in reading a burette
- b) Failure to clean pipette (or) burette properly.
- c) In ability to recognize certain colour changes that occur with indicators.
- d) Failure to make solutions homogenous.
- e) Carelessness in the transfer of liquids and solids.
- f) Mistakes in mathematical calculations.
- g) The errors due to prejudice.

**Instrumental Errors :**

As the name implies, these are due to instruments that are used.

1. Inaccurate weight : (uncalibrated/ improperly calibrated)
2. Unequal length of balance arms.
3. Uncalibrated volumetric glass ware.

These errors may also arise by the attack of foreign materials upon glass ware, porcelain etc. and by the loss in weight of platinum crucibles when strongly heated.

These errors can be avoided by careful calibration.

Similarly reagent error may arise by the use of impure reagents, which results in an inaccurate analysis. If the impure reagents are used in the absence of pure reagents, the degree of impurity must be measured, so as to apply suitable correction to the measurement.

**Errors of Method :**

These errors are due to such factors as

- i) the solubility of precipitate,
- ii) failure of reaction to proceed quantitatively,
- iii) secondary reactions
- iv) impurity of precipitate due to coprecipitation
- v) inadequate temperatures during drying and ignition and
- vi) neglect of indicator correction.

These errors are most serious in quantitative analysis and may be minimised by strict adherence to the well established procedures.

### Additive error (Constant error) :

Some times the magnitude of a determinate error is nearly constant in a series of analysis regardless of the size of the sample.

For Example : With use of an indicator blank that is not corrected for in a series of titrations. This type of error may be called as an Additive error (or) Constant error.

The significance of an error generally decreases as the size of the sample increases since usually we are not interested in the absolute value of an error.

For Example : A constant end point error of 0.1 ml in a series of titrations represents a relative error of 10% for a sample requiring 1 ml titrant but only 0.2% if 50 ml of titrant is used.

### Proportional Errors :

A proportional error is one whose absolute value depends upon the size of the sample, in such a manner that the relative error remains constant.

For Example : A proportional error may arise from impurity present in a standard substance, which leads to an incorrect value for the normality of a standard solution.

## II. INDETERMINATE (or) RANDOM ERRORS

These errors are accidental and more intangible errors, over which the experiment has little control. Their cause is not always known and hence corrections cannot be made. These errors are difficult to define, but their existence is revealed by small differences in the successive values of a measured quantity when the measurements were made by the same person with great care under nearly similar conditions.

They can be classified into two classes.

### 1. Variations within determinate errors :

A determinate error will arise when the knife edge of balance has become worn out. But when the error varies owing to load it becomes an indeterminate error.

Similarly temperature changes and variation in humidity in a balance room give rise to determinate error but if they are not controlled they become indeterminate.

### 2. Erratic Errors :

It is very difficult to notice them.

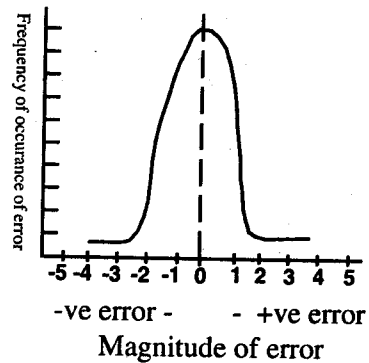
- a) Fluctuations in balance room can cause erratic errors in weighing.
- b) Accidental loss of materials during analysis.

A numerical relationship exists between the magnitude of a random error and the frequency of its occurrence.

The relationship is shown in the figure below. Which is known as "Normal Distribution Curve".

**Figure : 3.7**

**Normal Distribution Curve**



A statistical analysis of random errors reveals that

- Random errors of frequent occurrence are those of small magnitude
- Large errors are not likely to occur at all.
- Positive and negative differences are equally likely to occur.

The form of the error curve indicate the relative precision of the measurements made.

A narrow peaked curve with steep slopes indicate a relatively a high degree of precision.

A broad curve indicate a relatively low degree of precision.

**Minimisation of Errors :**

As discussed earlier determinate errors can be minimised by one of the following methods

- Calibration of apparatus and application of corrections.
- Running a blank determination.
- Running a control determination and correction can be applied as

$$\frac{\text{Result for standard}}{\text{Result for unknown}} = \frac{\text{Weight of the constituent in standard}}{x}$$

where 'x' is the constituent in the unknown.

The standards useful for this purpose are a) British chemical standards (BCS); b) Bureau of analytical samples (BAS) ; c) US Bureau of standards (US BS) and d) Analytical samples for students. (ASS)

- Using independent methods of analysis.
- Running parallel determinations ( precision)
- Standard addition methods.
- Isotopic dilution.

# STATISTICAL APPROACH

The mean (or average) deviation or the relative mean deviation is a measure of the precision.

## 1. Arithmetic Mean (or ) Average :

The mean is the numerical value obtained by dividing the sum of a set of measurements by the number of individual results in the set. It is also called the arithmetic mean or average.

**Explanation :**

	Data	Individual Deviations from average	
	0.973	0.001	
	0.976	0.002	
	0.971	0.003	
	<u>0.975</u>	<u>0.001</u>	
Average =	3.895 , 4	0.007	= Mean Deviation
=	0.973		

Thus the mean 'm' is given by  $m = \frac{\sum Mn}{n}$

where 'M' is the individual measurement and n is the total number of measurements.

## 2. Mean Deviation :

The agreement between a series of results is measured by computing their mean deviations. This is evaluated by determining the arithmetical mean of the results, then calculating the deviation of each individual measurement from the mean and finally dividing the sum of the deviations, regardless of the sign by the number of measurements.

The **relative mean deviation** is the mean deviation divided by the mean. This may be expressed in terms of percentage or in parts per thousand.

For example : The percentages of a constituent A in a compound AB were found to be 48.32, 48.36, 48.23, 48.11, 48.38 percent. Calculate the mean deviation and the relative mean deviation.

Results	Deviations
48.32	0.04
48.36	0.08
48.23	0.05
48.11	0.17
<u>48.38</u>	<u>0.10</u>
241.40 , 5	0.44 , 5
Mean = 48.28	Mean deviation = 0.088

$$\text{Relative Mean Deviation} = \frac{0.088 \times 100}{48.28} = 0.1822\% = 1.8 \text{ parts per thousand (ppt).}$$

If we consider a series of observations arranged in an ascending order of magnitude

$$x_1, x_2, x_3, \dots, x_{n-1}, x_n$$

$$\text{The Arithmetic mean is given by } \bar{x} = \frac{x_1 + x_2 + \dots + x_{n-1} + x_n}{n}$$

### 3. Standard Deviation

Another means of expressing precision is with standard deviation (s) of the sample. Which is also given by 'σ' is "defined as the square root of the sum of the squares of the absolute deviations of the individual samples" divided by one less than number of samples.

$$s \text{ or } \sigma = \sqrt{\frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + \dots + (x_n - \bar{x})^2}{n-1}}$$

$$= \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}} = \sqrt{\frac{\sum x_i^2}{n-1}}$$

Where  $x_i = x_n - \bar{x}$  and n may be 1, 2, 3, ..., n.

The square of the standard deviation is called variance (V)

A. more accurate measure of the precision is known as Coefficient of variation (C.V.) is given by

$$C.V. = \frac{S \times 100}{\bar{x}}$$

### Data Reduction / Distribution of Random Errors

#### Frequency Distributions :

When we get individual values which are in the unorganized form, the first step is that the results are to be arranged in the order from lowest to highest.

TABLE I - 3.1 (a) Individual Values, Unorganized

1.	0.458	21	0.462	41	0.450
2.	0.450	22	0.450	42	0.455
3.	0.465	23	0.454	43	0.456
4.	0.452	24	0.446	44	0.456
5.	0.452	25	0.464	45	0.459
6.	0.447	26	0.461	46	0.454
7.	0.459	27	0.463	47	0.455
8.	0.451	28	0.457	48	0.458
9.	0.446	29	0.460	49	0.457
10.	0.467	30	0.451	50	0.456
11.	0.452	31	0.456	51	0.455
12.	0.463	32	0.455	52	0.460
13.	0.456	33	0.451	53	0.456
14.	0.456	34	0.462	54	0.463
15.	0.449	35	0.451	55	0.457
16.	0.454	36	0.468	56	0.456
17.	0.456	37	0.458	57	0.457
18.	0.440	38	0.458	58	0.453
19.	0.457	39	0.456	59	0.455
20.	0.459	40	0.454	60	0.453

TABLE I-3.1 (b) Individual Values, organized

1.	0.440	21	0.454	41	0.457
2.	0.446	22	0.455	42	0.458
3.	0.446	23	0.455	43	0.458
4.	0.447	24	0.455	44	0.458
5.	0.449	25	0.455	45	0.458
6.	0.450	26	0.455	46	0.459
7.	0.450	27	0.456	47	0.459
8.	0.450	28	0.456	48	0.459
9.	0.451	29	0.456	49	0.460
10.	0.451	30	0.456	50	0.460
11.	0.451	31	0.456	51	0.461
12.	0.451	32	0.456	52	0.462
13.	0.452	33	0.456	53	0.462
14.	0.452	34	0.456	54	0.463
15.	0.452	35	0.456	55	0.463
16.	0.453	36	0.456	56	0.463
17.	0.453	37	0.457	57	0.464
18.	0.454	38	0.457	58	0.465
19.	0.454	39	0.457	59	0.467
20.	0.454	40	0.457	60	0.468

This is not just sufficient since the mind has no capacity to grasp about 60 numbers on a piece of paper even though they are arranged. Thus we need more compactness in order to make practical use of data.

**TABLE - 3.1 (c) Grouping of Individual Values into Cells**

Cell Midpoint	Cell Boundaries	Number of Values
0.4425	0.4405	1
0.4465	0.4445	3
0.4505	0.4485	11
0.4545	0.4525	21
0.4585	0.4565	14
0.4625	0.4645	7
0.4665	0.4685	2
0.4705	0.4725	1

The second step involves condensing the data by grouping them into cells. In this process we divide the results from lowest to highest value, into a convenient number of intervals or cells and then count the number of values falling within each cell. Of course this process involves some loss of information but this is more compensated by the increased efficiency with which the significance of the condensed data may be perceived.

In the present case out of 60 readings we can make them into 13 to 20 cells. But even 10 or fewer may be preferable if the number of values to be grouped is small say less than 250.

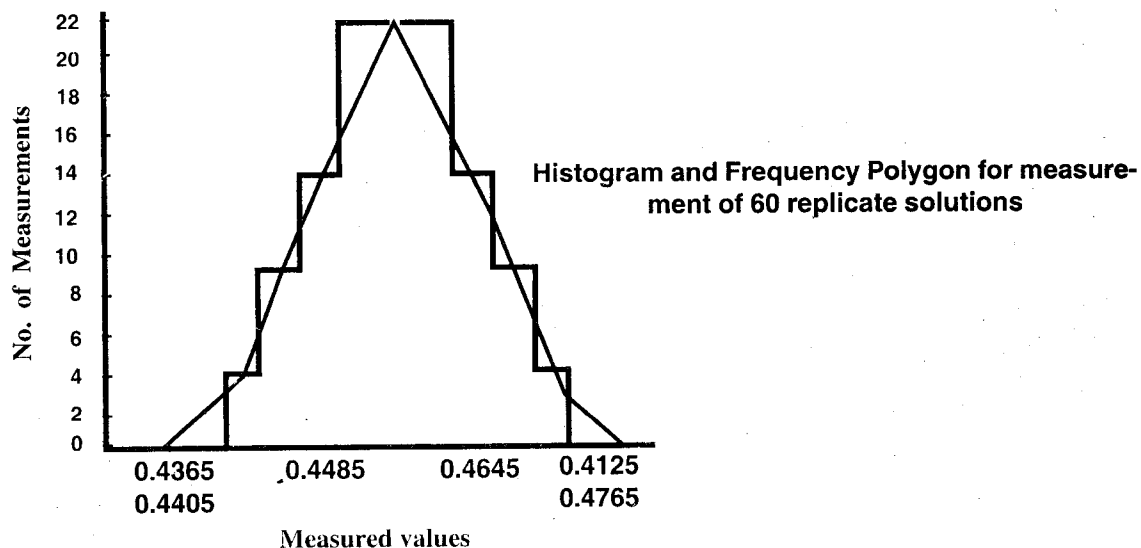
Thus let us assume that we have chosen to group the data into **eight cells**.

Thus we will get 9 boundaries and 8 cell mid points.

Ex : Suppose if the total 60 values range from 0.440 to 0.468 and if very few results are below 0.448 and above 0.464.

A Histogram can be plotted between measured value and number of measurements in each cell. A frequency polygon is also constructed by plotting frequencies at cell midpoints and connecting the point with straight lines.

Figure - 3.8 Frequency Polygon :



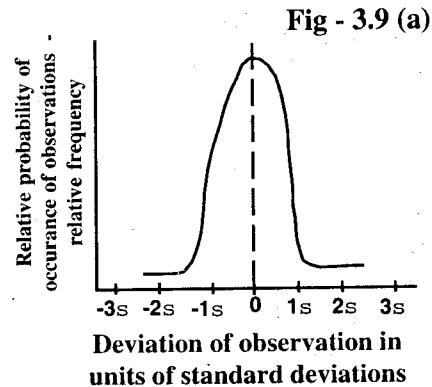
**The normal error curve / Gaussian distribution curve :**

The limiting case approached by the frequency polygon as more and more replicate measurements are performed is the normal or Gaussian distribution curve.

In statistics a finite number of observations of a given kind is considered to represent a sample of an infinite population (or) Universe of data.

The properties of the universe of random errors can be described by Gaussian distribution, which follows by equation.

$$p(x)dx = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x-\mu)^2}{2\sigma^2}\right] dx.$$



Where  $p(x)dx$  is the probability of a random error having a value in the interval 'x' to  $x+dx$ ,  $m$  is the average value of entire population and  $s$  is the standard deviation of the population. The distribution of errors for a particular population of data is given by two population parameters which are  $m$  and  $s$  i.e. properties of population such as  $m$  and  $s$  are known as population parameters. Analogous properties of finite sample are known as in statistics (parameter estimates).

For finite samples of 'n' observations the sample mean ( $\bar{x}$ ) is the arithmetic average of the 'n' observations.  $\bar{x}$  approaches the population mean  $m$  in the limit as  $n$  approaches infinity. Sample standard deviation 's' approaches the population standard deviation  $s$  in the limit.

The population mean  $m$  expresses the magnitude of the quantity being measured. The standard deviation  $s$  expresses the scatter and is therefore an index of precision. By introduction of variable 'y' as the deviation from the mean in units of standard deviation ( $\sigma$ )

$$y = \frac{x - \mu}{\sigma}$$

where  $x$  is the individual value

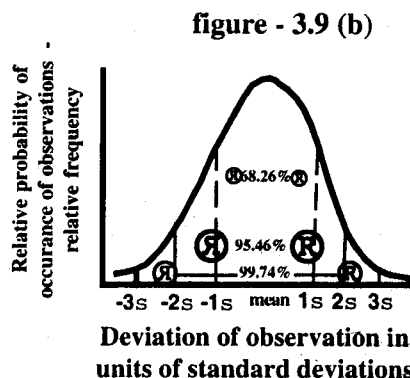
$m$  is the mean and

$s$  is the standard deviation.

A normalised expression of the Gaussian distribution in terms of a single variable is possible giving the equation.

$$p(x)dx = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{y^2}{2}\right) dy = f(y)dy.$$

which is plotted in the figure - 3.9 (b)



Areas under the curve for the function  $f(y)$  are listed in mathematical tables under a title such as cumulative normal distribution.

The total area under the curve of Figure - 3.9 (b) from  $-\infty$  to  $+\infty$  corresponds to a probability of unity for the entire population.

Thus the area under curve between any two values of 'y' (in units of  $s$ ) gives the fraction of the total population having magnitudes of 'y' between these two values.

(The area under the curve between any two values of  $(x - m)$  gives the fraction of the total population having magnitudes between these two values).

It may be shown that about two thirds ( $2/3$  rds) i.e. 68.26% of all the values in an infinite populations fall within the limit  $m \pm s$ , while  $m \pm 2s$  includes about 95% and  $m \pm 3s$  covers practically all of the values (99.74%).

Thus small errors are more probable than larger ones, since the normal curve is symmetrical, high and low results are equally probable once determinate errors have been dismissed.

The function  $f(y)$  has the property of being a maximum for  $y = 0$  and therefore  $x = m$ . Thus the average value is the most probable value of the population.

This probability forms the basis of a test for a Gaussian distribution.

### Statistical Treatment of Finite Sample

#### Applications to Finite Sample :

In spite of its mathematical reality, normal distribution of an infinite population appear to be fiction in the real laboratory work.

#### Measures of Central Tendency and Variability :

The central tendency of a group of results is simply that value about which the individual results tend to cluster.

For a infinite population, it is  $\mu$ , the mean of such a sample. The mean of a finite number of measurements,  $x_1, x_2, x_3, \dots, x_n$  is often designated as  $\bar{x}$  to distinguish it from  $\mu$ . However,  $\bar{x}$  approaches  $\mu$  as a limit when  $n$ , the number of measured values, approaches infinity.

Calculation of the mean involves simply averaging the individual results  $\bar{x} = \frac{x_1 + x_2 + x_3 + \dots + x_n}{n}$

$$= \sum_{i=1}^{i=n} \frac{x_i}{n}$$



The mean is generally the most useful measure of central tendency. It may be shown that the mean of 'n' results is  $\sqrt{n}$  times as reliable as any one of the individual results.

Thus there is a diminishing return from accumulating more and more replicate measurements.

The mean of four results is twice reliable as the result in measuring central tendency.

Mean of nine results is three times as reliable.

Mean of 25 results is five times as reliable etc.

Thus there is no need for more number of results.

The Median (M) of an odd number of results is simply the middle value when results are listed in order.

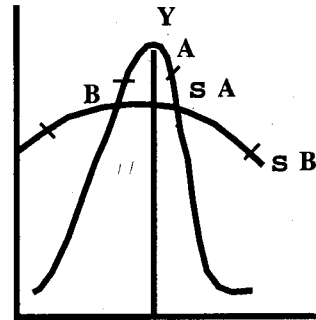
For even number of results the median is average of the two middle values.

In a truly symmetrical distribution, the mean and median are identical.

Generally speaking, the median is a less efficient measure of central tendency than is the mean, but in certain instances it may be useful, particularly when dealing with very small samples.

Since two parameters  $m$  and  $s$  are required to specify a frequency distribution. It is clear that two populations may have the same central tendency but differ in spread or variability (or dispersion) as seen in Fig.

Figure - 3. 10



Two populations with same central tendency  $m$ , but different variability

For a finite number of values the simplest measure of variability is the Range (R), which is the difference between the largest and smallest values.

The average deviation from the mean is often given as measure of variability which is given by

$$\text{Average deviation} = \bar{d} = \frac{\sum_{i=1}^{i=n} [x_i - \bar{x}]}{n}$$

$$\text{Relative average deviation} = \frac{\bar{d}}{\bar{x}} \times 100 = \frac{\sum_{i=1}^{i=n} (x_i - \bar{x}) / n}{\bar{x}} \times 100$$

$$\text{Standard deviation} = s = \sqrt{\sum_{i=1}^{i=n} (x_i - \bar{x})^2 / n - 1}$$

### Standard Deviation :

As 'n' is increased, the quantity  $n-1$  approaches  $N$  (the entire population) relatively more and more closely.

If a random sample is taken, the quantity 's' becomes a closer approximation to  $s$  as the size of the sample is increased.

$s$  should be reserved for the universe, or infinite population.

$$\sigma = \sqrt{\sum_{i=1}^{i=N} [x_i - \mu]^2 / N}$$

The standard deviation  $s$  of the population is the square root of the arithmetic mean of the squares of the deviations of the individual values  $x_i$  from the population mean  $m$ .

### Coefficient of variation :

If 'n' is large (say 50 or more), it is immaterial whether the term in the denominator is ' $n-1$ ' (which is strictly correct) or 'n'. When standard deviation is expressed as a percentage of mean, it is called coefficient of variation. (C.V).

$$C.V. = \frac{s \times 100}{x}$$

The variance which is  $s^2$  is fundamentally more important in statistics than 's' itself but later is much more commonly used in treating chemical data.

**EXAMPLE :** The amount of a particular constituent by four separate determinations is found to be 0.2041, 0.2049, 0.2039 and 0.2043. Calculate the mean, median, range, average deviation, relative average deviation, standard deviation and coefficient of variation.

$$\text{Mean : } \bar{x} = \frac{0.2041 + 0.2049 + 0.2039 + 0.2043}{4}$$

$$\bar{x} = 0.2043$$

$$\text{Median : } M = \frac{0.2041 + 0.2043}{2}$$

$$M = 0.2042$$

$$\text{Range : } R = 0.2049 - 0.2039$$

$$R = 0.0010$$

$$\text{Average deviation : } \bar{d} = \frac{(0.0002) + (0.0006) + (0.0004) + (0.0000)}{4}$$

$$\bar{d} = 0.0003$$

$$\text{Relative average deviation : } \frac{\bar{d}}{\bar{x}} \times 1000 = \frac{0.0003}{0.2043} \times 1000$$

$$= 1.5 \text{ ppt}$$

$$\text{Standard deviation : } s = \sqrt{\frac{(0.0000)^2 + (0.0004)^2 + (0.0006)^2 + (0.0002)^2}{4-1}}$$

$$s = 0.0004$$

$$\text{Coefficient of variation : } = \frac{0.0004}{0.2043} \times 100$$

$$= 0.2\%$$

### Students 't' test :

Although  $s$  and  $m$  are defined for normal distribution of an infinite population, we deal with  $\bar{x}$  and  $s$  which are only estimates of  $\mu$  and  $m$  in practical work due to limited observations.

In 1908, a British Scientist by name W.S. Gosset under pen name 'student' studied the problem of making predictions based upon a finite sample drawn from an unknown population.

The quantity 't' (often called student's 't') is defined by the expression

$$\pm t = (\bar{x} - \mu) \frac{\sqrt{n}}{s}$$

Tables of 't' values relating to various odds or probability levels and for varying degrees of freedom

TABLE - 3.2 Some Values of Student's t

NUMBER OF OBSERVATIONS N	NUMBER OF DEGREES OF FREEDOM, N-1	PROBABILITY LEVELS			
		t 50%	t 90%	t 95%	t 99%
2	1	1.000	6.314	12.706	63.66
3	2	0.816	2.920	4.303	9.925
4	3	0.765	2.353	3.182	5.841
5	4	0.741	2.132	2.776	4.604
6	5	0.727	2.015	2.571	4.032
7	6	0.718	1.943	2.447	3.707
8	7	0.711	1.895	2.365	3.500
9	8	0.706	1.860	2.306	3.355
10	9	0.703	1.833	2.262	3.250
11	10	0.700	1.812	2.228	3.169
21	20	0.687	1.725	2.086	2.845
$\mu$	$\mu$	0.674	1.645	1.960	2.576

may be found in statistical compilations.

Degree of freedom is one less than  $n$ ,  $(n-1)$  the number of observations.

The values of 't' are given in Table 3.2

### Confidence Interval of Mean :

By rearranging the equation of student's t test, we obtain the confidence interval of the mean, or confidence limits.

$$\pm t = (\bar{x} - \mu) \frac{\sqrt{n}}{s}$$

We obtain the confidence interval of the mean, or confidence limits.

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

This equation may be used to estimate the probability, that the population mean  $\mu$ , lies within a certain region, centered at  $\bar{x}$ , the experimental mean of measurements.

Value of 't' is essential for calculation confidence interval of mean.

It is observed that the 't' values increase with decrease in 'n' values (or) 't' values decrease with increase in 'n' values.

This is reasonable, since the smaller 'n' becomes, the less information is available for estimating the population parameter. Increase in 't' exactly compensate for the lessing of information.

In some cases where analyses have been repeated extensively, a chemist may have a reliable estimate of the population standard deviation ' $\sigma$ '. In such case there is no uncertainty in the value of  $\sigma$ , and the confidence interval is given by

$$\mu = \bar{x} \pm \frac{z\sigma}{\sqrt{n}}$$

where 'z' is simply the value of 't' at  $n = \infty$

when  $n = \infty$ , then

$$\mu = \bar{x} \pm C_n \cdot \frac{\sigma}{\sqrt{n}}$$

$$= \bar{x} \pm 1.96 \frac{\sigma}{\sqrt{n}} \text{ for 95\% confidence}$$

$$\text{and } \mu = \bar{x} \pm 2.58 \frac{\sigma}{\sqrt{n}} \text{ for 99\% confidence}$$

**Precision of the mean :** for mean  $\bar{x}$  of  $n$  measurements, the population mean  $\mu$  lies within the limits

$$= \bar{x} \pm 1.96 \frac{\sigma}{\sqrt{x}} \text{ for 95\% confidence}$$

$$\text{and } \mu = \bar{x} \pm 2.58 \frac{\sigma}{\sqrt{n}} \text{ for 99\% confidence}$$

It is possible to calculate a confidence interval from the range 'R' of a series of measurements using the relationship.

$$\mu = \bar{x} \pm C_n R$$

[ where 'R' is range that is difference between maximum value and minimum value.

Example Range (R) of : 26.28, 26.33, 26.36, 26.24

$$R = 26.36 - 26.24 = 0.12.]$$

Values of  $C_n$  for various number of observations are based upon estimates of 's' obtained from the range.

Table : - 3.3

Some values of  $C_n$  for calculating confidence intervals from the range.

No. of observations	Probability	Levels
	95%	99%
2	6.353	31.828
3	1.304	3.008
4	0.717	1.316
5	0.507	0.843
6	0.399	0.628

### Precision of Standard Deviation:

To obtain a measure of the precision of a standard deviation, we calculate a value 'q'

$$q = \sqrt{\frac{s^2(n-1)}{n}} = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n}}$$

**Example :** Ten replicate measurements of nitrogen in soil samples gave a mean of 0.1362% with a standard deviation of 0.0072%. Calculate the 95% confidence interval of the mean and the standard deviation.

Answer : Degrees of freedom = 9

t value for 95% = 2.262 (from table)

(t-value will be given along with the question during examination).

$$\bar{x} = 0.1362$$

$$s = 0.0072$$

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

The 95% confidence interval of the mean

$$= 0.1362 \pm 2.262 \times \frac{0.0072}{\sqrt{10}}$$

$$= 0.1414 \text{ to } 0.1311$$

For standard deviation :  $q = \frac{\sqrt{s^2(n-1)}}{n}$

$$q = \sqrt{\frac{(0.0072)^2 \cdot 9}{10}} = 0.0068$$

The 95% confidence interval for the standard deviation.

$$= 0.0072 - (0.66 \times q) \text{ and } + (1.77 \times q)$$

The values 0.66 and 1.77 are the values to be used with q for n degrees of freedom for various levels of the highest density regions. (Whenever necessary such values will be given in the question paper)

$$= 0.0072 - (0.66 \times 0.0068) \text{ or}$$

$$= 0.0072 + (1.77 \times 0.0068)$$

$$= 0.0027 \text{ to } 0.0192$$

#### Criteria for rejection of an observation :

When one of the results in a set of replicate measurements seems to be out of line with others. Then one must be able to decide whether to exclude this result from further consideration or not.

The frequency will be lessened with experience and practice.

It is not correct to reject results which were subject to known errors when they appear to be not in agreement with others. The only way to avoid unconscious introduction of bias into the measurements is to reject every result where an error was known to be made regardless of its agreement with others.

When the number of replicate values is large, the question of rejecting one value is not an important one. Since first, a single value will have only a small effect upon the mean and second, statistical considerations give a clear answer regarding the probability that the suspected result is a member of the same population as others.

The real dilemma arises when the number of replicate measurements is too small. The divergent result exerts a significant effect on the mean.

But there will be insufficient data to present real statistical analysis.

However, the question of rejecting or retaining one divergent value from a small sample really cannot satisfactorily be answered.

It is to be just decided, how large the difference between the suspected result and the other data before the result is to be rejected (discarded).

If the minimum difference is made too small, valid data may be rejected too frequently.- This is an error of first kind.

On the other hand setting minimum difference too high leads to errors of second kind, that is too frequent retention of highly erroneous values.

## Test for Significance :

### (i) Comparison of two means :

Suppose that a sample is analysed by two methods each being repeated several times and the mean values are different from each other. In such circumstances statistics cannot say which one is the right value.

It can only say whether the difference between the two values is significant or not. The statistical approach to this problem is so called **null hypothesis**.

This hypothesis states in the present case that the two means are identical.

The test 't' gives yes or no answer to the correctness of null hypothesis with a certain confidence such as 95% or 99%.

### Explanation :

Suppose a sample has been analysed by two different methods, yielding means  $\bar{x}_1$  and  $\bar{x}_2$  and standard deviations  $s_1$  and  $s_2$ ,  $n_1$  and  $n_2$  are the number of individual results obtained by two methods.

The first step is to calculate 't' value using the formula.

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{s} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

Treating  $s_1$  and  $s_2$  as same which will be tested later.

Then we have to go to table for 't' values at a degree of freedom ( $n_1 + n_2 - 2$ ) and at desired probability level.

If the value of 't' in the table is greater than the calculated 't' from the data, the null hypothesis is substantiated i.e.  $\bar{x}_1$  and  $\bar{x}_2$  are same with certain probability.

If 't' value in table is less than the calculated 't', we can say that null hypothesis **is incorrect**.

## ii) Comparison of two standard deviations :

'F' test : (named after R.A. Fisher)

If  $s_1$  and  $s_2$  are really different, much more complicated procedure is to be used.

A test is available for deciding whether the difference between  $s_1$  and  $s_2$  is significant or not.

This is the variance-ratio test or F test. The procedure involves calculation of ratio of  $s_1^2$  and  $s_2^2$ .

i.e.  $F = \frac{s_1^2}{s_2^2} = \frac{v_1}{v_2}$   $v_1$  and  $v_2$  are variances placing the larger 's' value in the numerator such that  $F > 1$ ,

then go to table of F values.

If the F value in table is less than the calculated F value then the two standard deviations are significantly different, otherwise they are not.

Table - 3.4 F Values at the 95% probability level.

n-1 for Smaller $s^2$	n-1 For Larger $s^2$					
	3	4	5	6	10	20
3	9.28	9.12	9.01	8.94	8.79	8.66
4	6.59	6.39	6.26	6.16	5.96	5.80
5	5.41	5.19	5.05	4.95	4.74	4.56
6	4.76	4.53	4.39	4.28	4.06	3.87
10	3.71	3.48	3.33	3.22	2.98	2.77
20	3.10	2.87	2.71	2.60	2.35	2.12

### Q - test :

Suggested by Dean and Dixon - is satisfactorily correct and is very easy to apply.

When Q test calls for rejection, confidence is high (90%) that the suspected result was indeed subject to some special error.

Using the Q-test for rejection, errors of the first kind are highly unlikely.

However, when applied to small sets of data (say 3 to 5 results), the Q-test allows rejection of only results that deviate widely and frequently lead to errors of second kind. (Retention of erroneous results)

Thus Q test provides excellent justification for the rejection of grossly erroneous values, but it does not eliminate the dilemma with suspicious but less deviant values.

### The Q-test is applied as follows :

1. Calculate the range of the results



2. Find the difference between the suspected result and its nearest neighbor.
3. Divide the difference obtained in step 2 by the range from step 1 to obtain the rejection quotient, Q.
4. Consult a table of Q-values. If the computed value of Q is greater than the value in the table, the result can be discarded with 90% confidence that it was indeed subject to some factor which did not operate on the other results.

Some Q - values are given in Table 3.5

**TABLE - 3.5 Values of Rejection Quotient, Q**  
**NUMBER OF**  
**OBSERVATIONS**

	Q <sub>0.90</sub>
3	0.90
4	0.76
5	0.64
6	0.56
7	0.51
8	0.47
9	0.44
10	0.41

The following example illustrates application of the Q-test.

**EXAMPLE :** Five determinations for calculating the normality of solution gave the following results : 0.318, 0.319, 0.330, 0.315 and 0.320. Apply the Q-test to see if the 0.330 value can be discarded

The value of Q is

$$Q = \frac{0.330 - 0.320}{0.330 - 0.315}$$

$$Q = 0.67$$

The value of Q in Table - 3.5 at n = 5, is 0.64. Since 0.67 > 0.64, the rule says that the result can be discarded that is the value 0.330 can be safely discarded.

### Control chart :

A control chart is a sequential plot of some quality characteristics. It is developed as a system for keeping track of quality during large scale operations. Especially it is useful as individual inspection of each item is not possible and in some cases the quality test is destructive and hence cannot be applied for each specimen produced by a company. Under such circumstances some sort of spot checking of a few samples coming out of the production line is essential and decision is to be made whether the production process is under control or not.

The control chart method is also useful in monitoring of performance of analytical methods in laboratories where the same types of samples are analysed continuously day after day over long periods of time. The control chart method helps to ascertain with a high degree of efficiency, definite trends or periodically recurring anomalies from random fluctuations.

Let us suppose the company manufactures some material. As a part of quality control programme, the analytical laboratory performs each day a certain analyses on samples coming out of the plant for any parameter like percent moisture. Mass of the sample etc., can be taken for the purpose of ascertaining the quality of the material.

The control limits can be assigned with the following formulae :

$$\text{Upper/lower control limit} = \mu \pm \frac{3\sigma}{\sqrt{n}}$$

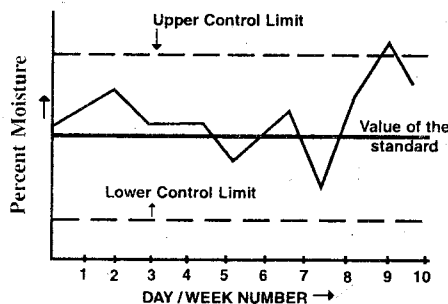
where  $\mu$  = population mean

$\sigma$  = population standard deviation

n = no. of replicates

The plant/company could also use a control chart method based upon the laboratory reports for monitoring the quality of the products. The percent moisture in the standard sample is indicated on the chart by horizontal line. The standard sample is analysed every day and the average of weekly result(s) what ever may be the case is plotted on the chart.

**Figure : 3.11 CONTROL CHART**



The control limits, shown above and below the standard values are designated to have a reasonable tolerance either in the product or the method selected for estimation of a particular component. As long as the results fall within the limits we can safely say the product/method is under control.

Any point that is falling above and below the boundary control limits on either sides indicate that the product/method failed at that point and gives a clue to the concerned authorities to check the flow. Parallel control charts using range, standard deviation etc. may be employed to help the laboratory personal to keep track of the precision of an analytical method.

### Propagation of Errors :

Precision and Accuracy are essential things in analytical measurements however it is the duty of the scientist to know how the errors in individual systems are propagated into the final result. The study of propagation of errors can be considered in case of both the determinate errors and indeterminate errors.

**Determinate errors :** Let us consider a computed result 'R' based upon the measured quantities A, B and C. Let  $\alpha$ ,  $\beta$  and  $\gamma$  represent the absolute determinate errors in case of A, B and C respectively. Let 'r' represent the maximum resulting error in 'R'. Let us see how errors are transmitted through addition and subtraction supposing that

$$R = A + B - C$$

on changing each quantity by amounts of its error we can write

$$R + \rho = (A + \alpha) + (B + \beta) - (C + \gamma) \text{ or}$$

$$R + \rho = (A + B - C) + (\alpha + \beta - \gamma)$$

On the other hand subtracting

$$R = A + B - C \text{ gives } \rho = \alpha + \beta - \gamma$$

On the other hand suppose the multiplication and division are involved that is let

$$R = \frac{AB}{C}$$

Substituting the appropriate errors

$$R + \rho = \frac{(A + \alpha)(B + \beta)}{(C - \gamma)} = \frac{AB + \alpha B + \beta A + \alpha \beta}{(C - \gamma)}$$

The term  $\alpha\beta$  can be neglected because it is going to be too small when compared with the measured values.

Then subtracting  $R = \frac{AB}{C}$  gives

$$\rho = \frac{AB + \alpha B + \beta A}{(C - \gamma)} - \frac{AB}{C}$$

taking L.C.M.

$$\rho = \frac{\alpha BC + \beta AC - \gamma AB}{C(C - \gamma)}$$

The relative error in the case that is  $\rho/R$  leads to

$$\frac{\rho}{R} = \frac{\alpha BC + \beta AC - \gamma AB}{AB(C - \gamma)}$$

Since ' $\gamma$ ' is very small when compared with ' $C$ ' the denominator on right hand side reduces to  $ABC$  and return

$\rho/R$  takes the following form

$$\frac{\rho}{R} = \frac{\alpha}{A} + \frac{\beta}{B} - \frac{\gamma}{C}$$

Then it can be concluded that the determinate errors are propagated as follows.

01. The absolute determinate errors are transmitted directly into the result, where addition (or) subtraction are involved.
02. The relative determinate errors are transmitted directly into the results where multiplication or division is involved.

### Indeterminate errors :

Indeterminate errors are manifested by a scatter in the data when a measurement is performed more than once. In considering the propagation of indeterminate errors it is to be examined how scatter in measurement of quantities A, B, C etc., is translated into random variation in the final result R.

Let us consider  $R = A + B - C$  and  $R = AB/C$

The result of the statistical theory leads to the following conclusions

1. The variance (square of standard deviations) of the measured values are additive in case of addition or subtraction that is

$$R = A + B - C, \quad S_R^2 = S_A^2 + S_B^2 + S_C^2$$

2. In case of multiplication (or) division, the squares of the relative standard deviations are transmitted i.e.

$$\text{for } R = \frac{AB}{C}$$

$$\text{i.e. } \left(\frac{S_R}{R}\right)^2 = \left(\frac{S_A}{A}\right)^2 + \left(\frac{S_B}{B}\right)^2 + \left(\frac{S_C}{C}\right)^2$$

### Regression Analysis :

In the analysis of data it is often desirable to determine whether two variable quantities are interdependent and express their relation quantitatively.

Let us constrain for linear relation. If two variables are proportional then a linear plot should have an intercept of zero and a log-log plot of one against the other must yield a straight line with a slope of unity.

Regression methods can be used when the dependence treated has regression character, that is when independent variable 'x' is known precisely, only the dependent variable 'y' is subject to an error. Thus a functional relationship is sort between the mean values of variables 'y' and 'x'. Generally the variable that is subject to a large error is selected as dependent. If the error of the dependent variable have normal distribution, the least square method can be used.

If the two variables x and y are related, one of the following two different situations may be recognised.

1. Both variables are subject to comparable experimental error.
2. One variable may be regarded as being determinable to so high degree of precision that its uncertainty can be ignored. The second is more frequently encountered in analytical chemistry.

Usually we are interested in determining whether a statistically significant trend in result exist with some variable (temperature, pH (or) sample size) that exerts only a small effect and therefore can be fixed as accurately needed.

Let us assume that the data fit the equation  $y = mx + c$  where 'x' is the concentration of standard solution and 'y' is the measured property of it. 'm' is the slope of the straight line and 'c' its intercept on the Y-axis (ordinate).

When values of 'm' and 'c' have been determined the proper straight line has been established and it can be drawn through the points. It can be shown statistically that the best straight line through the series of experimental points is that line for which the sum of the squares of the deviations of the points from the value on the line (S) is a minimum. This is known as **Method of Least Squares**. If  $x_e$  and  $y_e$  are the experimental data (co-ordinates) and  $y_e^*$  (expected value) is the value of 'y' on the straight line for the parameter  $x_e$ , then the expression for method of least squares can be written as

$S = \sum_e (y_e - y_e^*)^2$  substituting  $(mx_e + C)$  for the expected value  $y_e^*$  yields.

$$S = \sum_{e=1}^n [y_e - (mx_e + c)]^2 \dots\dots\dots(1)$$

And the best straight line occurs when 'S' is a minimum. By applying differential calculus to this it can be shown that 'S' is a minimum when -

$$m = \frac{\sum (x_e - \bar{x})(y_e - \bar{y})}{\sum (x_e - \bar{x})^2} \dots (2)$$

$$c = (\bar{y} - m\bar{x}) \text{, which is nothing but } y = mx + c, (3)$$

where

n = no. of points,

$\bar{x}$  = is the average of all the values of  $x_e$ .

$\bar{y}$  = average of all the values of  $y_e$ .

To illustrate let us take the following data pertaining to the determination of metal concentration by spectrophotometry.

Table - 3.6

Concentration of metal	Absorbance	$(x_e - \bar{x})(y_e - \bar{y})$	$(x_e - \bar{x})^2$
$(x_e)\mu\text{g/ml}$	$y_e$		
0.0000	0.0000	3.2500	32.215
1.1126	0.132	2.0078	20.823
3.3360	0.346	0.5302	5.475
5.5630	0.594	0.0024	0.012
7.7888	0.786	0.4521	4.464
10.0130	1.005	1.8757	18.818
Ave.	Ave :	Sum = 8.1182	Sum = 91.807
$\bar{x}_e = 5.67592$	$\bar{y}_e = 0.5725$		

$$m = \frac{8.1182}{91.807} = 0.08842$$

$$y = mx + c$$

$$c = 0.5725 - (0.8842)(5.6759)$$

$$= 0.5725 - 0.5017$$

$$c = 0.0708$$

The average  $\bar{x}$  of the values  $x_e$  (concentration of metal) is  $5.67592 \mu\text{g/ml}$  and the average  $\bar{y}$  of the values of  $y_e$  (absorbance) is  $0.5725$ . The above table also indicates the squares of the deviations of  $x_e$  and their sum, and product of the deviations of  $x_e$  times the deviation  $y_e$  and their sum

Thus from the equation .....(2)

$$m = \frac{\sum (x_e - \bar{x})(y_e - \bar{y})}{\sum (x_e - \bar{x})^2} \text{ and equation .... (3)}$$

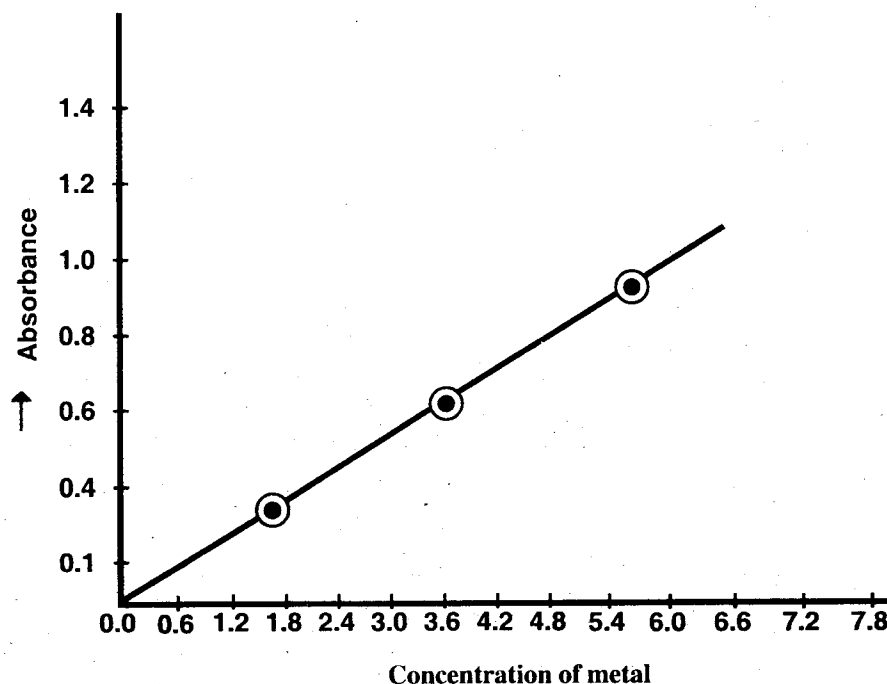
$$c = (\bar{y} - m\bar{x})$$

giving for the equation of the line through these data points  $y = mx + c$ ,

$$y = 0.8842x + 0.0708$$

The fig. - 3.12 shows the plot of data and the line drawn through them according to the above equation.

**Significant figures and Computation Rules :**



**Significant Figures :**

The use of significant figures procedure will be helpful in making a crude estimate of uncertainty involved in the final result. It is less laborious than the calculation of actual uncertainties particularly those based on determinate errors. The principal disadvantage is that only rough estimate of uncertainty is attained.

The term significant figures can be defined as follows :

“All digits that are certain plus one, which contain some uncertainties are said to be significant figures”.

The general rule used in chemistry, states that the last digit of a number and only the last digit of the number has any uncertainty in it. All of the other digits in the number contain no uncertainty.

For example the mass of an object is measured on a rough balance which can measure to the nearest of 0.1 g. If the weight of the object is found to be 64.2 g, the 6 and 4 are known exactly (certain figures) but '2' is uncertain figure. If the value of 64.2 g is written without specifying the magnitude of uncertainty. It is evident that the limits of errors are  $\pm 0.1$  in the last digit, so that the value is  $64.2 \pm 0.1$  g. The same object is weighed on an analytical balance 64.2164g, the uncertainty is understood to be  $\pm 0.0001$  gms (here also the last figure '4' is uncertain). In analytical calculation the following examples explain the importance of significant figures.

A significant figure is a digit which has some practical meaning. For example in case of number 643, the figure signifies that there are '6' hundreds, 4 tens and 3-units and therefore all of them are significant. For example the numbers 0.643, 6.43 and 643 all contain three significant figures but if these values have been obtained through multiplication and (or) division of measured quantities, the values 6 and 4 are reasonably certain while '3' is an uncertain value. The character 'zero' may (or) may not be a significant figure. Zero is not a significant figure when it is used to locate a decimal point. While it is a significant figure when it indicates that the quantity in the place in which it stands is known to be nearer zero than to any other value.

For example in the number 0.05300 the zero's to the left of the digit 5 are not significant since they are used only to locate the decimal point. But the zero's beyond the digit 5 are significant. In other words the number 0.05300 contains '4' significant figures. In another measurement the weight of the residue after digestion is found to be 0.00002 g, here zero's are not significant because they serve only to locate the decimal point.

\* \* \*

## UNIT - IV

### LESSON – 1

#### ELEMENTS OF COMPUTER PROGRAMMING

##### 4.1 (i) INTRODUCTION:

The computer is a digital electronic calculating device, which can accept data, process this data and display the output.

Computers have become very common in our daily life. Computers have a wide range of uses and play an effective role in our society.

Computers are sophisticated calculating devices which are capable of performing a large number of mathematical operations in a short time. Today computers are used in various applications such as weather forecasting, controlling robots and issuing tickets. They are used media publications. They help in diagnosing diseases. They are used to find documents in archives. Companies use them for accounting, invoicing, stock control and payroll, billing. They are used by architects to design buildings, dams, monuments and various structures.

The computer is changing many aspects of the sciences, and chemistry is no exception from the general revolution that is now underway. To the modern chemist, a user's knowledge of the capabilities of the high-speed digital computer is rapidly becoming indispensable.

Computers are used in a great variety of ways.

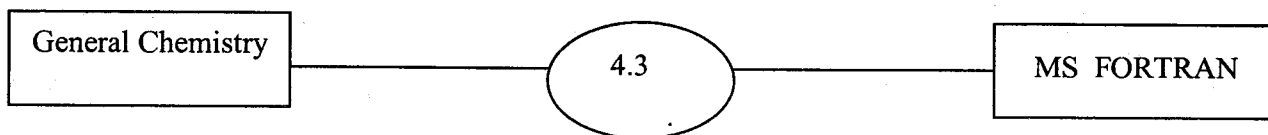
1. Computers can routinely and conveniently perform numerical calculations more rapidly and accurately than if performed by hand. ( A third generation computer of the IBM 370 class can perform approximately the equivalent of a person-life of calculations every 15 minutes, and more advanced computers are even faster.)
2. Computers can produce answers that would be useless if the time for hand calculations were required. (For example, the necessary calculations for correcting the trajectory of a spacecraft must usually be accomplished within a limited time. By the time a hand calculation could be done the answer might be only academic.)



3. Certain types of experiments may be optimized or simulated by computer calculations. (For example, knowledge of the functionality of the variable involved will often allow a computer simulation of a plant process. From such simulations the model may be optimized and the optimum plant constructed without a costly trial-and-error process of development.)
4. Computers are routinely used for information storage and the retrieval, organization, management, and presentation of large data banks. (Thousands of spectra may be searched and compared to that of an unknown, for example. The 10 nearest matches might then be presented. Such operations may be accomplished in a matter of seconds or minutes with a portion of the computer's various memory devices acting as a permanent file for all the library data.)
5. Computers can be used to gather data from experiments as produced (in real time), and they can often be incorporated into experimental apparatus so that they direct the experiment. For example, computerized X-ray diffractometers are sufficiently automatic to collect data for many days unattended.
6. Computers can be programmed to display intelligence by learning to perform tasks while improving their success as their experience increases. (Some advocates of machine intelligence go so far as to say that computers are essentially a new life form with nearly limitless possibilities.)

#### 4.1 (ii) COMPUTER APPLICATIONS

**Business Applications:** Business applications involve repetitive routines and handling of large volumes of data, computers have created a great impact on business. In an office environment, preparation of reports, documents require comprehensive editing and several revisions to be done repetitively.



**Scientific Applications:** Today a computer has become a basic necessity for any scientific establishment. There are worldwide networks linking universities and research & development Laboratories.

**Medical Applications:** Computers are used for planning and control purposes by Doctors. They are used for treatment planning and monitoring patient in hospitals. Medical diagnosis is another area, which has greatly benefited by the advent of computers. Computers are also used in more traditional information handling areas such as patient management, inventory management and billing.

**Engineering Applications:** Engineers design a circuit, later analyse the same report on defects such as unconnected components by using computers. Architects are coming to rely heavily on the computers ability to show possible design, décor patterns, simulate landscapes to help their clients judge other wise unimaginable visual appeal. Computers, which help design engineers to design a new component, like a gear, and then drive a set of CNC.

**Education Applications:** Computers, when used in the field of education lead to improved student performance in thinking logically and in problem solving to the extent of affording high school physics students, the use of a program that simulates moon landing! Gravity and Newton's Laws of motion.

In short, computers are now an integral part of modern life. As we have seen there are very few areas of human endeavour untouched by computers.

#### 4.1 (iii) CAPABILITIES OF A COMPUTER

**Speed:** Computers can perform arithmetic calculations and logical comparisons at an incredible speed with remarkable accuracy. The processing speed of a computer is generally measured in nanoseconds.

**Storage:** Computers have a large storage capacity. We could store say the contents of around two hundred sheets of paper, on a medium which is not even half the size of one sheet of paper. What would typically take large storage cabinets can be comfortably stored in a storage device of the size of the lunch box.

**Accuracy:** The accuracy of computers is consistently high. Errors in computing are generally due to human negligence.

**Diligence:** Computers, being machines, do not suffer from concentration. If five million calculations have to be performed, a computer would perform the five millionth calculations with the same speed as the first.

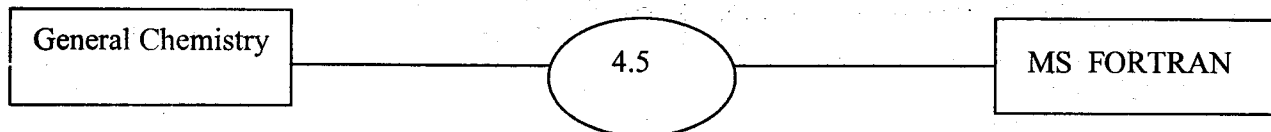
**Versatility:** A major strength of computers is that they can do a very wide range of jobs, both related and unrelated –with speed, accuracy and diligence.

#### LIMITATIONS OF COMPUTERS

**Lack of commonsense:** The computer is only a tool. It cannot think. It does not have commonsense or intelligence as we all have.

**Inability to correct:** When we give instructions to a computer we must give the correct instructions. A computer cannot correct wrong instructions. This follows from the fact that a computer cannot use its brain because it does not have one!.

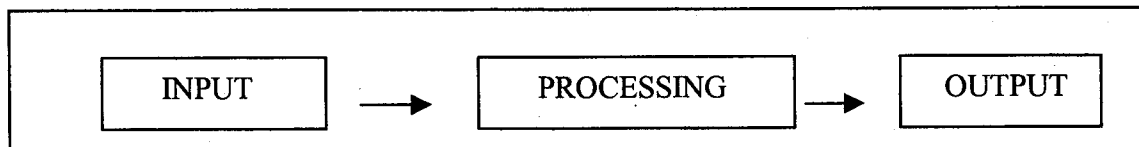
**Dependence on human instructions:** A computer cannot generate any information on its own. It can only do what it is told to do.



#### 4.1 (iv) Basic components of computers

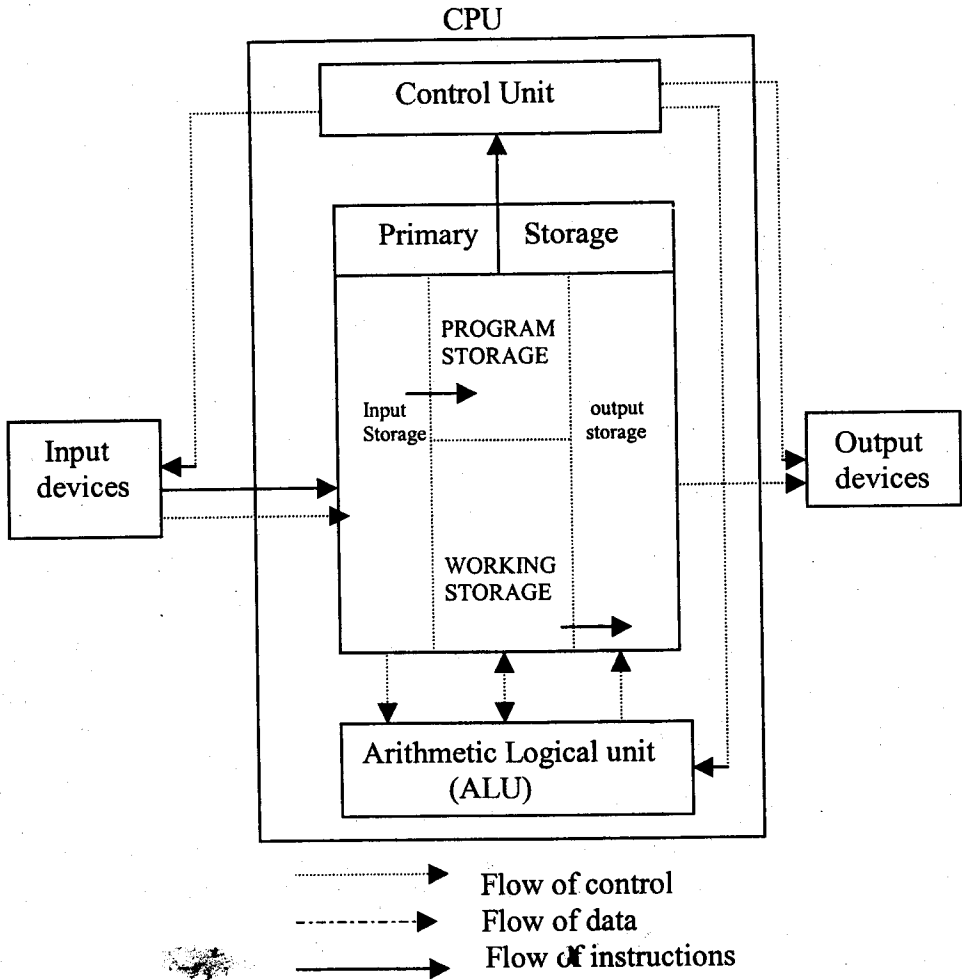
- The various components of a computer or PC are monitor, Keyboard, Printer, hard disc etc.
- The unit that resembles a TV screen is called the monitor, or more commonly, the VDU, an abbreviation of Visual Display Unit.
- The component that closely resembles a typewriter is called the Keyboard.
- The boxlike structure on which the VDU usually rests is called the system unit.
- The printer, as the name suggests, is used to print the results of any operation.
- The tiny device connected to the system unit through a cord resembling a tail is called a mouse. The movement of mouse produces a corresponding movement of an arrowhead on the monitor.
- All these devices collectively referred as hardware of PC.

#### Basic principles of computer



A computer can be accept data, process it and display, print the results. This forms the 'input', based on which the computer will perform some 'process' and 'output' the result. This Input-Output (I/O) cycle is an essential concept for understanding the working of any computerized system.

4.1 (v) ORGANISATION OF COMPUTER



The computer can be treated as a system, consists of various sub systems. The functional components of a computer are

1. Input Devices.
2. Central Processing Unit (CPU)
3. Output Devices

**INPUT DEVICES:** The devices, which are used to input the data into system are called input devices. Process of entering data and instructions (Program) into the computer system is called input. The common input devices are Floppy Drive, Key Board, Magnetic Disk Drive, etc.

**CPU:** The processes like calculations, logical comparisons controlling the operations are all made in the unit called Central Processing Unit.

1. Memory Unit
2. Control Unit
3. Arithmetic and Logic unit (ALU)

**MEMORY:** The storage area where data and instructions stored is called memory. The different types of memories are

- i) **INPUT STORAGE AREA:** The area in which input data is held until it is ready to processed.
- ii) **WORKING STORAGE AREA:** The area that holds the data being processed and the intermediate results.
- iii) **OUTPUT STORAGE AREA:** This is where finished results (output) are held until released to the output devices.
- iv) **PROGRAM STORAGE AREA:** While the above three areas are data related storage areas, the program storage area holds the processing instructions.

**CONTROL UNIT:** This is the central nervous system of the computer. It controls maintains order and directs the operations of the entire system. During execution they are transferred one by one to the control unit for execution.

**ARITHMETIC LOGIC UNIT:** The ALU performs all the arithmetic and logical operations on data selected from memory; i.e. it performs addition, subtraction, division, multiplication and

logical comparisons (such as  $A > B$ ) on the data sent to it from the memory. The ALU contains one or more storage locations called registers. The registers provide temporary storage for one or both of the operands that take part in the arithmetic or logical operations. Generally, the result is also produced in a register.

**OUTPUT:** The results of that data which is processed is called output. The output devices are instruments of communication between the user and the computer system. These devices are used to output results from CPU. The common output device is a printer, which prints the result on paper. Other output devices are magnetic tape drive, Magnetic disk drive, floppy disk drive, plotter, Visual display unit (VDU), etc.

#### 4.1 (vi) CLASSIFICATION OF COMPUTERS

The classification of computers, based on the type of data, is as follows:

1. Digital Computers
2. Analog Computers
3. Hybrid Computers

##### 1. DIGITAL COMPUTERS:

These computers operate on discrete data and are commonly used in business applications.

##### 2. ANALOG COMPUTERS:

This type of computer works on continuous data measured along a continuous scale. For example, a speedometer is a mechanical device that works on continuous data. Analog computers are commonly used in process control systems, which monitor pressure, temperature, flow, etc.

### 3. HYBRID COMPUTERS:

This type of computer has the properties of both analog and digital computers. A typical example is found in medicine, where analog properties are used to record the patient's data, while digital properties help in the analysis of the data as well as in monitoring the patient's health. Computers are also classified on the basis of their physical size, memory and processing speeds. Five of these categories are described below.

1. **MICROCOMPUTERS:** Microcomputers are systems based on the use of microprocessors. A microprocessor is a programmable large-scale integrated circuit chip containing all the elements required to process binary encoded data. In simpler terms, a microcomputer performs all arithmetic and logical functions of a computer. Quite often microcomputers are also called personal computers (PCs)
2. **MINICOMPUTER:** These systems are more powerful than microcomputers and are also more expensive. The word length is generally 16 bits or more. The processing speed of a computer is often measured in terms of MIPS, i.e. millions of instructions per second. These computers have a processing power of the order of 1.5 MIPS.
3. **MAINFRAME COMPUTERS:** These are machines with word lengths of 32 bits or more. The processing speed is of the order of 10 MIPS. These computers support a large main memory. In the time-sharing mode, due to fast processing speeds, they can support hundreds of terminals.
4. **SUPER COMPUTERS:** Super computers are the fastest computers and can be used to solve a wide range of large-scale problems, which require extensive numeric computations like complex molecular structural analysis, weather forecasting, etc. The processing speeds are of the order of 100 MIPS. These machines have word lengths of 64 bits or more.



**Short Answer Questions:**

1. Explain the basic components of a computer?
2. What is the difference between a Micro and a Mainframe computer?
3. List the capabilities of a computer?
4. Discuss briefly the computer Applications?

**Long Answer Questions:**

5. Draw a block diagram of a computer and discuss briefly the organization of computer briefly?

## LESSON - 2

### MS- FORTRAN

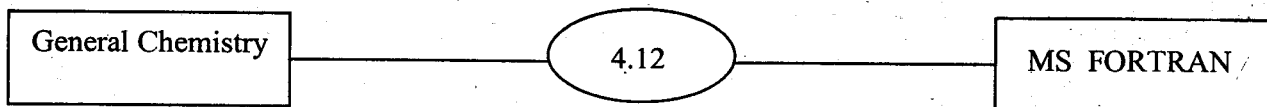
FORTRAN stands for **FOR**mula **TRAN**slation. This is the high level language used for most scientific and engineering calculations. Programs written using this language are called FORTRAN programs. FORTRAN language should not depend on a particular computer. We will emphasize in the examples the FORTRAN implementation on IBMPC computers called MS-FORTRAN 77.

#### 4.2.(i) Flow Charts

Certain amounts of planning is necessary before any problem is attempted. This planning is necessary whether it is a problem in mathematics or an everyday problem like shopping trip, one has to prepare a list of items to be purchased, the order in which various shops are to be visited, allocate time and money, etc., Most of this planning is done unconsciously. When a problem is to be solved on a computer, it is essential to work out in detail all the steps in the solution procedure and the order in which these steps are to be carried out. This step procedure to solve a problem is known as an **algorithm**.

The formulations of algorithms is aided by the use of **Flow Charts**. A Flow Chart is a picture which shows the sequence in which data are read, computing is performed, decisions are made and results are obtained.

Flow Charts are useful both for planning the solution to a problem and for documenting the method used. For each fundamental work there are certain standard symbols. Some flow chart symbol are shown in following figure.



Rectangle with rounded edges



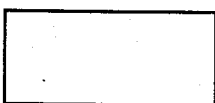
**Start / Stop**

Parallelogram



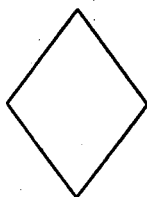
**Input / Output**

Rectangle



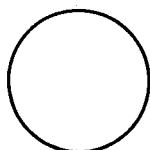
**Processing Box**

Diamond shaped Box



**Decision Box**

Circle



**Connector Symbol**

- In above symbols **Rectangle with rounded edges** is used to depict **START** and **STOP** operations in flow chart.
- **Parallelogram** is used to depict the operations of **READ** and **WRITE** ( **INPUT** and **OUTPUT** ) of data.
- **Rectangle** is used for computations and **Diamond Box** is used to show a comparison.
- **Circle** symbol is used as a connector .

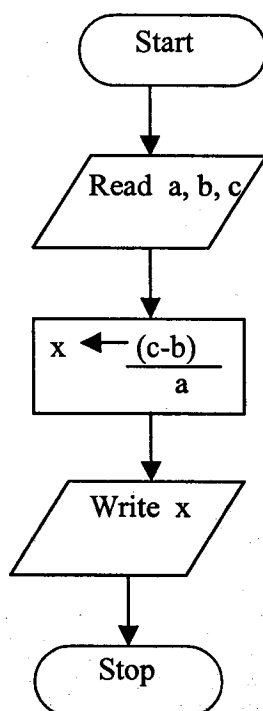
In development of a flow chart, all the symbols which are utilized must be connected with arrow symbol ( $\rightarrow$ )

**Example 1:**

To solve the equation  $ax + b = c$  ( $a \neq 0$ ), the steps in the solution are

1. Start
2. Read the values of  $a, b, c$
3. compute  $(c - b) / a$  and set  $x = (c - b) / a$
4. write the value of  $x$
5. Stop

These steps are pictorially depicted as the flow chart of Fig. 4.1



**Fig. 4.1** Flow chart for solving an equation  $ax + b = c$

If  $a \neq 0$ , there is no solution for the above equation. Then the modified algorithm is

1. Start
2. Read the values of  $a, b, c$
3. If  $a = 0$  write "Incorrect equation, No solution" and Stop
4.  $x \leftarrow (c - b) / a$
5. stop

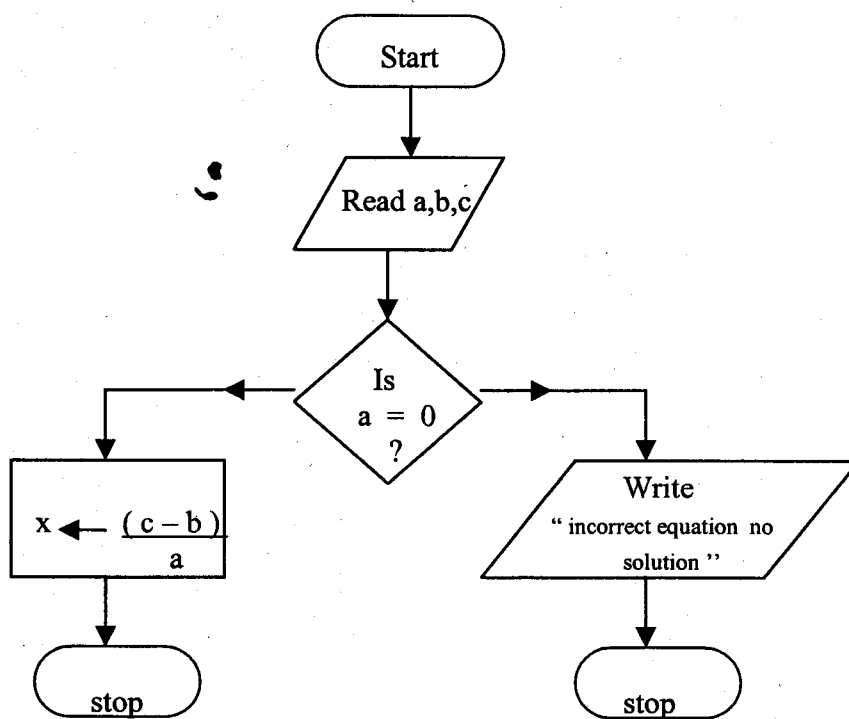
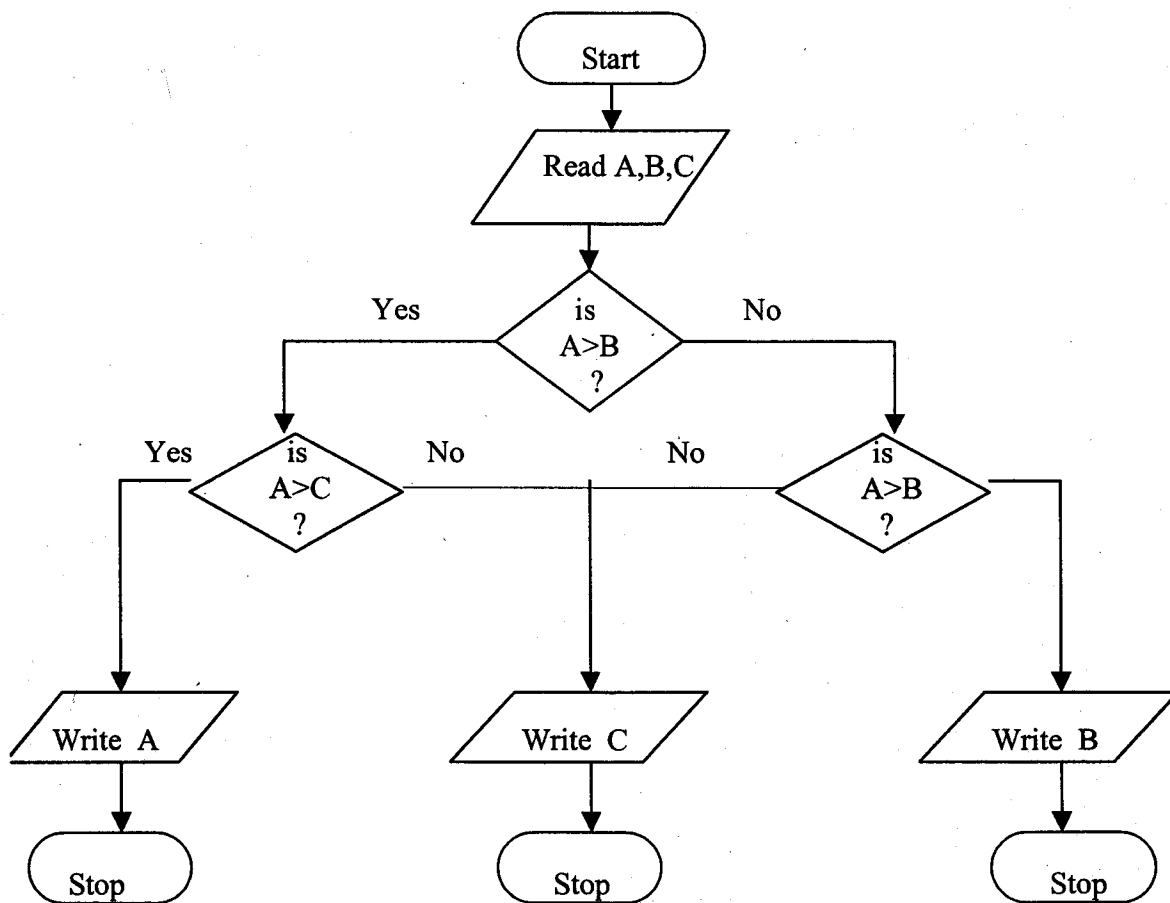


Fig 4.2 Flow Chart for solving the an equation  $ax + b = c$ , where  $a = 0$

**Example 1: Flow Chart to pick the largest of three numbers****4.2.(ii) Characters used in FORTRAN**

The following are the set of allowed characters in FORTRAN

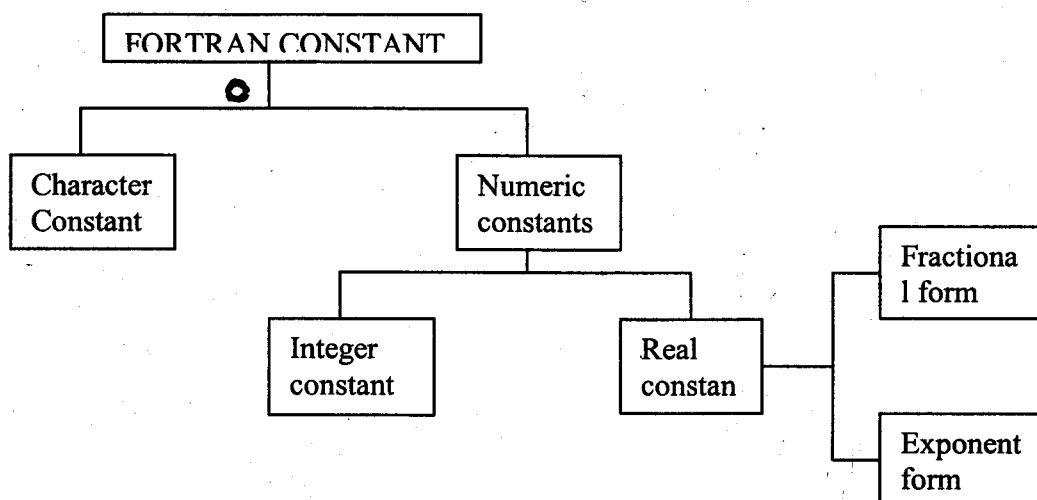
**Capital alphabets** : A B C D E F G H I J K L M N O P Q R S T U V W X Y Z

**Digits** : 0 1 2 3 4 5 6 7 8 9

**Symbols** : + - / \* . \$ , = ' ( )

**4.2.(iii) Constants in FORTRAN :**

A number on a string of FORTRAN characters are called constant. Numbers are called Numeric constants. A string of characters is called a character constant.



**4.2.(iv) Integer Constant :**

Integer Constants are whole numbers without any fractional part. The following rule define a Integer constant.

1. An integer constant is formed with digits. It must be written without a decimal point. It may have either + or - sign. If no Sign precedes the constant, it is assumed to be +ve.

Examples: Valid Integer constants

- (1) 1234
- (2) +123
- (3) -985

Invalid Integer constants

- (1) 123.4
- (2) + - 123
- (3) .985
- (4) 1,234

The maximum length of the integer depends upon the word length of the computer. For IBM pc the range of Integer constant is  $\pm 32767$

**4.2.(v) Real Constants:** A real constant is a string of digits which includes a decimal point.

A real constant can be expressed in any one of the following two forms

- i) Fractional form
- ii) Exponential form

The following rules apply for the real constants in **Fractional form**.

- 1) A real constant is written in the decimal form with the digits 0,1,2,.....9 and the decimal point.
- 2) There should be only one decimal point. It may have either sign + or - . If there is no sign, the numbers is assumed to be positive.
- 3) No special symbols such as \*, etc are allowed in a real constant.

Examples: Valid Fractional form constants

- 1) 1.00
- 2) -12222.
- 3)12345.67
- 4) +12345.67

Invalid fractional form constant

- 1) 1
- 2) -12222
- 3)1,2345.67
- 4) 12\*345.67

**Exponent form :**

Consider the number 123 000 000 000 00. This constant has 14 digits. This number can be written as  $0.123 \times 10^{14}$ . This is known as exponent form. In this exponent form 0.123 is called the mantissa and 14 is called exponent.

In FORTRAN this number can be written as 0.123E14. The letter E is used in between mantissa and the exponent.



The above same number can be written as  $0.0123 \times 10^{15}$  or  $1.23 \times 10^{13}$ . In Fortran we can write these numbers as 0.0123E15 and 1.23E13 respectively.

The following rules apply to the Exponential form of real constant.

1. The exponential form must have two parts
  - i) Mantissa
  - ii) Exponent
2. The letter E is written in between mantissa and exponent, ie. Mantissa E exponent.
3. The mantissa must be a valid real constant in fractional form. All the rules of the fractional form applied to the mantissa.
4. The exponent must be an integer and can have a sign + or -

Examples :--	Number	mathematical form	FORTRAN form
1.	-117000 000 0000	$-0.117 \times 10^{13}$	-0.117 E 13
2.	0.000 00000001005	$-0.1005 \times 10^{-10}$	-0.1005E -10
3.	0.000 000 516977	$0.516977 \times 10^{-6}$	0.516977 E -6

#### 4.2.(vi) Character Constants :

Character constants are any string of character enclosed within quotes. The only single quote (') must be used and not the double quote (").

Examples:-

Valid	Invalid
1) 'RAMAN'	"RAMAN"
2) ' X VALUE '	"X VALUE"
3) 'COUNT='	"COUNT="

#### 4.2. (vii) FORTRAN Variables :

In FORTRAN a quantity which may vary during program execution is called a variable. Each variable has a specific storage location in memory where its numerical value is stored.

A variable is said to be defined if a number is stored in the storage location identified by the name of the variable.

There are two types of variable names

1. Integer variable

2. Real variable

#### Rules for naming variables:

1. Variable names can be form one to six characters in length.
2. The first character of the variable name must be an alphabet and succeeding characters can be alphabets or numeric digits.
3. No special character is allowed in a variable name.
4. FORTRAN verbs which have special meaning in FORTRAN cannot be used as variable names.

**1. Integer Variable:** An integer variable name is a string of one to six letters or digits. The first character in the name must be one of the following letters, I,J,K,L,M, or N.

Eg:



#### Valid

1. IREG
2. I235
3. K5ABC
4. MIKL2X

#### Invalid

1. AIKM
2. IABC+D
3. I \* BCD
4. K \$,M

**2. Real Variable:-** A real variable name is any combination of one to six letters or digits. The first character must be one of the following letters A,B,C,D,E,F,G,H,O,P,Q,R,S,T,U,V,W,X,Y,Z.

Examples:

<b>Valid</b>	<b>Invalid</b>
1. THETA	1. AB-CD
2. DIG24	2. IAB
3. A123	3. ABC.DOG
4. EINK	4. AB *2

#### 4.2.(viii) Arithmetic Expressions :

An expression in FORTRAN is a series of variables and constants connected by arithmetic operation symbols namely addition, subtraction, multiplication, division and exponentiation.

The following symbols are used to represent arithmetic operations :

<b>FORTRAN operator symbol</b>	<b>Arithmetic operation</b>
+	Addition
-	Subtraction
*	Multiplication
/	Division
**	Exponentiation

Expressions in FORTRAN are classified into two types. i) **Integer Expression**  
ii) **Real Expression**

#### Integer Expressions :

The following rules must be followed to form an Integer expression.

- Rule 1. A signed or unsigned integer variable name or an integer constant is an integer expression. Eg: I, -K, -4, 4
2. An integer expression connected by an arithmetic operator on its right to an unsigned integer variable name or an unsigned integer constant is an integer expression.  
Eg: - IA \* IB , -IA \* IB + IC, IA \* IB + IC/J

3. An integer expression enclosed in paranthesis is an integer expression.

Eg:-  $(-K*I+J)$ ,  $(KAT * MAT /NAT)$ ,  $(MAT * NAT)$

4. Two integer expressions connected by an arithmetic operator is an integer expression.

5. Two arithmetic operators should not occur in succession in an integer expression.

Eg:-  $IA * -IB$  is an invalid expression.

### Real Expressions :

Rules for forming real expressions are identical to those given for forming integer expressions. The rules are obtained by substituting the word Real instead of Integer in all the 5 rules mentioned above.

Examples : for Rule 1. ABE, -ABE, -4.5, 2.2

2.  $-ABE+BAT+A*B$ ,  $ATE *BA/CA$

3.  $(BAT+4.5)$ ,  $(ABE *ALL)$

4.  $ABE * ALL + COUNT + DATE * (ARE*AL)$

5.  $A**-I$  is not valid expression.

The additional rule which is valid for forming real expressions but not for integer expressions is

**Rule 6:** A real variable or constant may be exponentiated by an integer expression.

Eg:  $ABE **I$ ,  $5.2 **K$ ,  $2.5 **2$ ,  $BABE ** (I+J)$

### 4.2. (ix) Hierarchy of Arithmetic operations :

The value of any expression is calculated by executing one arithmetic operation at a time.

The order in which the arithmetic operations are executed in an expression is called the **hierarchy of operations**.

The following are the rules of Hierarchy arithmetic operators in FORTRAN

1. Exponentiation is given the top priority and evaluated first in an expression.
2. Multiplication and Division are given the next priority .
3. Addition and Substraction are performed finally.

### Example

1.  $A ** B / C + D$  in this expression the exponentiation done first, the result is divided by C and then D is added, which is equivalent to

$$\frac{A^B}{C} + D$$

2.  $A ** B / C + D ** E * F - H / P * R + Q$

In first evaluation

$$A^B \quad D^E$$

Second evaluation

$$\frac{A^B}{C} \quad D^E F \quad \frac{H R}{P}$$

Third evaluation

$$\frac{A^B}{C} + D^E F - \frac{H R}{P} + Q$$

**Note :** All the expressions are examined from left to right. All exponentiations are done first. After completion of exponentiations the expression is examined again from left to right; Now all divisions and multiplications are executed. Finally all additions and Substractions are done starting again from left of the expression.

**4.2. (x) Use of Parenthesis :**

Expressions inside the parenthesis are evaluated first. Within the parenthesis the evaluation is governed by the rules of Hierarchy.

- i.e., I) Exponentiation (\*\*) First  
 II) Multiplication (\*) and Division (/) Second  
 III) Addition (+) and Subtraction (-) Last.

Eg:- Consider the expression  $\frac{A+B}{A-B}$ , It is converted into FORTRAN notation as A+B / A-B.

According to Hierarchy the expression evaluated as  $A + \frac{B}{A} - B$ , which is not correct evaluation.

In this case, the use of parenthesis is important to make the correct evaluation i.e., (A+B) / (A-B).

**4.2. (xi) Arithmetic Statements:-**

The FORTRAN arithmetic statement is used to evaluate a valid FORTRAN expression and store the result at a desired variable. The general form of an arithmetic statement is,

**Variable name = Expression.**

This is also known as Assignment Statement.

- Eg: 1)  $I = J + K ** 3$   
 2)  $X = Y + Z$   
 3)  $Z = A + B$

There are four types of arithmetic statements in FORTRAN.

- 1) Integer Variable = Integer expression ( Loss = I+J-K )
- 2) Integer Variable = Real expression ( Loss = A+B-C )
- 3) Real Variable = Integer expression ( ABC = I + J - K )
- 4) Real Variable = Real expression ( ABC = D+E-F )

In an arithmetic statement, the right side expression is evaluated and the result is stored (Assigned) in the memory location of variable, which is present in the left side. So that these statements can also be considered as Assignment Statement.

- Eg:-
1.  $C = A * B + 15.0$
  2.  $K = I - 2 * J + 50.$

#### 4.2(xii) Replacement Statements :-

In these statements the initial value is replaced by the another value.

For example in the statement

$$J = J + 1$$

If the initial value of J is replaced by J + 1, then  $J = J + 1$  is said to be a replacement statement.

Initially Count = 1

Count = Count + 1, then Count = 2

So Count = Count + 1 is said to be a replacement statement

**Exercise :-**

1) Write the FORTRAN expressions corresponding to the following algebraic expressions :

$$\text{i) } \frac{Ax+B}{Ax-B}$$

$$\text{ii) } ax^2 + bx + c$$

$$\text{iii) } \frac{mv^2}{x^2+K^2}$$

2) What is the value of I calculated in the following arithmetic statements ?

$$\text{i) } I = J * 2/3 + K/4 + 6 - J ** 3/8 \quad (J=2, K=5)$$

$$\text{ii) } I = B/2.0 + B * 4.0/A - B + A ** 3 \quad (A = 1.5, B=3)$$

$$\text{iii) } I = J/2 * 4 + 3/8 + J ** 3 \quad (J = 3)$$

$$\text{iv) } I = I + J/K - L \quad (I = 2, J = 2, K = 2, L = 2)$$

$$\text{v) } I = (I + J) / K - L$$

Answers :-

$$1) \text{ i) } (A * X + B) / (A * X - B)$$

$$\text{ii) } A * X * X + 2.0 * B * X + C$$

$$\text{iii) } AM * V * V / (X * X + AK * AK)$$

$$2) \text{ i) } I = 2 * 2/3 + 5/4 + 6 - 2 ** 3/8 = 1 + 1 + 6 - 1 = 7$$

$$\text{ii) } I = 3.0/2.0 + 3.0 * 4.0/1.5 - 3.0 + 1.5 ** 3$$

$$= 1.5 + 8.0 - 3.0 + 3.375$$

$$= 9.875$$

$$I = 9$$

$$\text{iii) } I = 3/2 * 4 + 3/8 + 3 ** 3$$

$$= 4 + 0 + 27 = 31.$$

$$\text{iv) } I = 2 + 2/2 - 2 = 2 + 1 - 2 = 1$$

$$\text{v) } I = (2 + 2)/2 - 2 = 2 - 2 = 0$$



**Short Answer Questions:**

1. Define an Algorithm. State and discuss its properties?
2. Define Flow Chart and mention their symbols with an example?
3. Explain different forms of FORTRAN constants with examples?
4. Define real variable name. Give two examples?
5. State different types of operators available in FORTRAN?
6. How do you define assignment and Replacement statements in FORTRAN?

**Long Answer Questions:**

7. Draw a flow chart to find the largest of three integers?
8. Draw a flow chart to find the smallest of three integers?
9. Explain the significance of flow charts and algorithms in preparing a program?
10. Write the FORTRAN expressions corresponding to the following algebraic expressions:

$$\text{i) } \frac{Ax+B}{Ax-B}$$

$$\text{ii) } ax^2 + bx + c$$

$$\text{iii) } \frac{mv^2}{x^2+K^2}$$

11. What is the value of I calculated in the following arithmetic statements?

- i)  $I = J * 2/3 + K/4 + 6 - J ** 3/8$  ( J=2, K=5 )
- ii)  $I = B/2.0 + B * 4.0/A - B + A ** 3$  ( A = 1.5, B=3 )
- iii)  $I = J/2 * 4 + 3/8 + J ** 3$  ( J = 3 )
- iv)  $I = I + J/K - L$  ( I = 2, J = 2, K = 2, L = 2 )

## LESSON - 3

### CONTROL STATEMENTS

#### 4.3(i) Relational Operators :-

The following are the relational operators and their symbols used in Fortran to express the logical condition.

Relational Operators	Symbol used in Fortran
Greater than ( $>$ )	<b>.GT.</b>
Greater than or equal to ( $\geq$ )	<b>.GE.</b>
Less than ( $<$ )	<b>.LT.</b>
Less than or equal to ( $\leq$ )	<b>.LE.</b>
Equal to ( $=$ )	<b>.EQ.</b>
Not equal to ( $\neq$ )	<b>.NE.</b>

#### 4.3(ii) Control Statements :-

A program is a set of instructions for doing a job. When a program is given to the computer, the order in which the statements in a program are executed is extremely important. Normally the statements are executed sequentially as written in the program. This is called Normal flow of control.

The normal flow of control can be altered by the use of some statements. The statements used to change the control flow are called the "**Control Statements**".

The following are the control statements used in Fortran ,

- i.e., a) Logical IF Statement,  
b) Arithmetic IF Statement,  
c) Go To Statement.

**a) Logical IF Statement :-**

The logical IF condition checks any given logical condition and transfer the control accordingly.

The general form of a logical IF Statement is :

```
IF (e) THEN
  St1
  St2
  --
  --
  Stn
ELSE
  Sf1
  Sf2
  --
  --
  Sfn
ENDIF
```

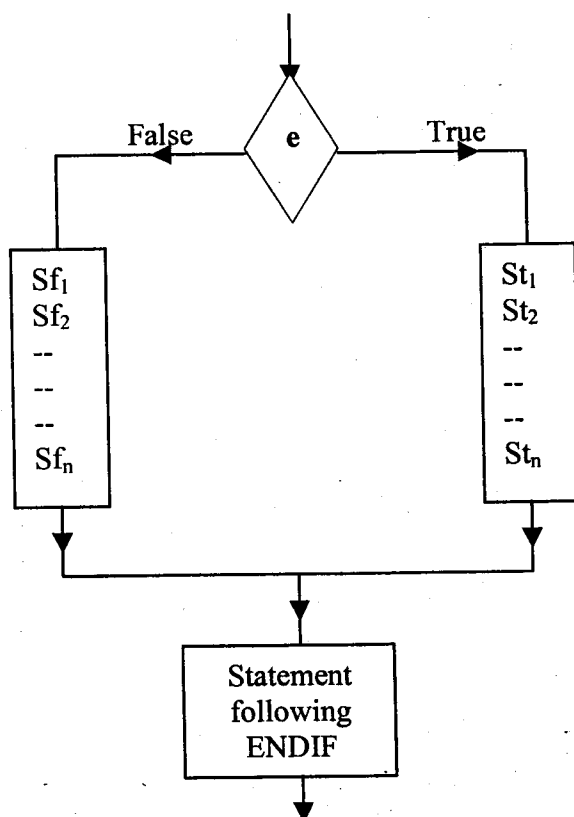
Where 'e' is a logical expression and St<sub>1</sub>, St<sub>2</sub>, -----St<sub>n</sub> and Sf<sub>1</sub>, Sf<sub>2</sub>,-----Sf<sub>n</sub> are Fortran Statements. ENDIF indicates the physical end of the IF Statement.

The above logical IF Statement is interpreted as follows :

If the expression 'e' is true then the statements  $St_1, St_2, \dots, St_n$  are executed and control passes to the statement following ENDIF.

If the expression 'e' is false then the statements  $Sf_1, Sf_2, \dots, Sf_n$  are executed and control passes to the statement following ENDIF.

The flow chart of above logical statement is



Ex:- 1) IF ( A.GT. B ) THEN

X = M+N

P = K+L

ELSE

X= M-N

P = K\*L

ENDIF

-----

-----

-----

2) IF ( MARKS.LT.40 ) THEN

WRITE (\*,\*) 'FAIL'

ELSE

WRITE (\*,\*) 'PASS'

ENDIF

Some times when the logical expression e is true one would like to execute only  $St_1, St_2, \dots$   
Stn. In such cases one may use the following form of the IF statement

IF ( e ) THEN

St<sub>1</sub>

St<sub>2</sub>

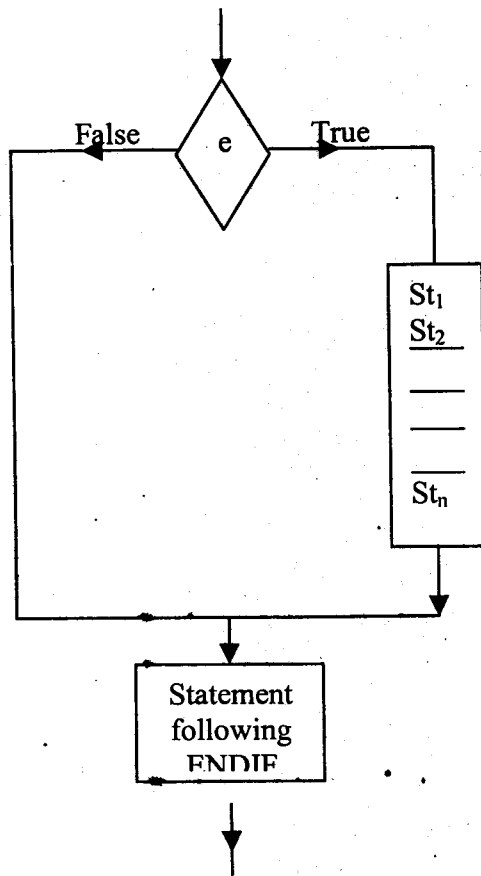
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--

St<sub>n</sub>

ENDIF

The flow chart of this statement is .



IF ----- THEN Structure

The following is invalid logical IF statement

```
IF ( A.GE.B )  
THEN X= Y+Z  
ELSE X= Y-Z  
ENDIF
```

Because THEN must be in first line. ELSE must be in a Separate line,

i.e.,

```
IF (A.GE.B) THEN  
    X=Y+Z  
ELSE  
    X=Y-Z  
ENDIF
```

**Nested IF-----THEN-----ELSE :-**

In Certain cases we may have to use one IF-----THEN-----ELSE Structure within another IF-----THEN. This is called Nested usage of IF-----THEN-----ELSE.

This can be classified as two types.

**Type 1:** In this type of usage it is proposed to use all the nested structures in the If clause.

**Type 2:** In this type of usage, all the nested structures are proposed to be included in the ELSE clause.

**b) Arithmetic IF Statement :**

This Statement transfer the control depending upon the value of an expression whether negative, zero or positive. This statement is rarely used.

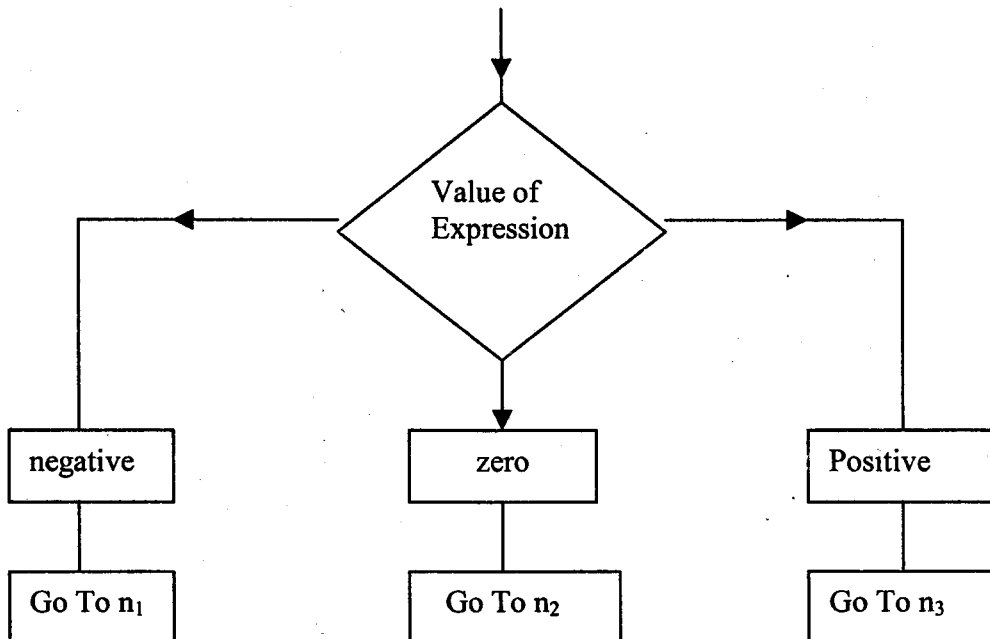
The general form of an arithmetic IF Statement is:

**IF ( Arithmetic expression )  $n_1, n_2, n_3$**

Where A. expression is a valid arithmetic expression enclosed within parenthesis and  $n_1, n_2, n_3$  are statement numbers.

The value of the expression is evaluated first. If the value is negative the control goes to statement number  $n_1$ , If it is zero, it goes to  $n_2$  and if it is positive, it goes to  $n_3$

The following flow chart depicts the action of this IF statement.





Ex:-

- 1) IF (I—J) 10,5,10
- 2) IF (A\*B-10.0) 15,20,100
- 3) IF ( M+N-5.0) 12,12,24

#### 4.2 (iii) Go To Statement :-

Go To statements are two types,

- i.e.,
- a. Unconditional Go To statement
  - b. Computed Go To statement

##### a. Unconditional Go To statement :

This statement is used to transfer the control to any other statement unconditionally.

The general form is            Go To n

Where n is the statement number to which the control must be transferred. The blank between Go and To is optional and also between Go To and the statement number.

Ex.    Go To 75 or GoTo 75 or GoTo75

The statement number may be before c after the Go To statement.

For example

```

1) 75 -----
    -----
    -----
        Go To 75
  
```

In this case, statement 75 is prior to the Go To statement.

```

2) -----
   -----
   Go To 75
   -----
   -----
75 -----

```

Here the statement number 75 is after the Go To statement both the above examples are valid.

**b. Computed Go To Statement :**

The Computed Go To Statement causes the transfer of control depending upon the value of an integer variable. The destination ( Where to go ) is decided by the value of integer variable.

The general form is

```
Go To ( n1, n2, -----nk ), I
```

Where i is the integer variable

n<sub>1</sub>,n<sub>2</sub>,-----n<sub>k</sub> are statement numbers.

This statement transfers the control to any one of the statement n<sub>1</sub>,n<sub>2</sub>,----- (or) n<sub>k</sub> depending on the value of i.

```

If i=1, the control is transferred to statement n1
i=2,           "           n2
-----
-----
i= k           "           nk

```

if i < 1 or i > k then this statement itself is ignored and the control goes to the next line.



Where  $n$  is a statement number,  $i$  is an integer variable. The parameters  $m_1, m_2, m_3$  are integer expressions or integer constants. Another valid form for the DO statement is :

$$\begin{array}{l} \text{DO } n \text{ } i = m_1, m_2 \\ \text{-----} \\ \text{-----} \\ n \text{ } \text{-----} \end{array}$$

in the above form  $m_3$  is assumed to be 1.

Examples : **Valid DO Statements**

DO 50 I = 1, 20

DO 990 J = K+1, L\*N, M-L

DO 25 J = 2, M, N

DO 80 IX = 2, -30, -8

**Invalid DO statements**

DO 50 I = 4.5

DO 40 A = 1, 24.5

DO 30 I = 0, 5, A(K)

DO 35 I = K(J), 25, 4

The DO statement is a command to execute all the statements following it upto and including the statement number  $n$ . This set of statements is called the **domain** or the **range** of the DO statement. When the DO statement is executed the number of times the domain is to be repeated ( $m_r$ ) is calculated using the formula :

$$m_r = (m_2 - m_1 + m_3) / m_3$$

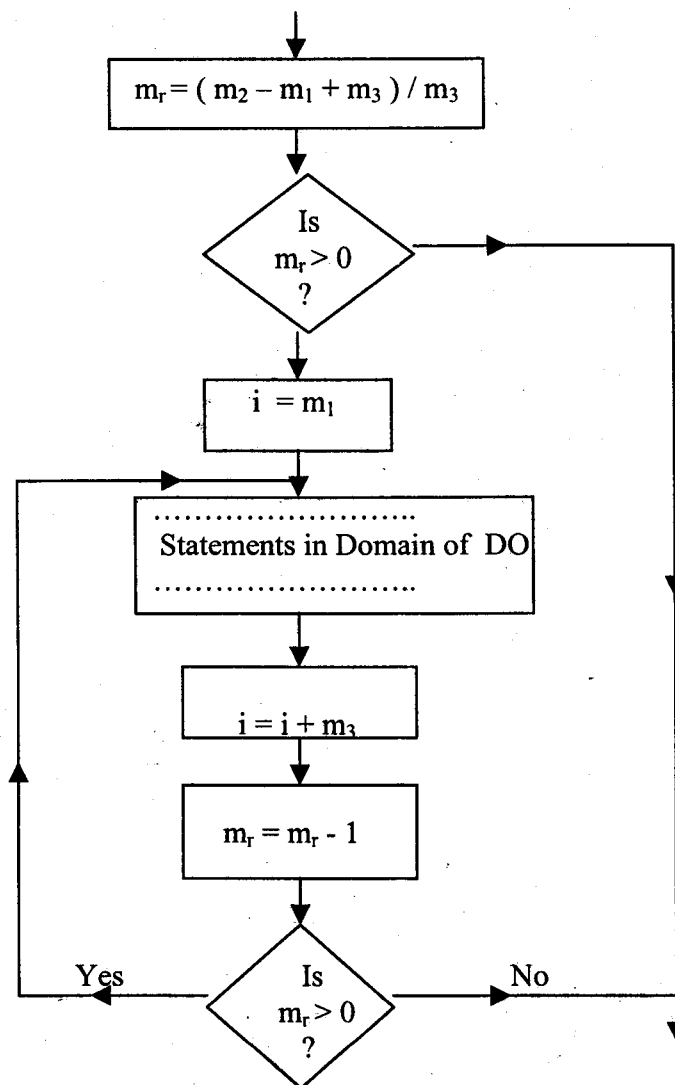
(where the division is integer division)

$$m_r = 0 \text{ if } m_2 < m_1 \text{ and } m_3 > 0$$

$$= 0 \text{ if } m_2 > m_1 \text{ and } m_3 < 0$$

Initially the repetition count  $m_r$  is checked. If it is 0 then control branches to the statement following the terminal statement  $n$  of the DO loop. If  $m_r$  is greater than zero then the DO loop index  $j$  is set equal to  $m_1$ . The domain of DO is executed with this initial value. After executing the DO loop statements,  $m_3$  is added to the index  $i$ . One is subtracted from the repetition count  $m_r$ .

If  $m_r$  is  $> 0$ , control branches back to statement following the DO statement and the domain is executed again with  $i = i + m_3$  and  $m_r$  is replaced by  $(m_r - 1)$ . As soon as  $m_r$  becomes 0 control branches to the statement following the terminal statement of the DO loop. It is thus seen that the DO loop is repeated  $m_r$  times, with index values  $i = m_1, i = m_1 + m_3, i = m_1 + 2m_3, \dots$  etc.,



Flow chart illustrating the DO statement

**Short Answer Questions:**

1. Write the general form of Logical IF statement and its functioning with an example?
2. Discuss the functioning of Do statement?
3. Write the format of GO-TO statement in FORTRAN?

**Long Answer Questions:**

4. Explain the syntax of DO-LOOPS. Discuss the rules to be followed while transferring the control in to out of a DO-LOOP?
5. Write a FORTRAN program to solve a Quadratic equation using Arithmetic If statement?
6. State and explain the syntax of control statements of FORTRAN. State which control statement is used when?

**LESSON – 4****LIST DIRECTED INPUT AND OUTPUT STATEMENTS**

In order to solve a problem on a digital computer it is necessary to transfer the required data from one of its input units to its memory. This is done by input – statements. Information may be transferred to the memory from one of several types of input units. This is performed by the statement called the READ statement.

After a program is executed the results of the computation are to be transferred from the memory of the computer to one of several output units. This is achieved by output-statements. We will consider in this chapter one type of output statement namely the WRITE statement, which causes the results to be displayed on a VDU.

Fortran I / O statements which do not need explicit FORMAT specification are known as list-directed I / O statements. We will now discuss these statements.

**4.4 (i) List – directed Input Statements**

The general form of a list – directed input statement is :

`READ ( * , * ) List`

This statement causes data to be read from the keyboard and assigned to the variables named in the List.

Examples : `READ ( * , * ) A, B, C, D, I, J, K,`

In this example the list is A, B, C, D, I, J, K,

The values to be assigned to the variables in the list of a READ statement are typed on successive columns starting from column 1. The values are in the same sequence as in the List and are separated by a comma of a line they may be continued on the next line. A single value, however, should not be split between two lines.

In the example above if the values to be assigned to A, B, C, D, I are respectively 8.95,  $9 \times 10^{-3}$ , -.68457, 342, 583 they should be typed on a line as shown below.

8.95,  $9 \times 10^{-3}$ , -.68457, 342, 583

The following restrictions should be remembered while preparing data

1. The values should be typed in the same order as specified in the List. While typing a particular value no column should be left blank. For example the number .89675 is typed incorrectly in the following line.

1	2	3	4	5	6	7
.	8	5	X	9	3	5

2. The numerical values should be within the allowed range of values of the real and integer variables. For example an integer data 123456 is illegal as it exceeds the allowable limit. The real data .89E - 99, for example is also illegal as it is outside the range of allowed real numbers.
3. When an E is punched to assign an exponent at least one number should follow it. For example, .77E is illegal.
4. No value should be split between two lines. For example the value .85935 should not be typed as shown below:

<b>First line</b>	:	77	78	79	80
			8	5	
<b>Next line</b>	:	1	•	2	3
		9	3	5	

5. A READ statement always causes a new line to be read, thus the values corresponding to the lists of two different READ statements should not be typed on the same line.



#### 4.4 (ii) LIST – DIRECTED OUTPUT STATEMENT

The general form of a list – directed output statement is :

WRITE (\*,\*) List

This statement causes the values of the variables specified in the List to be displayed on the video display screen.

Example : WRITE (\*,\*) X, Y, I

In the example the list is X, Y, I

Real numbers are displayed using the exponent notation or a fraction depending on their value. A variable is displayed in either of the forms given below.

The form :

$$b \pm n_1 n_2 n_3 n_4 n_5 n_6 . n_7 n_8 n_9 n_{10} n_{11} n_{12} n_{13}$$

is used when the variable magnitude is between 1 and  $10^7$

The form :

$$b \pm n_1 n_2 n_3 n_4 n_5 n_6 n_7 E \pm m_1 m_2$$

is used when the variable magnitude is  $> 10^7$  or less than 1.

Integer variable are displayed as shown below :

$$\pm n_1 n_2 n_3 n_4 n_5$$

←-----12 columns----->

for each variable value

In the example considered in this section if the variables in the list X, Y, I have the values  $.12452467 \times 10^6$ ,  $-.0034 \times 10^6$ , 452 they are displayed as shown below :

~~b b~~ 124524.67 b - 0.340000E-08 ~~b b b b b b b b~~ 452

#### 4.4 (iii) FORMAT specification

When data are to be input or the results to be output. We fully mention the type of the data ( integer, real or character ) and also its size. The specification of the types of the data and its size is called FORMAT specification.

#### FORMAT statement

The general form of a FORMAT statement is

$$N \text{ FORMAT } ( s_1, s_2, \dots, S_r )$$

When  $n$  is the statement number

$s_1, s_2, \dots, S_r$  are the format specifications.

#### Rules :-

1. The format specifications  $s_1, \dots, S_r$  must be enclosed within Parenthesis.
2. The specifications  $s_1, \dots, S_r$  must be separated by commas.
3. Every FORMAT statement must be given a statement number.

#### 4.4 (iv) I Format

The symbol **I** is used to denote the **integer** quantities. The general **I** format specification is

$$I w$$

Where  $w$  is the width of the integer data, including the +ve or -ve sign. In the width one space is allowed for the sign.

Example : 1) -756, 678, 158, this data can be described by the FORMAT statement.

FORMAT ( I4, I3, I3 ) this can be written as FORMAT ( I4, 2I3 )

2) +135, -235, +155, 12345 :- FORMAT ( I4, I4, I4, I5 )  
or FORMAT ( 3I4, I5 )

3) 12, 123, 1234, 12345, 123456 : FORMAT ( I2, I3, I4, I5, I6)

**4.4 (v) F Format :-**

The symbol **F** is used to denote the real data expressed in decimal form. The general form of the **F** format is

**Fw.d**

Where **w** is the total width of the number

**d** is the decimal width

Example : 1. Consider the number -15.1234

The total width of the number is **8** ( including sign and decimal point)

Decimal width **4**

So , this is represented by the format **F 8.4**

2. 

	1	5	.	6	-	5	.	7	9	-	8	5	5	.	6	5
--	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---

Column	Number	Format
1 to 5	15.6	F 5.1
6 to 10	-5.79	F 5.2
11 to 17	-855.65	F 7.2

So , this data is represented by the statement

FORMAT ( F5.1, F5.2, F7.2 )

**4.4 (vi) E Format :-**

The alphabet **E** is used to denote a real data expressed in the exponential form  
Its general form is

$$Ew.d$$

Where **w** is the total width including mantissa and the letter **E** and the exponent  
and the sign of the exponent.

**d** is the decimal width of the mantissa.

Example :- 1. Consider the number  $-0.567890E-15$

here the total width is 13, decimal width of mantissa is 6, so it can be written as **E13.6**

11.  $-45.234E15$ ,  $+10.2345E12$  can be written as **E10.3**, **E11.4**

**4.4 (vii) Multi Record FORMATS**

If input – output lists are to be obtained in more than one record then a **multi record format** is to be specified. In order to understand this specification it is helpful to know how the compiler interprets **FORMAT** statements.

**Record Spacing** : Whenever it is necessary to read a line next to the current line a slash (/) is used. The slash (/) is also used if printing is to be done in the next line.

The Statement

```
WRITE (*, 55) A, B, C, K, L, M, N
```

```
55 FORMAT (1X, 3F10.2 / 4 I5)
```

When type A,B, C on first line and K,L,M,N on the next line. The specification

```
FORMAT (1X, / 3F10.2 / (4 I8) /
```

Will leave a blank line, type 3 fields on the second and will type four integer fields on all succeeding lines.

**Short Answer Questions:**

1. Give an account of I, F, E formats of Read and Write statements?
2. What is an input statement? State the syntax of input statements of FORTRAN?
3. Define Format statement? Explain format codes I, F, E?

**Long Answer Questions:**

4. Write in detail the format of READ and WRITE statements?

**LESSON – 5**  
**FORTRAN PROGRAMMES**

**4.5 (i) ROOTS OF A QUADRATIC EQUATION**



$[\text{H}^+]$  = hydrogen ion due to acid + hydrogen ion due to ionization of  $\text{H}_2\text{O}$

$$[\text{H}^+] = \text{Ca} + K_w / [\text{H}^+], \quad \text{Ca} \longrightarrow \text{Concentration of acid}$$

$$\text{Or } [\text{H}^+]^2 = \text{Ca} [\text{H}^+] + K_w$$

$$\text{Or } [\text{H}^+]^2 - \text{Ca} [\text{H}^+] - K_w = 0$$

This is in the form

$$\text{AX}^2 + \text{B X} + \text{C} = 0$$

$$\text{ROOT} = \frac{-\text{B} \pm \sqrt{\text{B}^2 - 4 \text{AC}}}{2 \text{A}}$$

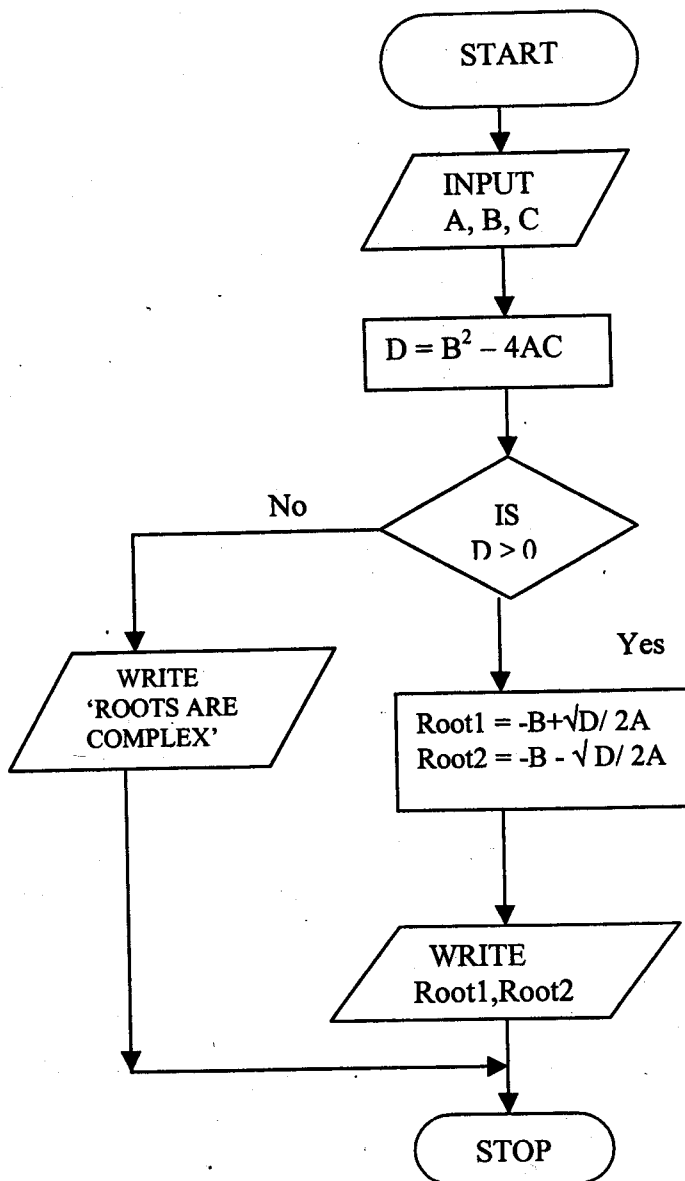
If  $\text{B}^2 - 4 \text{AC} = 0$ ; roots are real and equal

If  $\text{B}^2 - 4 \text{AC} > 0$ ; roots are real and unequal

If  $\text{B}^2 - 4 \text{AC} < 0$ ; roots are complex

## FLOW CHART:

## ROOTS OF A QUADRATIC EQUATION



**PROGRAM :****C (\*, \*) ROOTS OF A QUADRATIC EQUATION**

READ (\*, 10) A, B, C

10 FORMAT (3F<sub>10.4</sub>)

D = B \* \* 2 - 4.0 \* A \* C

IF (D. LT. 0.0) GO TO 30

ROOT1 = (- B + SQRT (DISC)) / 2 \* A

ROOT2 = (- B - SQRT (DISC)) / 2 \* A

WRITE (\*, 20) ROOT1, ROOT2

20 FORMAT (1X, ' ROOT1 = ', F<sub>10.4</sub>/1X 'ROOT2 = ', F<sub>10.4</sub>)

GO TO 50

30 WRITE (\*, 40)

40 FORMAT (1X, ' ROOTA ARE COMPLEX')

50 STOP

END



**4.5 ( i a) C (\*, \*) USING IF-ELSE CONDITION TO FIND THE QUADRATIC ROOTS**

```
      READ (*, 10) A, B, C
10     FORMAT (3F10.4)
      D = B ** 2 - 4.0 * A * C
      WRITE (*, 20)
20     FORMAT (1X, ' COMPLEX ROOTS')
      GO TO 40
      ELSE
      ROOT1 = (- B + SQRT (DISC)) / 2 * A
      ROOT2 = (- B - SQRT (DISC)) / 2 * A
      WRITE (*, 30) ROOT1, ROOT2
30     FORMAT (1X, ' ROOT1 = ', F10.4/1X 'ROOT2 = ', F10.4)
40     STOP
      END
```

#### 4.5 (ii) RATE CONSTANT OF A FIRST ORDER REACTION OR BEER'S LAW BY LEAST-SQUARE METHOD

$$K = 2.303/t \log a/a-x \quad \text{or} \quad Kt/2.303 = \log a - \log (a-x)$$

$$\text{Or } \log (a - x) = \log a - Kt/2.303$$

$$\text{Or } \log (a - x) = (-K/2.303) t + \log a, \text{ this is in the form; } y = m x + c$$

$$\text{Beer's Law } A = \epsilon t \cdot c$$

If blank is not compensated

$$A = \epsilon t c + b$$

This is in the form

$$y = m x + c$$

Where A = Absorbance

$\epsilon$  = Molar extinction coefficient

t = Path length or cell length

c = Concentration

**For paired Data** -The method of least-square is used to estimate SLOPE and INTERCEPT

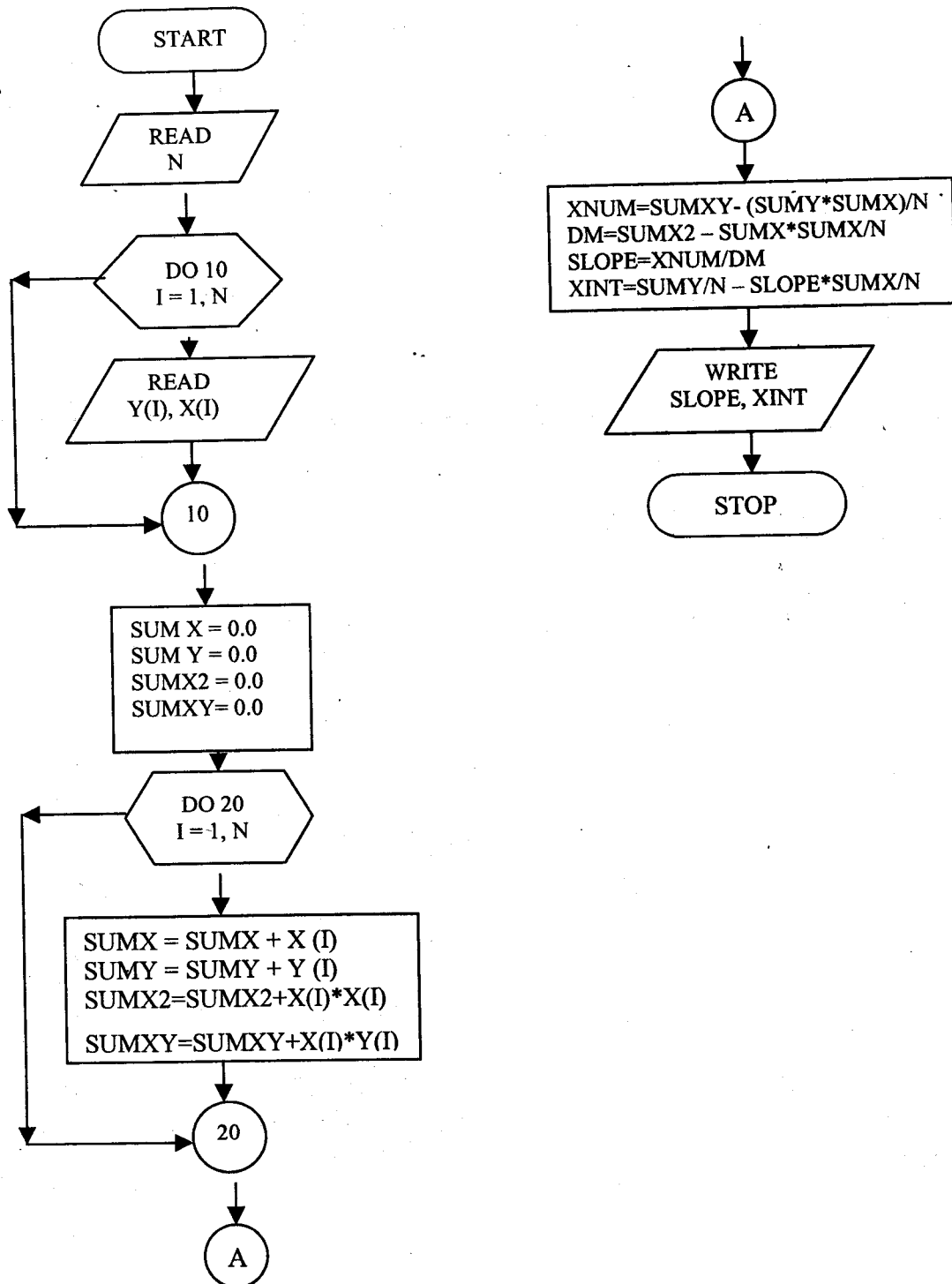
$$\text{SLOPE: } \frac{\sum_{i=1}^n y_i x_i - \frac{(\sum y_i)(\sum X_i)}{n}}{\sum_{i=1}^n x_i^2 - \frac{(\sum X_i)^2}{n}}$$

$$\text{INTERCEPT: } 1/n \sum y_i - \text{SLOPE} * 1/n \sum X_i$$

$$Y - \text{SLOPE} * X$$

Where n is the number of pairs

## FLOW CHART: RATE CONSTANT OF A FIRST ORDER REACTION OR BEERS LAW



**PROGRAM :**

C (\*, \*) RATE CONSTANT OF A FIRST ORDER REACTION OR BEER'S LAW BY

C (\*, \*) LEAST-SQUARE METHOD

DIMENSION X (100), Y (100)

READ (\*, 100) N

100 FORMAT (I<sub>3</sub>)

DO 10 I = 1, N

READ (\*, 200) X (I), Y (I)

200 FORMAT ( 2F<sub>10.4</sub>)

10 CONTINUE

SUM X = 0.0

SUM Y = 0.0

SUM X<sub>2</sub> = 0.0

SUM X<sub>4</sub> = 0.0

DO 20 I = 1, N

SUM X = SUM X + X (I)

SUM Y = SUM Y + Y (I)

$$\text{SUM } X_2 = \text{SUM } X_2 + X(I) + X(I)$$

$$\text{SUM } XY = \text{SUM } XY + X(I) + Y(I)$$

20 CONTINUE

$$X \text{ NUM} = \text{SUM } XY - \text{SUM } Y * \text{SUM } X / N$$

$$DM = \text{SUM } X_2 - \text{SUM } X * \text{SUM} / N$$

$$\text{SLOPE} = X \text{ NUM} / DM$$

$$X \text{ INT} = \text{SUM } Y / N - \text{SLOPE} * \text{SUM } X / N$$

WRITE (\*, 300) SLOPE, X INT

300 FORMAT (1X, ' SLOPE = ', F<sub>10.3</sub>/1X, ' INTERCEPT = ', F<sub>10.3</sub>)

STOP

END

\* SLOPE \* 2.303 give, Rate constant in the case of first order reactions

- SLOPE / CELL LENGTH gives extinction coefficient for Beer's Law.

**4.5 (iii) STANDARD DEVIATION AND VARIANCE OF UNIVARIENT DATA**

If there are N replicate values

$$\text{Arithmetic mean} = \frac{\sum_{i=1}^N X_i}{N} \equiv \bar{X}$$

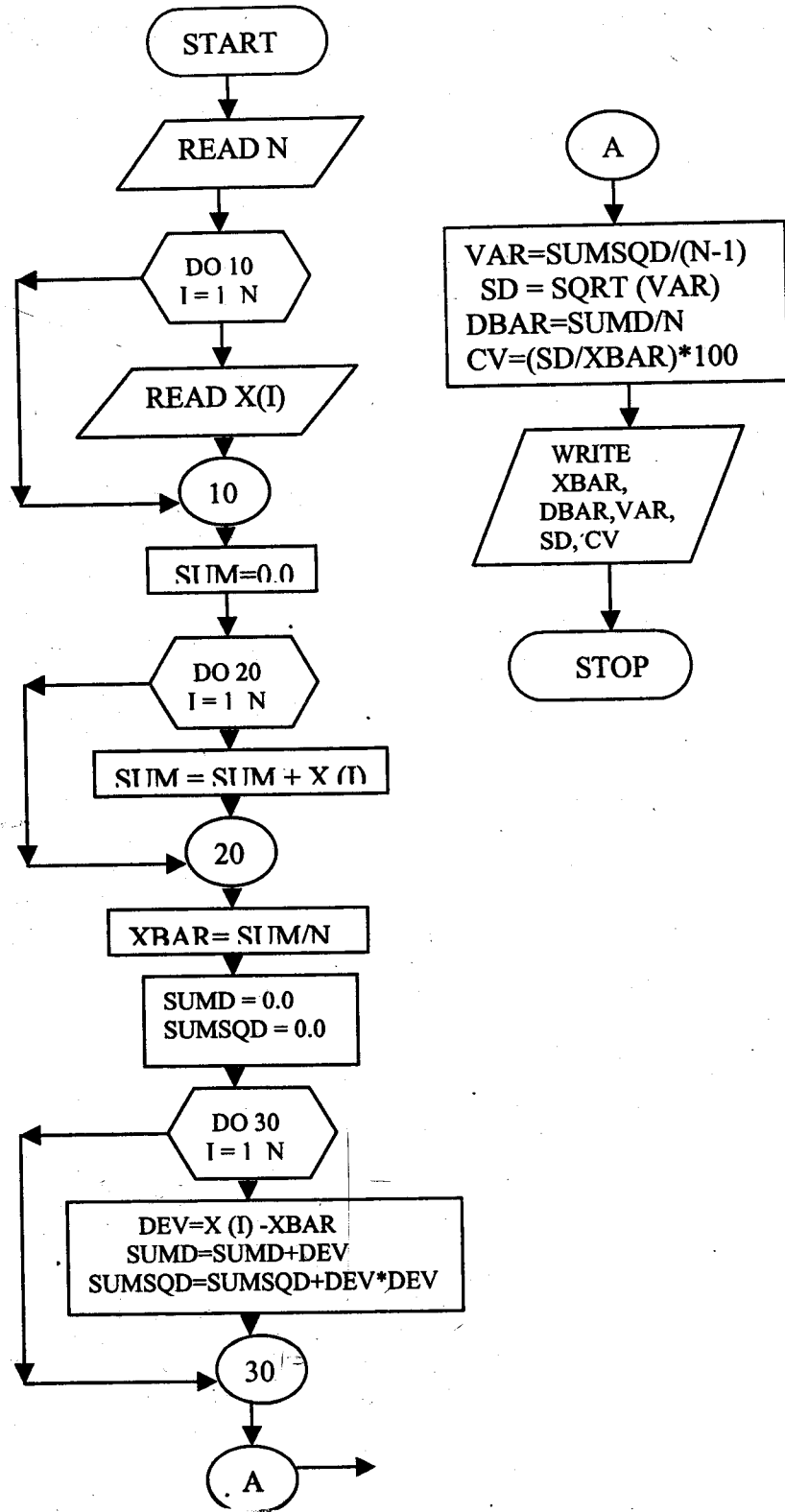
$$\text{Mean Deviation} = \sum_{i=1}^N (X_i - \bar{X}) \equiv \bar{d}$$

$$\text{Variance around mean} = \sum_{i=1}^N \frac{(X_i - \bar{X})^2}{N-1}$$

$$\text{Standard Deviation} = \sqrt{\text{Variance}} = \sigma$$

$$\text{Coefficient of Variance} = \sigma / \bar{X} * 100$$

**FLOW CHART:**  
STANDARD DEVIATION AND VARIANCE OF UNIVARIENT DATA



**PROGRAM: STANDARD DEVIATION AND VARIANCE OF UNIVARIENT DATA**

```
DIMENSION X (100)
  READ (*, 100) N
100  FORMAT (I3)
      DO 10 I = 1, N
          READ (*, 200) X (I)
200  FORMAT (F7.4)
10   CONTINUE
      SUM = 0.0
      DO 20 I = 1, N
          SUM = SUM + X (I)
20   CONTINUE
      X BAR = SUM / N
      SUM D = 0.0
      SUM SQD = 0.0
      DO 30 I = 1, N
          DEV = X (I) - X BAR
          SUM D = SUM D + DEV
          SUM SQD = SUMSQD + DEV * DEV
30   CONTINUE
      VAR = SUM SQD / (N-1)
      SD = SQRT (VAR)
      D BAR = SUM D / N
      CV = (SD / X BAR) * 100
      WRITE (*, 300) X BAR, D BAR
301  FORMAT (1X, ' X BAR = ', F10.4/1X, ' MEAN.DEV = ', F10.4/)
      WRITE (*, 400) VAR, SD, CV
400  FORMAT (1X, ' VARIANCE = ', F10.4/1X, ' STAND.DEV = ', F10.4/1X, ' CV = ', F10.4)
      STOP
      END
```



#### 4.5.(iv) VANDER-WAALS EQUATION (HYDROGEN ION CONCENTRATION OF A WEAK MONOPROTIC ACID)

$$(P + a / V^2) (V-b) = RT$$

$$\text{Or } PV^3 - V^2 (Pb + RT) + aV - ab = 0$$

This is a cubic equation in V. This is in the form  $f(x) = a_0 + a_1 \cdot x^1 = 0$

For a cubic equation  $n = 3$

Let  $x$  be an approximate root of the equation. Then  $x+h$  must be a better approximation to the root.

Where  $L$  is a shift in the value of  $x$

$$\text{Therefore } f(x+h) = f(x) + L f^1(x) + \frac{h^2}{2!} f^{11}(x) + \dots = 0$$

This explanation is called Taylor's expansion

As  $L$  is very small we can neglect the higher order terms. Here  $f^1(x)$  and  $f^{11}(x)$  are the first and second derivatives of  $f(x)$ .

$$f(x+h) = f(x) + h f^1(x) = 0 \text{ neglecting higher order terms}$$

$$\text{or } h = -f(x) / f^1(x)$$

$x + h$  (i.e.)  $x - \frac{f(x)}{f^1(x)}$  is a better approximation to the root and therefore can be taken as new

as a new value of ' $x$ '. A further improved value of ' $x$ ' may be obtained by determining

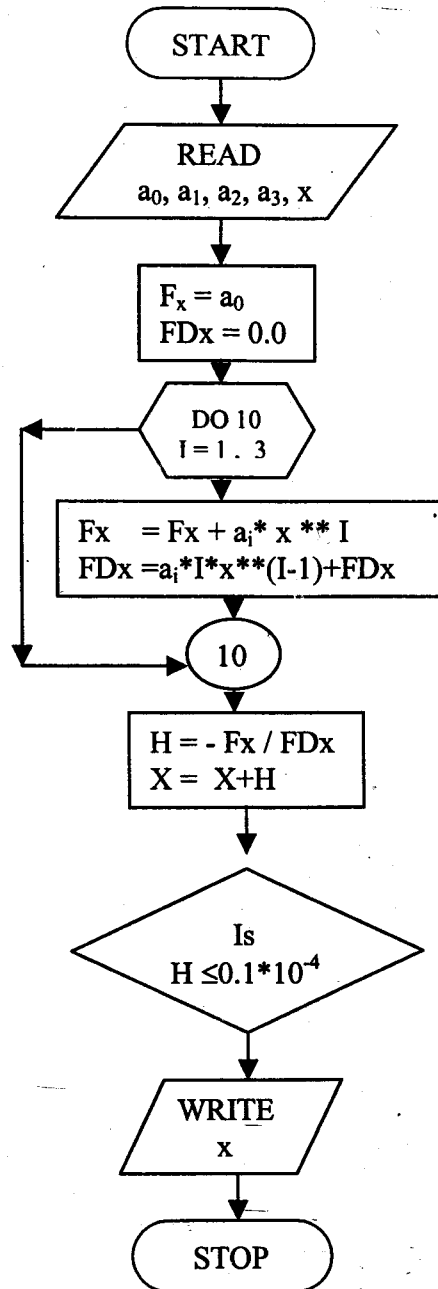
$$h^1 = -f(x+h)$$

$$\frac{f^1(x+h)}$$

This iterative procedure should be continued as long as the improvement in the root continues to be significant (i.e.)

If  $W < 0.1 \times 10^{-4}$  the integration may be terminated

## FLOW CHART: VANDER-WALLS EQUATION

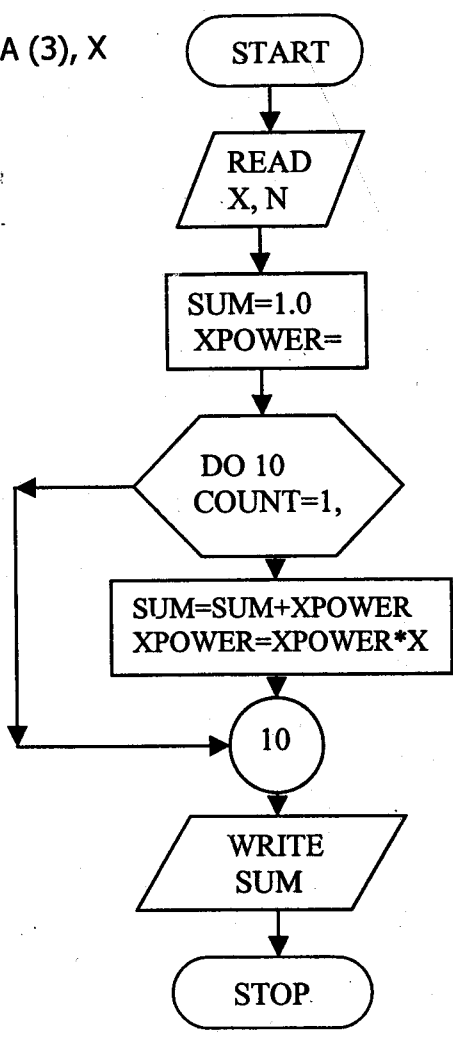


**PROGRAM:**

```

C (*, *) VANDER-WAALS EQUATION
      DIMENSION  A (10)
      READ (*, 100) A0, A (1), A (2), A (3), X
100  FORMAT (5 F10.4)
20   FX = A0
      FDX = 0.0
      DO 10 I = 1, 3
      FX = FX + A (I) * X ** (I)
      FDX = A (I) * I * X ** (I-1) + FDX
10   CONTINUE
      H = - FX / FDX
      X = X + H
      IF ( H .GT. 0.1E-04) GO TO 20
200  WRITE (*, 200) X
      FORMAT (1X, ' ROOT = ', F10.4)
      STOP
      END

```



FLOW CHART: SUMMING OF SERIES

**PROGRAM FOR SUMMING OF SERIES**

$$1 + X + X^2 + X^3 + \dots + X^n$$

**PROGRAM:**

C (\*, \*) SUMMING OF SERIES WITH DO STATEMENT

```
    READ (*, *) X, N
    SUM = 1.0
    X POWER = X
    DO 10 COUNT = 1, N
    SUM = SUM + X POWER
    X POWER = X POWER * X
10  CONTINUE
    WRITE (*, *) ' SUM = ', SUM
    STOP
    END
```

**Questions**

1. Write a FORTRAN program to solve Vander wall's equation.
2. Write a FORTRAN program to evaluate rate constant of a first order reaction.
3. Write a FORTRAN program to find the summing of a power series
4. Write a FORTRAN program for the application of Hydrogen ion concentration of a strong acid.
5. Write a FORTRAN program for standard deviation and variance of univariate data.

**M.Sc. DEGREE EXAMINATION, DECEMBER 2004**  
**First Year, Chemistry**  
**Paper – I GENERAL CHEMISTRY**

Time: Three hours

Maximum : 100 marks

*Answer the following questions*

**UNIT – I**

1. a) Discuss the rotational spectra of diatomic molecules (10)  
Or  
b) Evaluate the allowed transitions between rotational energy levels.
2. a) Explain the energy transitions that occur in molecules when  $\gamma$ -ray, UV-visible, Infra-red, microwave and radiowave radiations interact with them. (15)  
Or  
b) Describe the radiation sources and detectors in UV-visible, Infra-red, ESR and NMR spectro photometers

**UNIT- II**

3. a) Give an account of rotational fine structure of electronic vibrational transitions (10)  
Or  
b) Elucidate the vibrational spectrum of a diatomic molecule assuming it as a simple harmonic oscillator.
4. a) Write notes on :
  - i. Electronic spectra of diatomic molecules. (8)
  - ii. Quantization of vibrational motion (7)Or  
b) Describe the different types of electronic transitions observed in UV-visible spectroscopy with examples.

**UNIT – III**

5. a) Define the terms 'accuracy' and 'precision' with examples. Describe the standard deviation method to evaluate the precision of a set of data. (10)  
Or  
b) Explain the techniques involved in the preparation of gaseous, liquid and solid samples.
6. a). What are significant figures? Determine the number of significant figures in the following : (15)

- I. 0.002065
- II. 46052.37
- III.  $16.4 \times 0.3745$
- IV.  $64.25 / 0.125$
- V.  $\log 4.4 \times 10^3$

Or

- b) i. Describe the least square fit method in preparing a calibration plot. (7)
- ii. What are types of errors? Give the sources of different systematic errors. (8)

#### UNIT - IV

- 7. a) What are the basic components of a computer? Draw the block diagram and sketch all the components. (10)

Or

- b) Explain the usefulness of IF, GOTO and Do statements in computer programming.

- 8. a) Write a computer programme for solving vander-waal's equation. (15)

Or

- b) List out the various steps required to generate a computer programme.

M.Sc. DEGREE EXAMINATION, JULY 2005.

First Year, Chemistry

Paper I - GENERAL CHEMISTRY

Time : Three hours

Maximum : 100 marks

Answer ALL questions.

UNIT I

1. (a) What are the different sources of radiation used in molecular spectroscopy? (10)  
Or  
(b) Discuss the difference between ESR and NMR with examples. (10)
2. (a) (i) Give an account of quantised energy levels in a rigid rotor. (7)  
(iii) Explain the origin of allowed transitions in microwave spectra of molecules. (8)  
Or  
(b) (i) Explain the rotational spectra of a non rigid rotor. (7)  
(ii) Give an account of rotational spectra of linear molecules. (8)

UNIT II

3. (a) How do you classify the UV-visible spectral bands? (10)  
Or  
(b) What is the difference between the vibrational spectra of simple harmonic and anharmonic oscillators? (10)
4. (a) What are normal modes of vibration? Explain them in H<sub>2</sub>O and CO<sub>2</sub> molecules. (15)  
Or  
(b) Discuss the vibrational and rotational spectra of diatomic molecules. (15)

UNIT III

5. (a) What are the techniques employed for the storage of different samples? (10)  
Or  
(b) What are *t*-test and *f*-test? Why are they performed on data? (10)
6. (a) Describe the method of least squares with an example. (15)  
Or  
(b) What are determinate errors and how are they caused? (15)

UNIT IV

7. (a) Describe the functions of all the components of a computer. (10)  
Or  
(b) Write the format and purpose of different control statements used in FORTRAN. (10)
8. (a) Write a FORTRAN program to calculate the sum of a power series  $1 + x + x^2 + \dots$ . (15)  
Or  
(b) Write a FORTRAN program to calculate the roots of a quadratic equation. (15)

M.Sc. (Previous) Degree Examination, December 2005  
First Year, **Chemistry**

**Paper I - GENERAL CHEMISTRY**

Time : Three hours

Maximum : 100 marks

Answer any FOUR Questions.

**Unit - I**

1. Explain briefly the origin of any four types of molecular spectra. (10)  
Or  
b) Discuss the allowed transitions in the rotational energy levels of molecules. (7)
- 2) a) i) Give an account of isotopic effect in rotational spectra. (7)  
ii) Describe the spectra of rigid and nonrigid rotor systems. (8)  
b) i) What are the sources of radiation and detectors used in recording the NMR and ESR spectra of molecules. (7)  
ii) Give an account of microwave spectra of linear molecules.

**Unit - II**

- 3) a) Explain the origin of electronic spectra of molecules. (10)  
Or  
b) Give an account of vibrational energy levels and transitions of a diatomic molecule. (10)
- 4) a) Give an account of vibrational structure of an electronic transition. (15)  
Or  
b) Discuss the vibrational and rotational spectra of diatomic molecules. (15)

**Unit - III**

- 5) a) Give the importance of sampling techniques used for different forms of substances (10)  
Or  
b) Explain the importance of 'Accuracy' and 'Precision' in analytical determinations. (10)
- 6) a) Discuss the types of errors encountered in chemical analyses. (15)  
Or  
b) What is meant by mean, median, average deviation relative deviation and standard deviation? Calculate the above parameters for the following data. The normality of a solution determined by four individuals is, 0.2041, 0.2049, 0.2039 and 0.2043. (15)

**Unit IV**

7. a) Compare the features of mainframe, micro and super computers (10)  
Or  
b) Describe the format of different assignment statements used in FORTRAN (10)
8. a) Write a Fortran program to calculate the rate constant of a first order reaction from the observed kinetic data. (15)  
Or  
b) Write a FORTRAN program to calculate and print the pressure of a van der Waal's gas, given the volume, temperature and van der Waal's constants. (15)



(కత్తిరించి పంపవలెను)

**అధ్యాపకుల, విద్యార్థుల సలహాలు, సూచనలు :**

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**Course**  
M.Sc. Chemistry

**Year**  
1st Year

**Paper No. & Title**  
Paper - I. General Chemistry

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