CHAPTER 12

ANALYTICAL CHEMISTRY

The branch of Chemistry which deals with the qualitative and quantitative analysis of matter is called analytical Chemistry. Analytical Chemistry deals with the identification of substances and finding their weights. In analytical Chemistry the analysis of matter is studied.

Chemical Analysis: Determination of type/kind of components and their amounts in a matter sample is called analysis. Analysis may be qualitative and quantitative.

1. **Qualitative analysis:**Determination of the kind/type of substances present in a matter sample is termed as quantitative analysis. For example, the identification of acidic and basic radicals in a slat is qualitative chemical analysis.
2. **Quantitative analysis:**Determination of the amount of substances present in a matter sample is termed as quantitative analysis. For example, volumetric analysis (titration) and gravimetric analysis is quatitative analysis.

Both the classical and instrumental methods may be gravimetric and volumetric.

1. **Gravimetric analysis:** Gravimetric analysis relies on the critical mass measurement. For example, solution containing chloride ions can be assayed by adding an excess of silver nitrate, silver chloride precipitate will form, it is filtered, dried and weighed. The mass of the precipitate can be used to calculate the amount of analyte present.
2. **Volumetric analysis:** Volumetric analysis relies on volume measurement. Usually a liquid solution of a chemical reagent of known concentration is placed in a buret, the titrant is added gradually to the analyte until the chemical reaction is completed. The added titrant volume is just sufficient to react with all of the analyte is the equivalence point and can be used to calculate the amount or concentration of the analyte that was originally present.

Chemical analysis may further be classical and instrumental analysis.

1. **Classical analysis:**It is also termed as wet analysis. It consists of those analytical techniques that use no mechanical or electronic equipments other than a balance. The method usually relies on chemical reactions between the material being analyzed and a reagent that is added to the analyte. These often depend on the formation of a product of the chemical reaction that is easily detected and measured. The product could be any coloured material or precipitate.

2. **Instrumental analysis:** In this case instrument is used to perform the analysis. In some cases the instrument is used to characterize a chemical reaction between the analyte and the added reagent and sometimes it is used to measure the property of the analyte.

Before studying the analysis of compounds and molecules we must have an overview of the chemical formula and its types.

Chemical Formula

The symbolic representation of a compound or molecule is called chemical formula. A formula is a collection of symbols of the elements of which it is made. Chemical formula tells us about the composition of a compound that which kind of elements are involved and in what ratio they are present. Expressing a compound or molecule in terms of formula saves our precious time and space.

H_2O is the formula of water while H_2SO_4 is the formula of sulphuric acid. The subscripts indicate the number of atoms of the element present in the formula of that compound.

Types of Chemical Formula

There are three types ofchemical formula.

1. Molecular formula

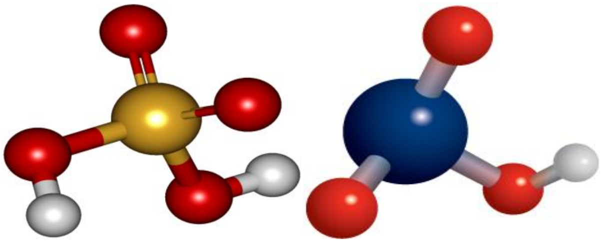
Molecular formula shows us the actual number of atoms present in a molecule or compound. It is also called true formula for a compound or molecule. For example C_6H_6 is the molecular formula of benzene which shows us that there are 6 carbons and 6 hydrogen atoms, means a total of 12 atoms in one molecule of benzene. Similarly the molecular formula of glucose is $C_6H_{12}O_6$.

2. Empirical formula

Empirical formula shows us the simplest combining ratio between atoms in a compound or molecule. It is also called experimental formula because it can be experimentally determined. The empirical formula of benzene is C_1H_1 or CH, this shows us that in benzene the simplest ration of C and H is 1:1. Similarly the empirical formula of glucose is CH_2O.

3. Structural formula

Structural formula shows us the arrangement or orientation of atoms in a molecule or compound. It is also called spacial formula as it shows us the arrangement of atoms of a molecule in three dimensional space. Structural formula of sulphuric acid (H_2SO_4) and nitric acid (HNO_3) are given below.



Relationship between molecular and empirical formula

The relationship between molecular and empirical formula is given as follows.

Molecular formula = n × Empirical formula

where $$n = \frac{\text{Molecular formula mass}}{\text{Empirical formula mass}}$$

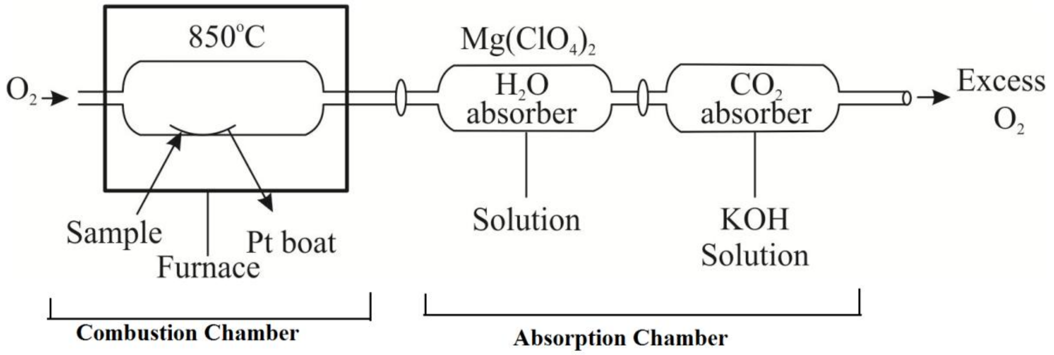
Classical Method of Analysis (Combustion Analysis Method)

Combustion analysis method is used for the determination of empirical formula of a compound and from the empirical formula the molecular formula can be determined then.

With the help of this method the empirical formula of simple organic compounds containing C and H or C, H and O can be determined. It cannot be applied to complex organic compounds and to non combustable inorganic compounds.

Procedure of the combustion analysis method

1. Fix amount of the organic compound is mixed with CuO and the mixture is taken in the platinium boat.
2. The platinium boat is placed in the combustion chamber of the instrument.
3. The organic compound is combusted in the excess oxygen in the combustion chamber.
4. Carbon of the organic compound is converted into CO_2, while Hydrogen is converted into H_2O.
5. The amount of CO_2 and H_2O formed are determined by absorbing these vapours in the absorbing solutions in the absorption chamber of the instrument.
6. Water vapours are absorbed by pre-weighed $Mg(ClO_4)_2$ solution.
7. While CO_2 is absorbed by pre-weighed 50% KOH solution.



8. The amounts of water and carbon dioxide are determined by subtracting the masses of the solutions before absorption from the masses of the solutions after absorption.
9. From the amount of water formed, the percentage of Hydrogen present in the organic compound can be calculated.
10. From the amount of carbondioxide formed, the percentage of Carbon can be calculated.

    %age of C, H and O_2 are calculated by using the following formula.

$$\%\text{age of C} = \frac{\text{Mass of } CO_2}{\text{Mass of the compound}} \times \frac{12}{44} \times 100$$

$$\%\text{age of H} = \frac{\text{Mass of } H_2O}{\text{Mass of the compound}} \times \frac{2.02}{18} \times 100$$

$$\%\text{age of O} = \left(100 - \%\text{age of Carbon} + \%\text{age of Hydrogen}\right)$$

11. From the percentages of C, H and O, the number of moles of C, H and O can be determined. This can be done by dividing percentage of the element by its atomic mass.
12. If the moles are in fractions then dividethe number of moles by the least moles of the element.
13. If the moles are still in fractions then multiply it with a suitable integer to get the whole numbers.
14. Write down the element and write the number of moles of each element as its subscript to obtain the empirical formula of the compound.
15. Multiply the empirical formula with “n” to get molecular formula of the compound.

Example: The combustion analysis of 0.003g of aspirin produced 0.006g of CO_2 and .0012g of H_2O. Calculate the empirical formula of aspirin.

Solution:

(1) Calculate the %age of each element

$$\%\text{age of C} = \frac{\text{Mass of CO}_2}{\text{Mass of O. Comp}} \times \frac{12}{44} \times 100$$

$$\%\ \text{C} = \frac{0.006}{0.003} \times \frac{12}{4} \times 100 = 60\%$$

$$\%\text{age of H} = \frac{\text{Mass of H}_2\text{O}}{\text{Mass of O. Comp}} \times \frac{2.02}{18} \times 100$$

$$\%\ \text{H} = \frac{0.0012}{0.003} \times \frac{2.02}{18} \times 100 = 4.48\%$$

$$\%\text{age of O} = (100 - \%\ \text{C} + \%\text{H})$$

$$= 100 - 60 + 4.48$$

$$\%\ \text{O} = 100 - 64.48$$

$$= 35.52\%$$

(2) calculate the No. of moles of each element.

$$\text{Moles of C} = \frac{\%\text{age of C}}{\text{At. Mass of C}} = \frac{60}{12.01} = 4.99$$

$$\text{Moles of H} = \frac{\%\text{age of H}}{\text{At. Mass of H}} = \frac{4.48}{1.01} = 4.43$$

$$\text{Moles of O} = \frac{\%\text{age of O}}{\text{At. Mass of O}} = \frac{35.5}{16} = 2.21$$

(3) Divide the No. of moles by the smallest value of the No. of moles to get the No. of moles in the whole numbers.

C	H	O
4.99	4.43	2.21
$\frac{4.99}{2.21}$	$\frac{4.43}{2.21}$	$\frac{2.21}{2.1}$
2.25	2	1

(4) Now multiply the No. of moles with 4, to get the whole numbers.

$$(4\times 2.25) \ : \ (2\times 4) \ : \ (4\times 1)$$

$$9 \ : \ 8 \ : \ 4$$

$C_9H_8O_4$ is the empirical formula of aspirin.

Example: The Empirical formula of a compound is CH_2O. Molecular weight of this compound obtained from other experiments is 180.12g/mol. Find the molecular formula of the compound.

Solution:

Empirical Formula = CH_2O

$$\text{Empirical formula weight} = 12 + 2 + 16 = 30$$

$$\text{Molecular formula weight} = 180.12\text{g / mol}$$

As we know that M.F = n × E.F…………..(1)

$$n = \frac{\text{Molecular Formula mass}}{\text{Empirical formula mass}}$$

$$n = \frac{180.12}{30} = 6$$

Put the value of "n" in equation (1) we get.

$$\text{M. Formula} = n \times CH_2O$$

$$= 6 \times (CH_2O)$$

$$= \boxed{C_6H_{12}O_6}$$

So compound is Glucose.

Modern/Instrumental Methods of Analysis

In inorganic Chemistry, molecular formula is enough to distinguish one compound from another. However this is not the case in organic Chemistry where molecular formula may represent more than one compounds. For example C_2H_6O may represent ethanol or acetone. So in organic Chemistry, structural formula is often used to represent a particular organic compound.

Physical properties of a compound provide enough information about its structure. Like for example, C_2H_6O will be dimethyl ether if it is gas and has boiling point 248K, and it will be ethanol if it is liquid and has boiling point 341K.

Chemical properties of a compound also provide information about the structure (functional groups) of the compound. For example, C_2H_6O will be dimethyl ether if it did not react with sodium metal and if it react with sodium metal it will be ethanol.

For the determination of structures of organic compounds, spectroscopic methods are used. Modern methods of analysis are superior than classical methods because;

- These methods requires small amount of compound.
- These methods are quick and very sensitive.
- Chemicals are not wasted in large amount.
- These give more accurate results.
- These methods are simple and easy in handling.
- These methods are nondestructive and if needed the whole sample can be recovered.
- These methods do not involve much Chemistry compared to the classical

methods.

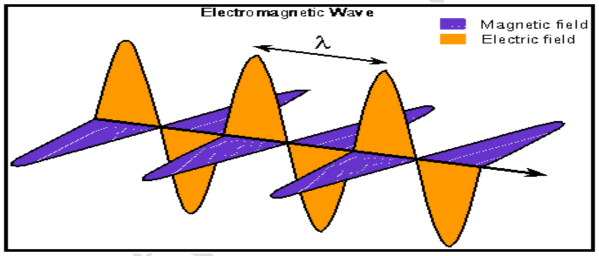
- Continuous monitoring of changes taking place is possible in spectroscopic methods which can give information on kinetics of changes.

Spectroscopy

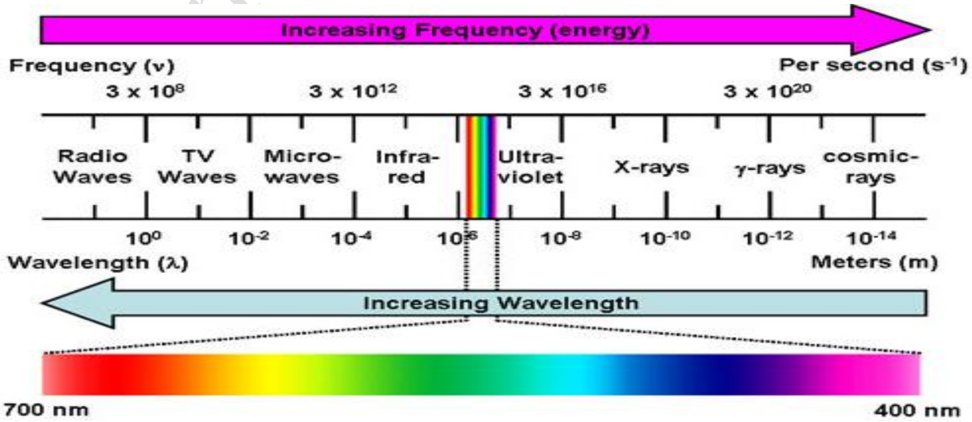
1. Spectroscopy is a technique used to identify different substances as a result of their interactions with electromagnetic radiations.
2. Spectroscopy is measurement of the amount of electromagnetic radiations absorbed by a substance at various wavelengths.
3. Spectroscopy is simply study of the interaction of light with matter.
4. Spectroscopy is a qualitative as well as a quantitative technique of analysis.

Spectrophotometer: The instrument used to record the wavelengths absorbed and concentration of the absorbing species is called spectrophotometer.

Electromagnetic radiations: Electromagnetic radiation consists of electric and magnetic components perpendicular to one another and to the path of propagation. Such type of radiation needs no medium for propagation.



EMR ranges from radio waves to cosmic rays. Radio waves being the least energetic (low frequency, larger wavelength) while cosmic rays the most energetic (high frequency, smaller wavelength).



Various regions of electromagnetic radiations

The wavelength of radio waves are about the size of human body, that of microwaves is about the size of honey bee, microwaves are of pinhole size, visible rays are protozoan's size, ultraviolet is of molecular size, X-rays are in the range of atomic size and gamma rays are of proton size.

Cosmic rays: These rays come from sun and are known to be the radiations of highest energy. They have wavelength less than 10^{-3} nm (nanometre).

γ-rays and X-rays: γ-rays and X-rays are less energetic than cosmic rays. Their wavelength ranges between $10^{-3} – 10^{-1}$ nm.

Ultraviolet light (U.V. light): These are the rays which are less energetic than X-rays but more energetic than visible light. The range of wavelength of U.V. light is 10—400 nm.

Visible light: It is ordinary sunlight and is comprized of seven different radiations (from red to violet). It has the wavelength range 400 nm—860 nm.

Infrared light: These are radiations weaker in energy but larger in wavelength than visible light. These have their wavelength in the range of $8 \times 10^2 – 3 \times 10^5$ nm.

Microwaves: These are radiations of still smaller energy but larger wavelengths lying in the range of $3 \times 10^5 – 1 \times 10^7$ nm.

Radiowaves: These have the longest wavelength, more than 10^7 nm.

The wavelengths of different constituents of visible light are given below:

Colour	*Wavelength, (nm)*
Violet, indigo	400–435
Blue	435–480
Green-blue	480–490
Blue-green	490–500
Green	500–560
Yellow-green	560–580
Yellow	580–595
Orange	595–610
Red	610–750

During the interaction of organic compound with EMR, certain wavelengths are absorbed which cause molecular rotation, bond vibration, electronic excitation and nuclear spin flipping. The nuclear spin flipping is caused by the absorption of radio waves. Molecular rotation and bond vibration occurs when IR radiations are absorbed. When UV-Visible radiations are absorbed, these will cause electronic excitation. The absorption of wavelength of radiation is selective for a particular transition which depends on structure of molecule. Thus spectroscopy helps us in elucidation of the structure of unknown compounds by measuring their absorption spectra.

Spectrum: The result of interaction of EMR and atoms/molecules is recorded as a plot of absorbance versus wavelength/wave number which is in the form of peaks and is known as spectrum.

Transmittance (T): It is ratio of the intensity of the transmitted radiations to the intensity of the incident radiations. If I^o is incident and I is transmitted radiation then $T = I/I^o$.

Absorbance (A): It is log of the ratio of the intensity of incident radiations to the intensity of the transmitted radiations. $A = \log I^o/I$.

Spectroscopic Methods of Analysis

Following spectroscopic methods of analysis are frequently used for the determination of structures of compounds.

1. Infrared spectroscopy
2. UV-Visible spectroscopy
3. Nuclear magnetic resonance spectroscopy
4. Atomic absorption spectroscopy
5. Atomic emission spectroscopy
6. Mass spectrometry
7. Raman spectroscopy
8. Electron spin spectroscopy

1. Infrared spectroscopy

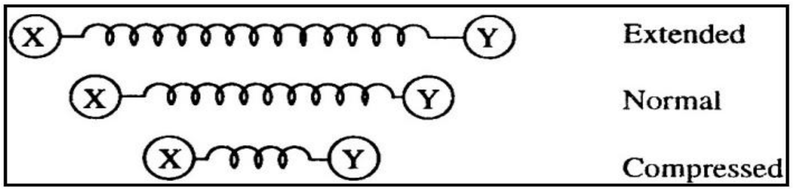
Infrared spectroscopy is used for the determination of functional groups in a compound. In infrared spectroscopy, infrared radiations are used whose range is from $5000cm^{-1}$ to $600cm^{-1}$.

When an organic compound is exposed to IR radiations in the range of $5000\text{-}667cm^{-1}$, rotation of molecules and vibration of bonds increases.

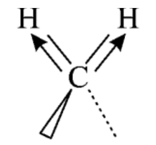
Rotational motion: The motion around a fix point is called rotational motion. Linear molecules have two types of rotations while non-linear molecules have many types of rotational motions.

Vibrational motion: The to and fro motion, back and forth motion or see saw motion is referred to as vibrational motion. It is motion about a mean position. It may be of two types.

A. Stretching vibrational motion: In this type of motion bond length changes while there is no change in bond angle. It may further be of two types.

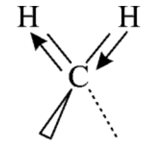


i. **Symmetric stretching:** In this type of stretching both the bonds stretches in the same direction. Both the bond lengths increases or decreases at the same time.

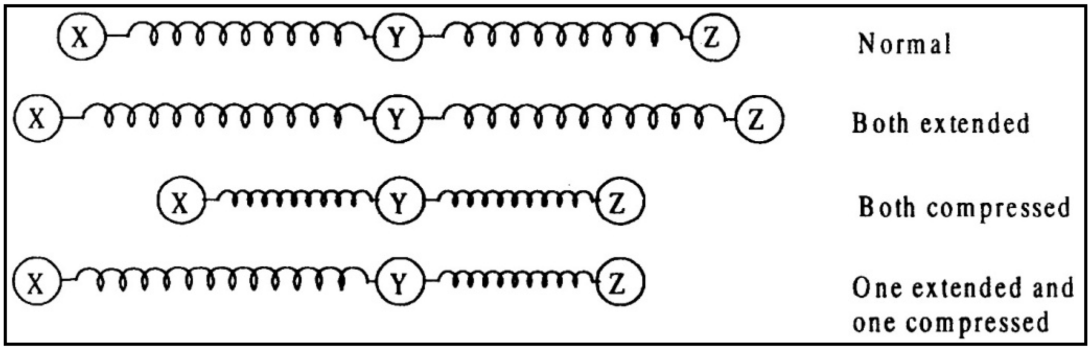


Symmetric Stretching

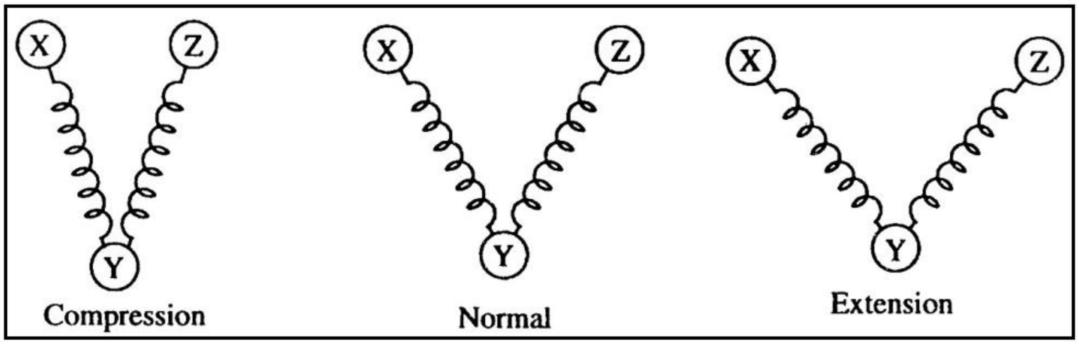
ii. **Anti-symmetric stretching:** In this stretching both the bonds stretches in opposite directions. Bond length of one bond increases and that of other bond decreases.

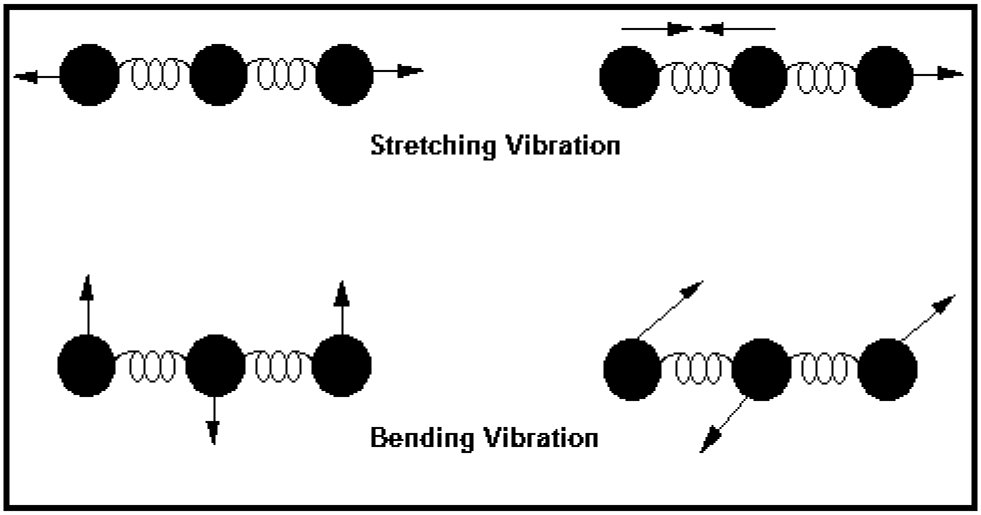


Anti symmetric Stretching

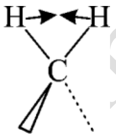


B. **Bending vibrational motion:** In this type of motion bond anglechanges while there is no change in bond length. It may further be of four types.

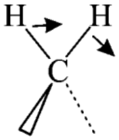




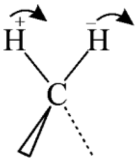
i. **Scissoring bending vibration:** It is anti-symmetric in plane bending. In such bending, the two bonded atoms either move towards one another or move away from each others like scissor.


Scissoring

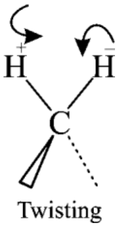
ii. **Rocking bending vibration:** It is symmetric in plane bending. In such bending both the atoms move in back and forth directions. Both the atoms either move towards one side or another, either to the right or to the left which is like a rocking chair.


Rocking

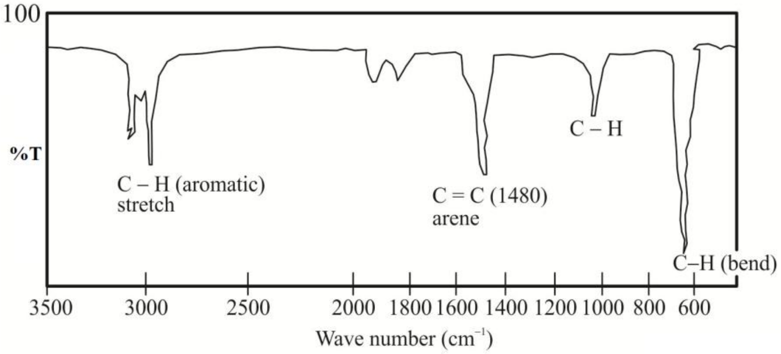
iii. **Wagging bending vibration:** It is symmetric but out of plane bending. Both the atoms swing back and forth but out of plane of the molecular axis. Both either come down to front or goes down to back side.


Wagging

iv. **Twisting bending vibration:** It is asymmetric and out of plane bending. In such case one atom moves in downward direction and the other moves opposite to it and thus these twist around the central atom like twisting of a wire.



IR spectrum: IR spectrum is a plot of wave number (cm^{-1}) on X-axis and % transmittance on Y-axis. Each dip in the spectrum is called a band or peak. 100% transmittance means no absorption. Every compound absorb a specific wave number radiation for its characteristic rotational and vibrational motion so each compound will give band or peak at a particular position. IR spectrum of an organic compound is characteristic of the structure of the compound and is of great assistance in establishing its identity. No two different compounds would give identical spectra.



IR spectrum of benzene

Regions in IR Region

The IR region is divided into two regions, finger print and functional group.

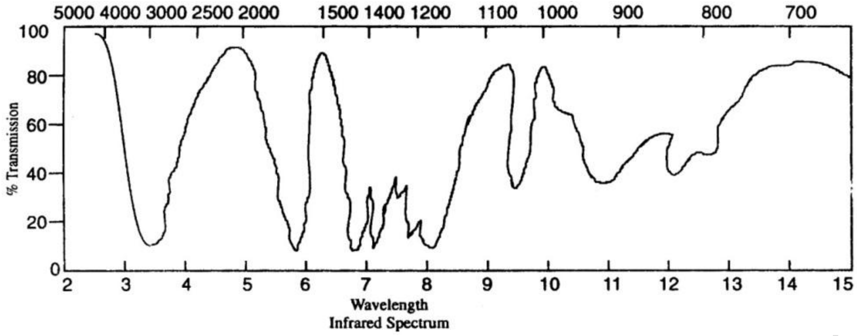
Finger print region: The region between 600 to 1500cm^{-1}is called finger print region because the absorption in this region is characteristic of a compound. Two different compounds will give different absorption peaks in this region. This region is used to identify a compound.

Functional group region: The region between 1500 to 4000cm^{-1}is called functional group region. Different functional groups show absorption at different frequencies/wave numbers in this region. All the functional groups shows absorption in this region which helps to determine the nature of functional group present in a particular compound. The IR absorption wave numbers of different functional groups are given in the table below.

Wavenumber [cm^{-1}]	Assignment
3500	O-H stretch of hydroxyl groups
3200	N-H stretch (amide A) of proteins
2959	C-H stretch (asymmetric) of –CH3
2934	C-H stretch (asymmetric) of >CH2
2921	C-H stretch (asymmetric) of >CH2 in fatty acids
2898	C-H stretch of C-H methane
2872	C-H stretch (symmetric) of CH3
2852	C-H stretch (symmetric) of >CH2 in fatty acids
1741	>C=O stretch of esters
1715	>C=O stretch of esters, RNA/DNA, OH-C=O
1695	Amide I band components
1685	resulting from antiparallel
1675	pleated sheets and b-turns of proteins
1655	Amide I of α-helical structure

Functional groups	Wave number (cm^{-1})
O-H aliphatic and aromatic	3600 to 3000
N-H primary, secondary, tertiary ammines	3600 to 3100
C-H aliphatic	3000 to 2850
C-H aromatic	2280 to 2200
C-C arene	1600
C-O	1300 to 1000
O-H free	3670 to 3580
C ≡ C alkynes	2250 to 2070
COOR ester	1750 to 1700
COOH carboxylic acid	1740 to 1670
C = O aldehydes, ketones and esters	1750 to 1680
$CONH_2$ amides	1720 to 1640

Q: Which of the following compounds could give rise to infrared spectrum in the figure below? Acetone, propionic acid, *n*-propyl alcohol or ethyl formate?



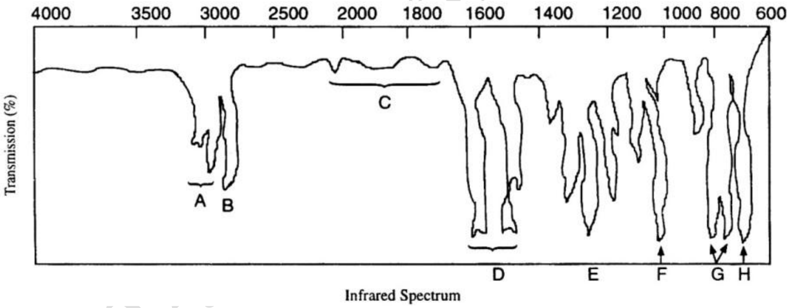
Ans: (*i*) We observe a band at 3000 cm^{-1}. This can be due to hydrogen bonded alcoholic or carboxylic group.

(*ii*) Since acetone and ethyl formate are not expected to give this band, the possibility of the compound being acetone or ethyl formate is ruled out.

(*iii*) The spectrum shows a band at 1700 cm^{-1} which is due to C = O of the propionic acid. No such group is present in propyl alcohol.

(*iv*) The band near 1300 cm^{-1} confirms the presence of propionic acid. Hence the spectrum relates to propionic acid.

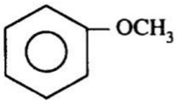
Q: Draw conclusion about the structure of the compound from the following IR spectrum. The molecular formula of the compound is C_7H_8O.



Ans: The absorption frequencies as observed in the spectrum are related to the groups as follows:

A	Aromatic C — H stretching	3060, 3030 & 3000 cm^{-1}
B	Methyl C—H stretching	2950, 2835 cm^{-1}
C	Overtone	2000–1650 cm^{-1}
D	C ——— C ring stretching	1590, 1480 cm^{-1}
E & F	C—O—C stretching	1245, 1030 cm^{-1}
G	C—H bending	800, 740 cm^{-1}
H	C ——— C bending	680 cm^{-1}

Based in the above observations the structure of the compound is



Anisole

Q: **How will you distinguish between the following pairs of compounds using IR spectra?**

(*a*) **$CH_3CH_2COCH_3$ and $CH_3OCH = CH_2$**

(*b*) **CH_3COOH and CH_3COCH_3**

(*c*) ***o*-OHC_6H_4COOH and *m*-$OH.C_6H_4COOH$.**

Ans: It is possible to distinguish between the compounds at given below:

(*a*) **$CH_3CH_2COCH_3$ and $CH_3OCH = CH_2$ (methyl ethyl ketone and methyl vinyl ether)**

(*i*) A strong absorption band at about 1715 cm^{-1} due to C—O stretching in methyl ethyl ketone will be obtained. No such band will be seen in the spectrum of methyl vinyl ether.

(*ii*) An absorption band at about 3050 cm^{-1} due to C—H stretching of $CH_2 = CH$ — groups and another band at about 1100 cm^{-1} due to C—O stretching will be observed in the IR spectrum of methyl vinyl ether. Such bands will not be formed in the spectrum of methyl ethyl ketone.

(*b*) **CH_3COOH and CH_3COCH_3 (acetic acid and acetone)**

(*i*) Both the compound will show an absorption band at about 1700 cm^{-1} due to C = O stretching.

(*ii*) Spectrum of acetic acid will show an absorption band between 2500 — 3000 cm^{-1} due to hydrogen bonded carboxyl group which will not be observed in the spectrum of acetone.

(*c*) ***o*-hydroxy benzoic acid and *m*-hydroxybenzoic acid**

In *o*-hydroxy benzoic acid, there is a possibility of hydrogen bonding between the two groups as they are quite near to each other. Hence, we shall observe a band in the range 2500—3000 cm^{-1} while in *m*-hydroxybenzoic acid (no hydrogen bonding) we shall see an absorption band in the range 3200—3400 cm^{-1}.

Uses of IR Spectroscopy

1. IR spectroscopy is helpful in the identification of unknown compounds.
2. It can easily detect the presence of an impurity due to shifting in the peak position of particular functional group. The presence of cyclohexanone is detected in cyclohexanol by intense C = O stretching.
3. It can be used to follow the progress of a reaction by withdrawing small

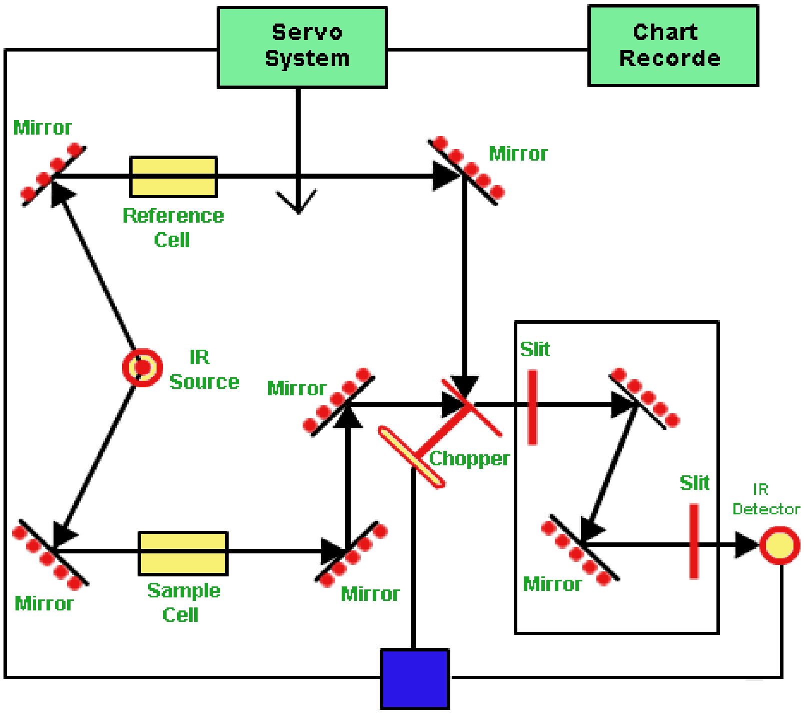
quantities from reaction mixture e.g. the oxidation of alcohols to aldehyde can be easily followed by disappearing absorption of OH group at 3600cm^{-1} and appearing of peak of C = O at 1715cm^{-1}.

4. It can be used to determine the percentage composition of a mixture.

Instrumentation of IR

IR spectrophotometer consists of the following parts.

(1) Radiation source
(2) Sample compartment
(3) Monochromator
(4) Detector
(5) Amplifier
(6) Readout devices
(7) Spectrum



2. **Ultraviolet visible spectroscopy**

In UV-Visible spectroscopy, quantized absorption of UV-Visible radiations cause electronic excitation due to which we obtain information about the presence and nature of unsaturation in conjugated molecules. As the UV-Visible radiations cause electronic excitation among the electronic energy levels of the molecules so it is called electronic spectroscopy.

In UV-Visible spectroscopy, radiations having wavelength in the range of 200 to 800nm are used. These are more energetic compared to IR radiations and therefore can change the distribution of loosely bonded (pi) and non-bonded electrons in the molecules or atoms.

UV-Visible range: UV-Visible radiations having wavelength from 200nm to 800nm. The region from 200 to 400nm is called ultraviolet while from 400 to 800nm is called visible. As all matter has electrons, almost all substances absorb certain wavelengths in this range. The absorption is according to Beer-Lambert law.

Beer-Lambert law: A = Ecl

Beer's law: According to Beer's law, absorption is directly proportional to the concentration of the sample solution. If "c" is the concentration and "A" is the absorbance then

$$A \propto C \text{.........................}(1)$$

Lambert's law: According to Lambert's's law, absorption is directly proportional to the path length of the sample solution. If "l" is path length in cm and "A" is the absorbance then

$$A \propto l \text{.........................}(2)$$

Beer-Lambert law: Combining equation (1) and (2) we get.

$$A \propto C.l$$

$$A = E.C.l$$

E = a constant, called molar absorptivity or molar extinction coefficient. It is characteristic of the solute at a given wavelength.

UV-Visible spectroscopy is both qualitative as well as quantitative analysis. For quantitative analysis Beer-Lambert law is used. Solutions of different concentrations are prepared and placed in quartz cell (cuvet) of known path length. UV-Visible light is passed through it and their absorbances are noted.

UV-Visible spectrum: It is a plot of concentration on X-axis and absorbance on Y-axis. The graph is called working curve. During this experiment a selected wavelength is used throughout the study at which maximum absorption occurs. This wavelength is called maximum wavelength (λ_{max}). When a solution of unknown concentration is placed in the spectrophotometer, its concentration is displayed on the screen.

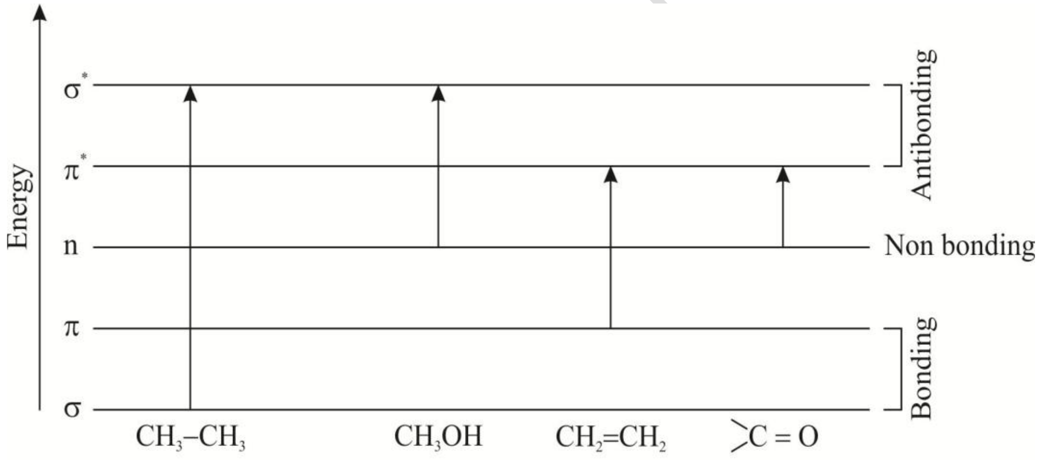
Electronic excitation/transition: The absorption of UV-Visible radiations causes electronic excitation/transition. Following types of transitions occurs.

(i) σ–σ* Transition: This is the type of transition in which σ electrons are excited to higher energy σ* orbitals by the absorption of UV-visible radiations. These transitions occurs in all saturated hydrocarbons i.e. alkane. Thus these transitions require higher energy. C–C bond absorbs 135nm while C–H bonds absorb 125nm light for sigma to sigma star transition.

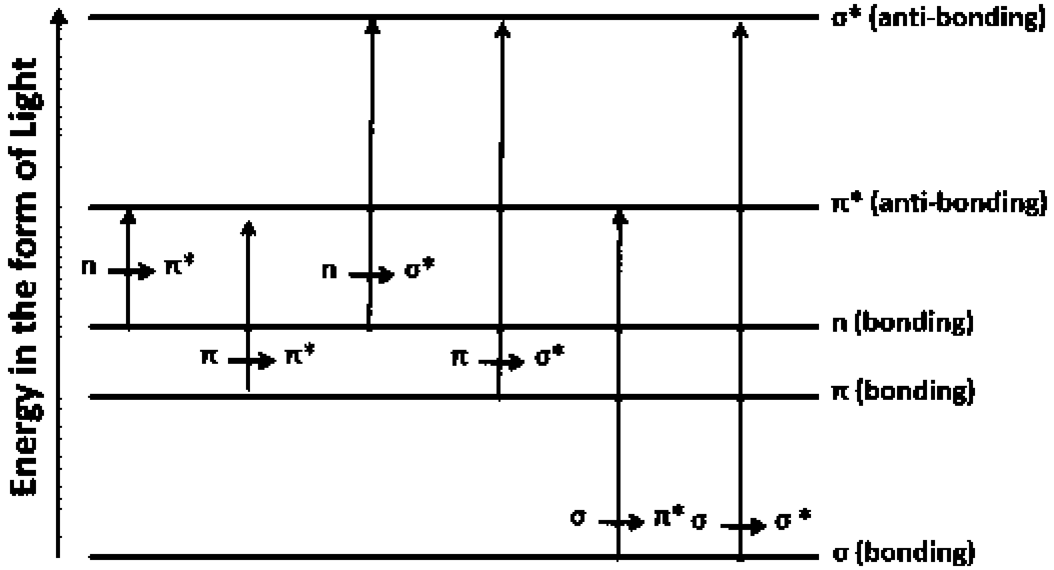
(ii) n–σ* Transition: This type of transition occur in saturated compounds having a heteroatom i.e. N, O, S, X. This involves the transition of electrons from non bonding orbital of heteroatom to an antibonding sigma* (σ*) orbital of the molecule. These transitions require less energy than σ–σ*. This transition requires light from 150 to 250nm. In methyl alcohol n–σ* transition occur at 183nm while in trimethyl amine at 227nm.

(iii) π–π* Transition: This type of transition takes place in unsaturated hydrocarbons i.e. alkene, alkyne or aromatic compounds. These transition involves the promotion of electrons from a π orbital to a π* orbital. Ethylene absorb at 171nm. However a conjugated system absorbs at much higher wavelengths. e.g. Butadiene ($CH_2 = CH - HC = CH_2$) absorbs at 217nm.

(iv) n–π* Transition: These transitions occur in molecules that contains double or triple bonds along with heteroatom i.e. O, N, S, X (halogen). In a given molecule the n—π* transitions require less energy and hence absorb in longer wave length. eg. C = O (aldehydes and ketones) shows absorption at 275-295nm. Therefore these are most useful transitions for analysis.



Energy changes involved in different electronic transition



From the position of the absorption peaks in the UV-Visible spectrum we can predict that for which type of excitation the specific wavelength has been absorbed and we can easily find out the nature of the compound.

Visible light absorption and color of the transition metal complexes

Transition metal complexes are usually colored due to d–d transition. Such compounds absorb radiations in the visible region. The light in the frequency equivalent to this energy will be able to cause electronic excitation. e.g. when a compound absorbs violet light (400–435nm) it reflects all other colors, which electively appears as complementary color. Complementary color of violet is yellow green. Thus the compound will appear yellow green to human eye. Similarly if a compound absorb green light from spectrum then this compound will appears to be purple. Thus UV visible spectroscopy can be used to predict the colour of the transition metal complexes.

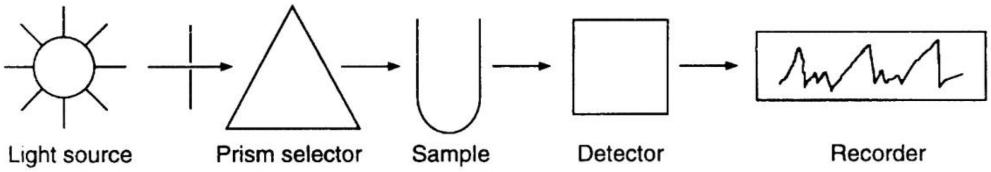
Color of light absorbed	Wave length (nm)	Color of complex
Violet	400 – 435	Yellow green
Blue	435 – 480	Yellow
Blue green	490 – 500	Red
Green	500 – 560	Purple
Yellow	580 – 595	Blue
Orange	595 – 650	Green Blue

Instrumentation in UV-Visible spectroscopy

Two types of spectrophotometers are used in VU-Visible spectroscopy.

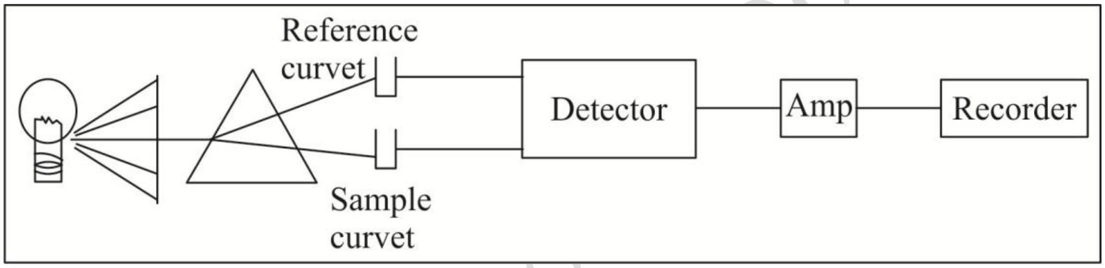
1. Single beam spectrophotometer
2. Double beam spectrophotometer

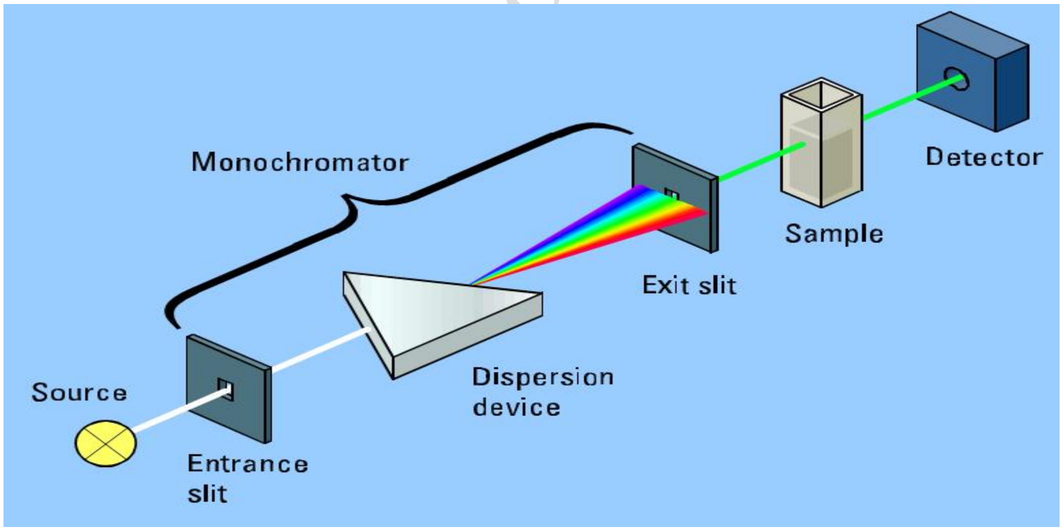
Simple sketch of single beam spectrophotometer is given below.



The components of double beam spectrophotometer are given below.

(1)	Source of radiations	(2)	Monochromator
(3)	Beam splitter	(4)	Sample cell and reference cell
(5)	Optical chopper	(6)	Detector
(7)	Amplifier	(8)	Recorder

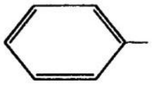




Applications of Ultraviolet Spectroscopy

The important applications of the study of UV spectra of compounds are as given below:

(*i*) Detection of conjugation: With the help of UV spectrum, we can establish the presence of conjugation in a compound. Conjugation can be

$— C = C — C =$ or $— C \equiv C — C \equiv$ or $C = C — C = O$ or  $— C = C$

By observing the λ_{max} values, we can also predict the location of substituents.

(*ii*) Detection of functional groups: It is possible to detect certain functional groups with the help of UV spectrum. The negative test is also of value. Absence of absorption above 200 nm is a sure indication of the absence of conjugation, carbonyl group and benzene rings in the compound.

(*iii*) Detection of geometrical isomers: When a compound exhibits geometrical isomerism, the trans isomer shows absorption at higher wavelength with larger values of extinction coefficients ($\in_{max}$) compared to cis isomers. Out of two stilbenes ($C_6H_5CH = CHC_6H_5$). The trans isomer shows absorption at 294 nm, ($\in_{max} = 24000$) while the cis isomer absorbs at 278 nm ($\in_{max} = 9350$).

(iv) Determination of the structure

(v) Determination of the ionization constant

(vi) Kinetic measurement

(vii) Stereochemical study

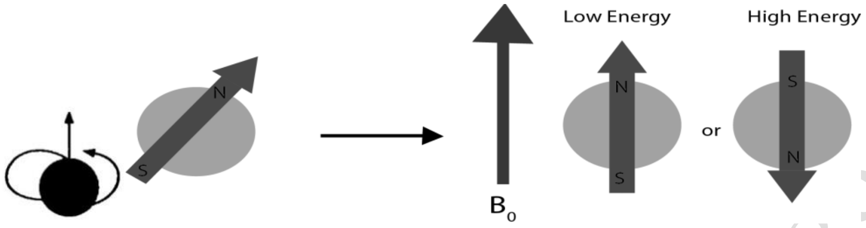
(viii) Analytical applications

3. Nuclear magnetic resonance (NMR) spectroscopy

1. NMR spectroscopy deals with the study of magnetic properties of atomic nuclei.
2. Measurement of the EMR required for the reversing of spinning of nucleus is called NMR spectroscopy.
3. NMR spectroscopy deals with the measurement of the energy required to excite a spinning nucleus from lower energy spin state (ground state) to high energy spin state (excited state) in an external magnetic field.

When a molecule is exposed to radio waves, quantized absorption takes place which leads to spin flipping in the presence of a magnetic field which give signals on the NMR spectrum. These signals give information about the environment and nature of the nucleus and about the number of protons in the molecule.

Like electrons, atomic nucleus also spins about its axis as nucleus is also charged body. The atomic nuclei behave like a tiny magnet as the spinning charged bodies produce magnetic field. The nuclear spin is quantized therefore the magnetic moment of nucleus is also quantized. In a proton (H) the spin quantum number is = ½. Other nuclei with odd atomic number like C^{13}, N^{15}, F^{19} and P^{31}also have a spin quantum number = ½. The nuclei with even atomic numbers have zero spin and zero magnetic moment like C^{12}, N^{14} and O^{16}. Such nuclei are invisible in NMR spectroscopy and are magnetically inactive.



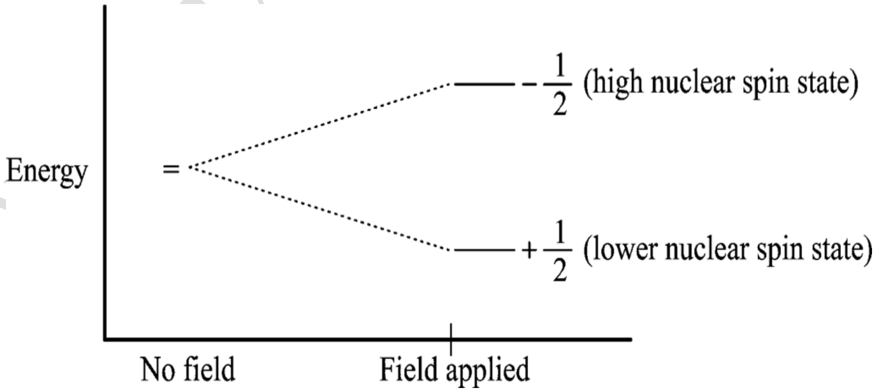
The spin states of a nucleus have equal energies in the absence of applied magnetic field. If magnetic field is applied, the spin states are no longer of equal energy. Thus two nuclear spin states, one of lower energy and other of high energy are produced.

Low energy spin state: It is represented by (+1/2). It is called alpha (α) state. Its magnetic field is aligned with the applied magnetic field.

High energyspin state: It is represented by (-1/2). It is called beta (β) state. Its magnetic field is aligned against the applied magnetic field.

Proton with magnetic field aligned with the applied field is at a lower energy than the one which aligns against the applied magnetic field. Nuclei with magnetic field aligned with the applied magnetic field can absorb energy and change their spin state (high energy state). The quantity of energy absorbed depends on the energy gap between the two states.

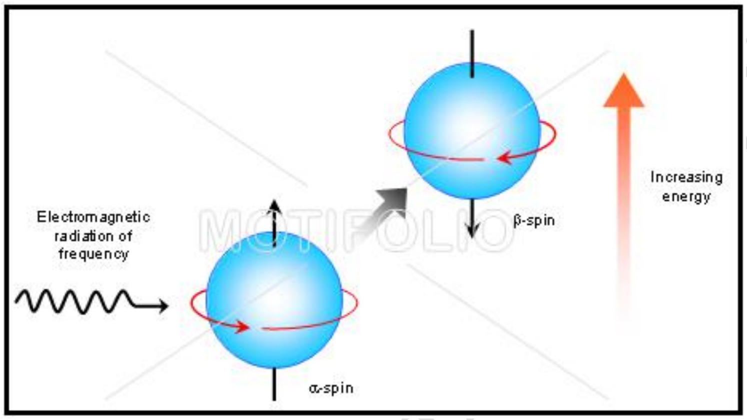
$$\Delta E_{\text{Absorbed}} = E_{(-1/2)} - E_{(+1/2)}$$



The absorbed energy is in the radiofrequency region (60 to 500Hz) of the electromagnetic radiations. When a sample is placed in the NMR spectrophotometer, the magnetic field is varied and energy of a specific frequency is absorbed.The absorption of energy is recorded on the chart paper.

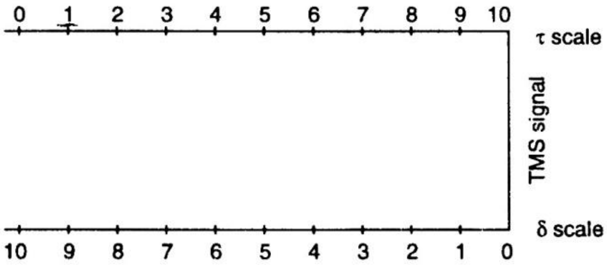
Spin flipping: The transition of nucleus from low energy spin state to high energy spin state by the absorption of EMR of suitable frequency from radio waves is called spin flipping.

$$_{+1/2}(\uparrow)_{\alpha} \xrightarrow{Radiowaves} {}_{-1/2}(\downarrow)_{\beta}$$

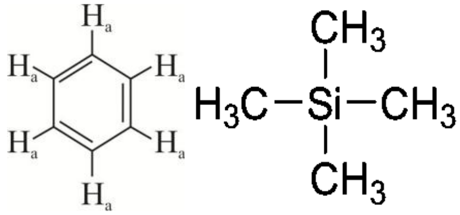


Chemical shift: The separation of absorption position of a particular proton from the absorption position of the reference standard is called chemical shift. It is expressed in hertz, also in smaller unit delta scale (σ). The delta value ranges from 0 to 12, where zero corresponds to TMS (standard). Another unit tau (τ) is also used. Chemical shift is indicated in ppm scale where TMS signal is at 10ppm, 10τ or 0σ.

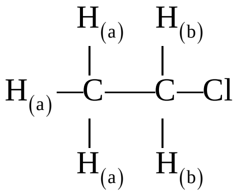
$$\tau = 10 - \sigma$$



Equivalent Protons: All protons which are in the identical environment in a molecule, having same chemical shift value are called equivalent protons. All the six protons of benzene and all the twelve protons of tetramethylsilane (TMS) are equivalent therefore the NMR spectrum of benzene and TMS show single single peak.

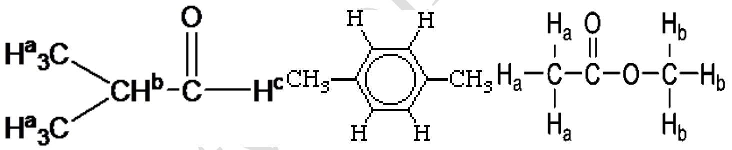


Non-equivalent protons: Protons which has different chemical environment and different chemical shif values are called non-equivalent protons. Like in ethyl chloride (CH_3–CH_2–Cℓ), there are two types of proton, i.e. methyl (CH_3) proton and methylene (–CH_2–) protons. Both have different environment and will appear at different positions in the NMR spectrum.



$$H_{(a)}-\overset{H_{(a)}}{\underset{H_{(a)}}{C}}-\overset{H_{(b)}}{\underset{H_{(b)}}{C}}-Cl$$

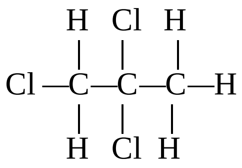
In above figure the two methylene (H_b) protons are attached with carbon having Cl atom. Whereas the methyl (CH_3) protons are attached to C which is not attached to Cl. So ethyl chloride will give two signals (peaks) in NMR spectrum.



Methyl iso-propnaldehyde has three types of protons. While xylene and methyl acetate has two types of protons.

Shielded Protons (less deshielded protons): Protons which are surrounded by high electron density and protected from the applied magnetic field are called shielded protons and the nucleus is said to be shielded. Such protons will require higher energy for spin flipping and appears up field i.e. at lower σ value. Examples of shielded protons are that of ethane, propane and butane.

Deshielded Protons (more deshielded protons): Protons in the vicinity of high electronegative atoms (like Cl, N, O, F) have lower electron density around them and require less energy for flipping, such protons are called deshielded and give peaks at higher σ value and appear downfield. Consider the example of 1, 2, 2-trichloropropane.

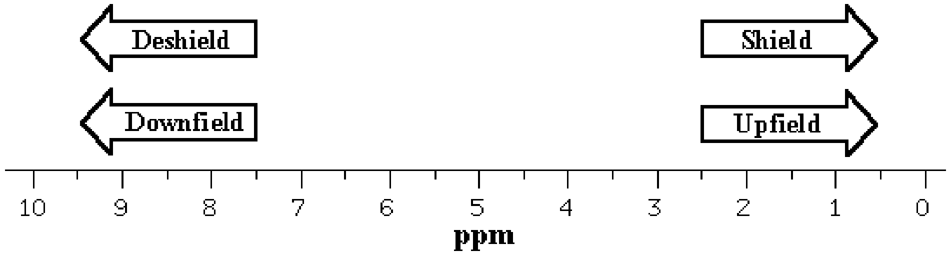


$$\begin{array}{ccccccc} & & H & & Cl & & H \\ & & | & & | & & | \\ Cl & — & C & — & C & — & C — H \\ & & | & & | & & | \\ & & H & & Cl & & H \end{array}$$

In this example the methyl protons are shielded and thus require high energy for spin flipping. Whereas the methylene (CH_2–) protons are attached to such carbon atom which having an electro negative chlorine atom, which will decrease the electron density on methylene protons and are less shielded or deshielded.

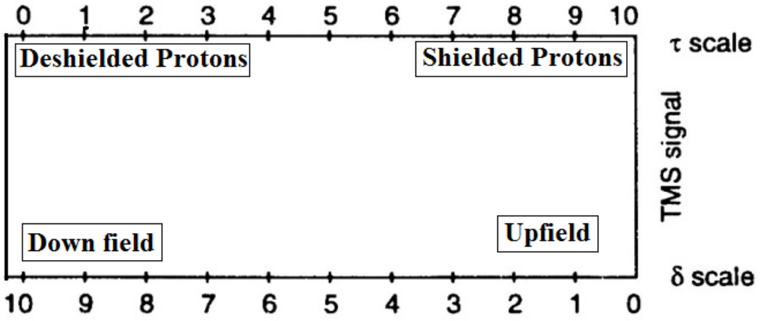
Up field region: Low σ value region in the NMR spectrum.

Down field region: High σ value region in the NMR spectrum.

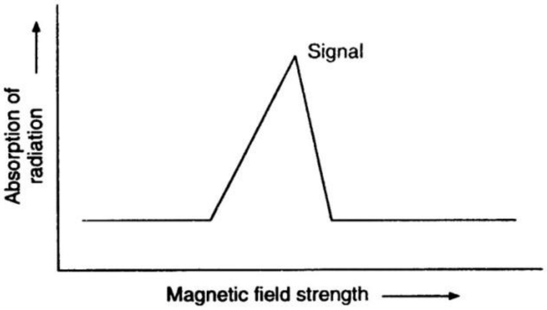


NMR spectrum: It is plot of absorption on Y-axis and chemical shift on X-axis. NMR spectrum is a rectangular chart paper with a linear scale of σ. For TMS the σ value is zero. Chemical shifts of other substances are compared with this reference value.

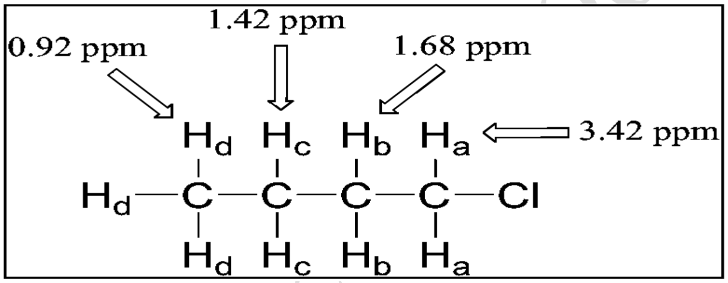
$$\delta = \frac{\text{Observed shift from TMS (Hz)}}{\text{Operating frequency of spectrophotometer (Hz)}} \times 10^{6}\,\text{ppm}$$



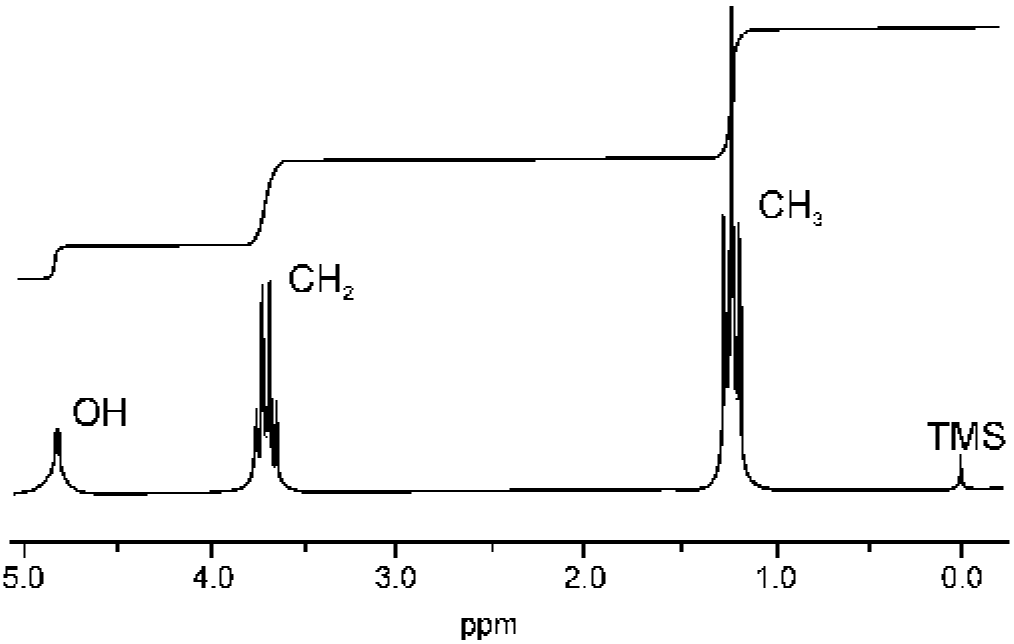
An NMR spectrum can be recorded by placing the substance containing hydrogen nuclei in a magnetic field of constant strength and passing radiations of changing frequency through the substance and noting the frequency at which the absorption of energy corresponding to flipping of proton, from lower to higher energy state, takes place. However for ease of operation, the frequency of radiation is kept constant (at 40, 60 or 100 megacycles/sec) and the strength of the magnetic field is changed. We obtain a graph of absorption of energy versus magnetic field strength. A signal is obtained which signifies the absorption of energy at particular field strength.



Chemical shift values of the protons of 1-chlorobutane



NMR spectrum of ethanol is given below



Tetramethylsilane is used as standard because.

- It is chemically inert and miscible with large range of solvents.
- Its twelve protons are magnetically equivalent.
- It is highly volatile and can be easily removed to get back the sample.
- It does not take part in the intermolecular associations with samples.
- Its chemical shift value is far away from the absorption position of other organic compounds.

Spin SpinCoupling

The interaction between the neighboring protons to cause spin spin splitting is known as spin spin coupling and the neighboring protons are said to be coupled.

Applications of NMR Spectroscopy

Various applications of NMR spectroscopic technique are given as under:

1. Identification of functional groups: Every functional group gives a characteristic signal in the NMR spectrum. By studying the chemical shift of compound, it becomes possible to establish what kind of functional group is present in the compound.

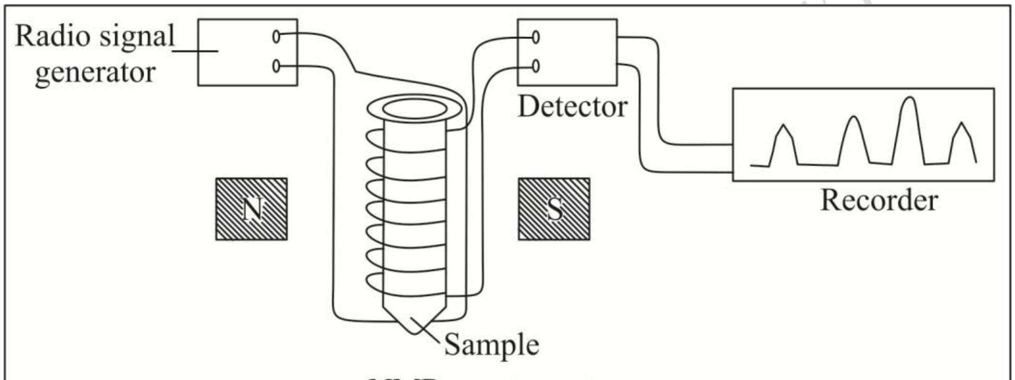
2. Structure of an unknown compound: It is possible to elucidate the structure of an unknown compound from the NMR studies. This is because protons under different environments give different chemical shifts. By observing doublets, triplets and multiplets, it is possible to place hydrogens at appropriate place in the formula and hence to establish the structure.

3. Comparison of two compounds: NMR spectrum is like fingerprint of a compound. Two compounds showing same NMR spectrum must be structurally identical.

NMR Instrumentation

NMR spectrophotometer consists of the following parts.

(1) Magnet
(2) Sweep coils
(3) Sample tube
(4) Radiofrequency transmitter
(5) Radiofrequency receiver
(6) detector and Amplifier
(7) Integrator
(8) Recorder
(9) Readout device



NMR spectrometer

Units for Expressing Chemical Shifts

Chemical shifts are expressed in frequency units (cycles per second). Frequency and magnetic field are related to each other by the following equation.

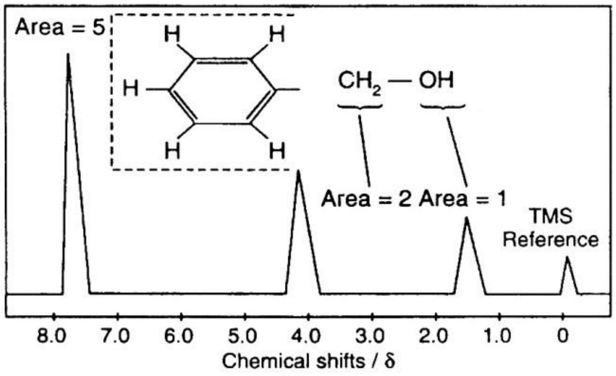
$$\nu = \frac{\gamma\ H_{20}}{2\pi}$$

Chemical shift expressed in cps (cycles per second) is directly proportional to the strength of applied field which in turn is equivalent to radiofrequency used. Since different PMR spectrophotometer used different radiofrequencies of 40, 60 or 100 magacycle/ sec (MCps) it is more appropriate to use units in which the radiofrequency of the instrument has been cancelled out. This is done by dividing the shift in cps by the radiofrequency employed and multiplying by a factor of 10^6 so that shifts are obtain in **parts per million (ppm).**

If a signal is obtained at 120 cps downfield with reference to TMS using 60 Mcps (or 60×10^6cps), then the chemical shifts is given by

$$\text{Chemical shift } (\delta) = \frac{120\times10^6}{60\times10^6} = 2 \text{ ppm.}$$

Q: Explain the various signals in the NMR spectrum of benzyl alcohol.



Ans: The no. of signals in a spectrum tells us how many different types of protons are present and the position of the signals (chemical shift) tells us about the nature of different protons (or their environments).

In the spectrum of benzyl alcohol shown above, we observe four signals which are due to the protons as detailed below:

(*i*) The small but sharp signal at $\delta = 0$ is the reference signal of TMS.
(*ii*) Signal at $\delta = 7.3$ is due to five equivalent ring protons.
(*iii*) The signal at $\delta = 4.6$ is due to two chemically equivalent methylene protons.
(*iv*) The peak at $\delta = 2.4$ is due to hydroxyl proton.

Q: How can NMR spectroscopy be employed in differentiating between ethane, ethylene and acetylene?

Ans: All the protons in ethane, ethylene and acetylene separately are equivalent. Hence we expect only one signal each in the above compounds. However the environments of protons in ethane, ethylene and acetylene are different. Hence absorption signals will be obtained at different positions. We can know the chemical shifts in the three compounds by consulting the table of chemical shifts. These are as follows:

$CH_3 — CH_3$	δ 0.9
$CH_2 = CH_2$	δ 5.3
$CH \equiv CH$	δ 2

Position of the signal can help us differentiate one compound from the rest.

Q: A compared having molecule formula $C_{10}H_{14}$ gives the following NMR data.

(*a*) Singlet τ 9.12 (δ 0.88), 9H

(*b*) Singlet τ 2.72 (δ 7.28), 5H

Assign a structure to the compound on the basis of above data.

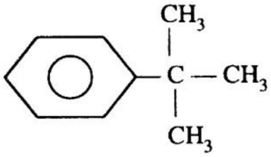
Ans: (*i*) The formula corresponds to the aromatic compounds general formula C_nH_{2n-6}. Hence it appears to be a substituted benzene.

(*ii*) There are nine protons of one kind and 5 protons of another kind. It suggests that there is mono-substitution in the benzene ring.

(*iii*) The two kinds of protons are not spin-spin coupled as we are getting the singlets.

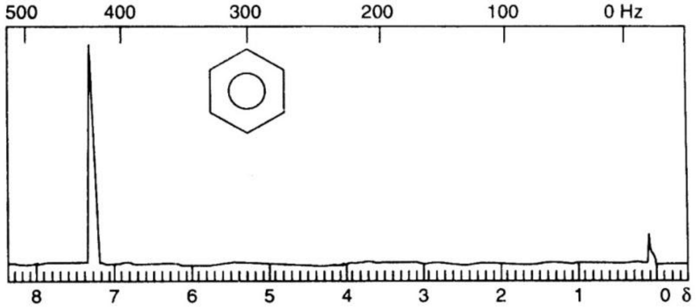
(*iv*) The singlet τ 2.72 (δ 7.28) can be due to C_6H_5 *i.e.* phenyl group, confirming monosubstitution.

(*v*) The remaining part of the molecule *i.e.* C_4H_9 can have nine equivalent protons only if it is in the form of a *t*-butyl group.



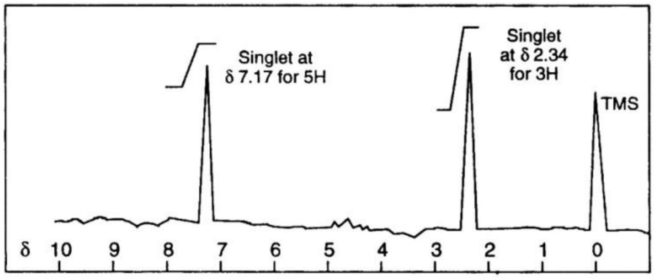
The singlet at τ 9.12 (δ 0.8) is due to the methyl protons.

NMR spectrum of benzene is reproduced as under.



The NMR spectrum of benzene exhibits only a sharp singlet at δ 7.37 from the six equivalent protons.

NMR spectrum of toluene is reproduced as under.



The following peaks are observed in the NMR spectrum of toluene:

(*a*) Singlet, δ 2.34, 3H

(*b*) Singlet, δ 7.17, 5H

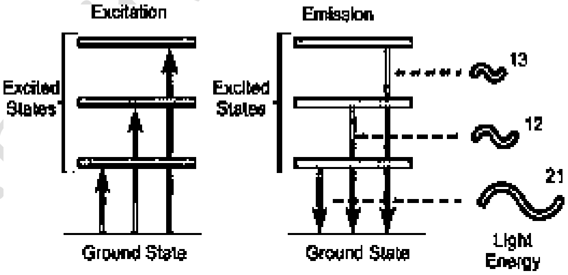
Toluene has eight protons, five of which are aromatic and remaining three form methyl group.

The signal for three protons of methyl group which is joined to an aromatic ring appears as a singlet at δ 2.34.

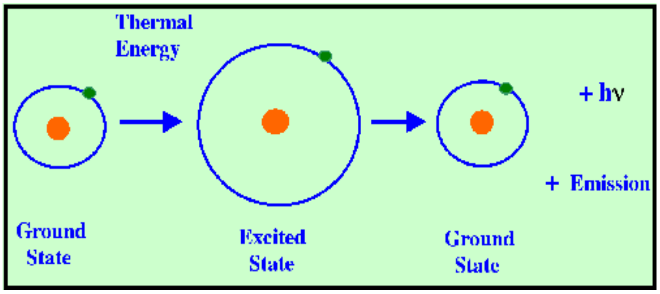
4. Atomic emission spectroscopy

Atomic emission spectroscopy is study of the emitted light during de excitation of electrons. It is a technique in which elements are determined from their line emission spectra.

When a metal is strongly heated, it starts glowing. The light emitted from the metal is when passed through a prism a continuous spectrum is obtained ranging from violet to red. Such a spectrum is called emission spectrum as it is obtained from the emitted light.



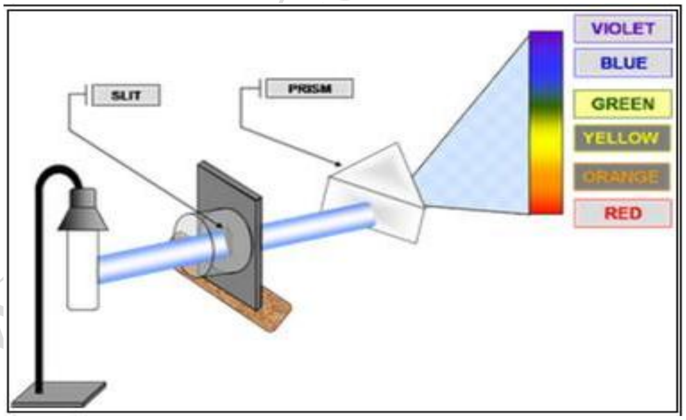
The emission spectra of atoms in the gas phase don't show a continuous spread of wavelength from red to violet, rather the atoms produce bright lines in different parts of the visible spectrum. Each element has a characteristic line spectrum.



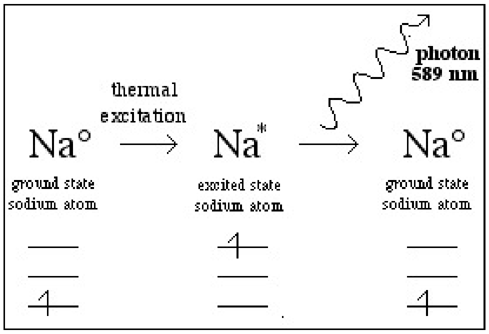
Line emission spectrum of hydrogen: When a hydrogen gas is taken in a discharge tube under low pressure it emits blue light. The light emission occurs when atoms go from excited states to ground state. When this blue light is passed through a prism, four bright lines against a dark background are produced. The colours and wavelengths of these lines are.

Red: 656.2nm	Blue green: 486.1nm
Blue violet: 434nm	Violet: 410.1nm

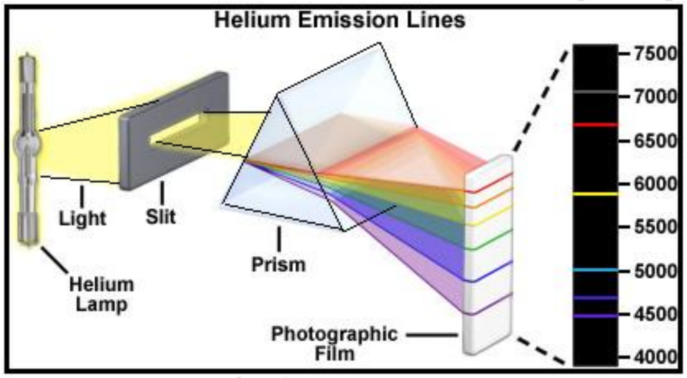
These lines of hydrogen spectrum are collectively called Balmer series as these are in the visible region. The red, blue green, blue violet and violet lines of Balmer series are actually due to the electronic transition from 6th, 5th, 4th and 3rd orbit to 2nd orbit respectively. In the invisible part of the hydrogen spectrum four more series are also obtained which are Lyman series (UV region), Paschen series (IR region), Brackett series (IR region) and Pfund series (IR region).



Line emission spectrum of sodium: When Sodium salt is placed on the Bunsen flame, yellow flame (light) is produced. When this yellow light is passed through a prism, two closely spaced yellow lines are obtained. These lines are called Sodium D lines. One is Sodium D_1 line (589nm) and other is Sodium D_2 line (589.6nm).

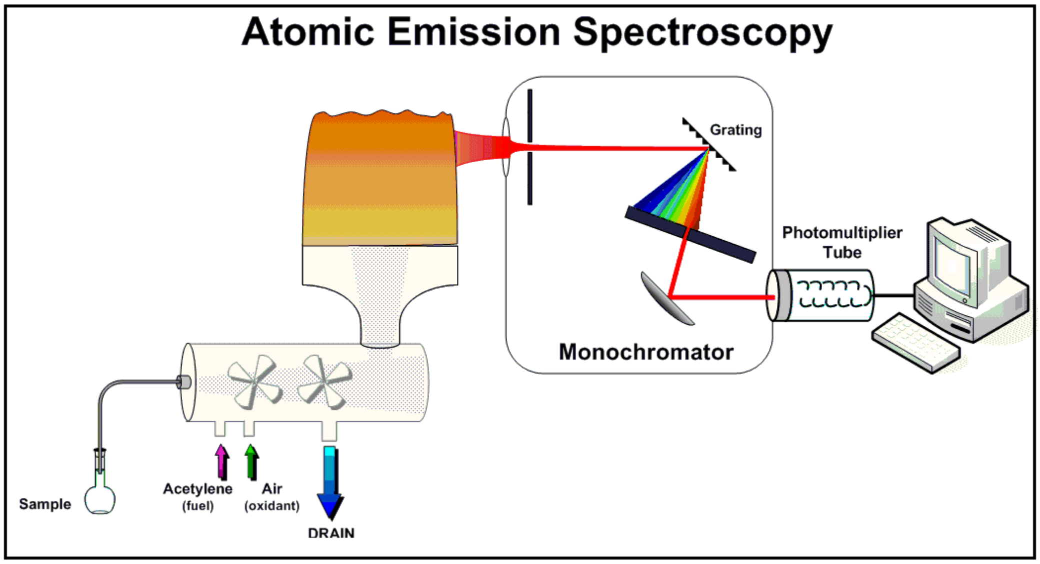


For every element there is a unique emission or absorption spectrum which is used as fingerprint to identify the element. Following is the line emission spectrum for Helium.



Flame photometry: One of the widely used emission spectroscopic technique is flame photometer. This technique is usually used to find the concentration of metals like Ni, Na, K etc. in the biological samples.

Procedure: An aqueous analyte is introduced into flame, water evaporates and solid salt is left behind. The salt breaks into constituent atoms. The atoms go to vapour state. The vapours get excites in the flame and during de-excitation light of characteristic wavelength is emitted which is dispersed by a grating or prism and detected in the spectrophotometer. The intensity of light emitted by the atoms is directly proportional to the concentration of the analyte.

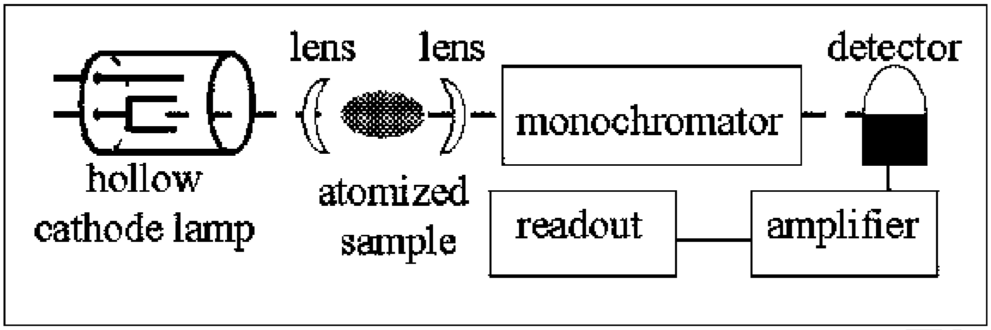


5. Atomic absorption spectroscopy

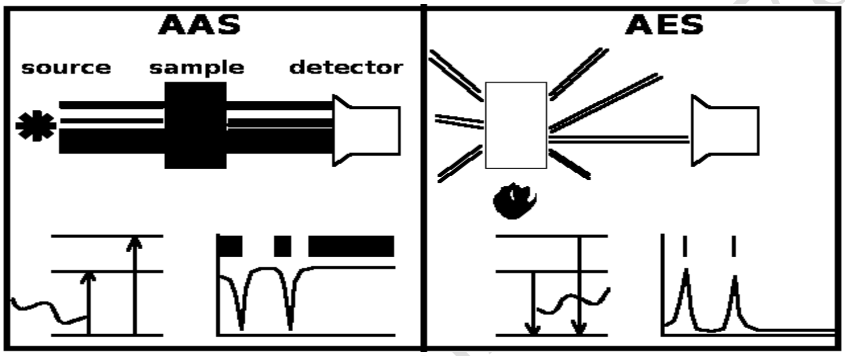
Atomic absorption spectroscopy is study of the absorbed light for the electronic excitation. Atomic absorption spectroscopy is used for the analysis of elements. In atomic absorption spectroscopy the absorbed light by the element is measured and the detection of element is carried out from the type of light absorbed by the element. Each element absorb characteristic wavelength of light for electronic excitation.

Procedure: The sample solution is evaporated on a flame and the sample is converted into atomic vapours. Some of the atoms in the flame get excited but majority of these are in ground state. When a light of particular wavelength from the hollow cathode lamp is passed through these atoms, these absorb the light for excitation from ground state to high energy state. The absorbance of light by atoms is directly proportional to the concentration of atomic vapours in the flame. For the analysis of different elements, different types of lamps are used which produce light of different wavelengths. Each element absorbs light of particular wave length.

Before introducing the sample of unknown concentration, solutions of known concentrations of that element are aspirated into the flame one by one. Their absorbances are recorded and a working curve is constructed. Then sample of unknown concentration is aspirated into the flame and its concentration is read out from the instrument. A simple diagram of an atomic absorption spectrophotometer is shown below.



Comparison of AAS and AES



6. Mass spectrometry

Mass spectrometry is a technique used for the determination of atomic masse and molecular masses. This technique also tells us about the percentage composition of a mixture by determining the percentage abundance of each component. This technique can also be applied in carbon dating and radioactive dating process. This technique is called spectrometry and not spectroscopy as there in no light absorption, when light absorption occur the technique is called spectroscopy.

With the help of mass spectrometry usually the atomic masses of isotopes present in an elemental sample and the percentage abundance of each isotope is determined. The instrument used in mass spectrometry is called mass spectrometer.

Structure and Function of Mass Spectrometer

Mass spectrometer consists of the following chambers.

1. Vapourization chamber

The sample is usually injected as gas but if liquid is introduced then it may be evaporated in the evaporation chamber by gentle heating. The vapours formed are collected in the vapours reservoir.

2. Ionization chamber

The sample vapours are ionized by electrons from the electron gun. Electrons (of energy 10 to 15 eV) from the electron gun when hit the sample electrons, these are ejected and cations are formed.

3. Acceleration chamber

The cations are accelerated by applying electric field from 500 to 2000V.

4. Separation/deflection chamber

The cations are separated from one another in the presence of magnetic field. The cations deflect in circular paths on the basis of difference in their m/e values. Lighter ions with low m/e value deflect to larger extent than heavier ions which has high m/e value.

5. Collection chamber

These separated ions are collected in ion collector called electrometer or Faraday cup. While striking the Faraday cup electric signals are produced by the ions.

6. Detection chamber

The current produced is detected by the detector and percentage abundance of each ion is calculated from it.

7. Amplifier

The electric signals are amplified by the amplifier by cascading effect.

8. Recorder

In the recorder the electric current operates a pen which traces peaks on a chart. The intensity of the electric signal is directly proportional to the number of ions striking the detector.

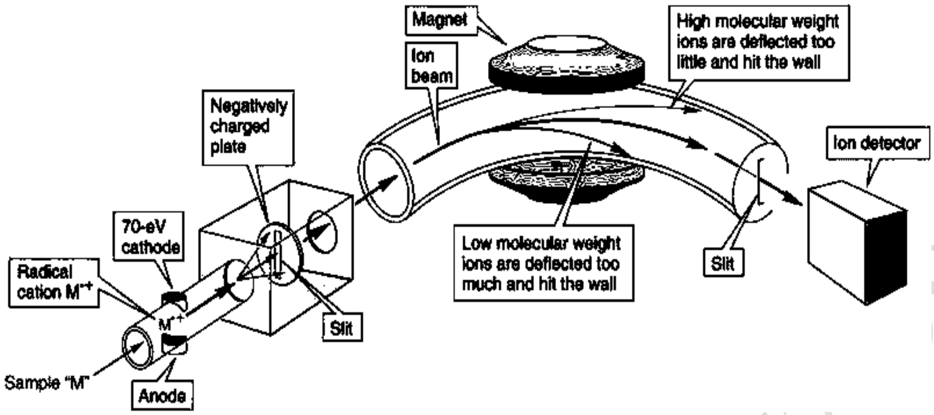
9. Comparison with C_{12}

The whole experiment is performed with C_{12} and comparison of the ions is carried out with C_{12} and hence their atomic masses are calculated.

10. Spectrum or graph

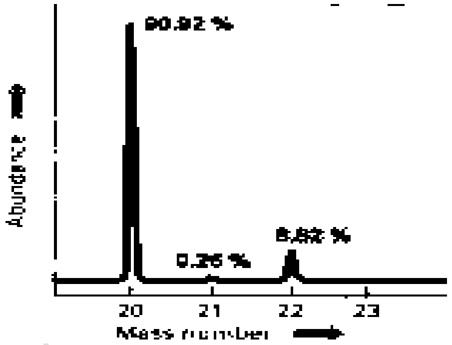
Mass spectrum is a plot of m/e or atomic mass on X-axis and relative abundance on Y-axis. Position of the peak on X-axis tells us about the atomic mass while height of the peak tells us about the percentage abundance on Y-axis.

When a molecule is introduced into mass spectrometer, molecular ion is produced due to the loss of electron. Also rupturing of the bonds takes place and more ions are produced due to fragmentation. The fragmentation pattern of a molecule gives an idea about the structure of the molecule. So mass spectrometry is helpful in the identification of molecular structure.



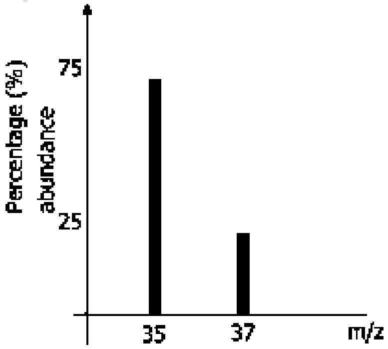
Mass Spectrum of Neon

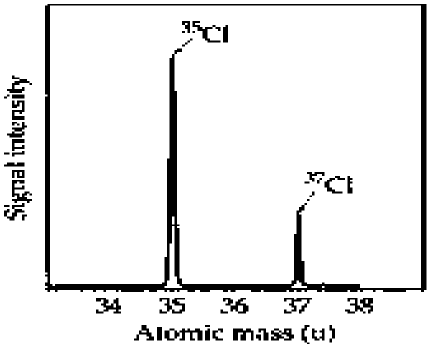
For Neon we get three peaks at atomic masses 20, 21 and 22 which correspond to Ne^{20}, Ne^{21} and Ne^{22}. Ne^{20} is the most abundant and Ne^{21} is the least isotope. The percentage abundance is noted from the height of the peak. The percentage abundance of Ne^{20} is 90.92%, that of Ne^{21} is 0.57% and of Ne^{22} is 8.82%.



Mass Spectrum of Chlorine

Two peaks are obtained for chlorine, the one at 35 and other at 37 on atomic mass scale. The percentage abundance of Cl^{35} is 75% and that of Cl^{37} is 25%.





Applications of Mass-Spectrmetry

1. Identification of substances: Mass spectrum is highly characteristic of a substance. The mass spectra of two identical samples superimpose exactly on each other. By comparing the spectra of an unknown substance with those of known samples, it is possible to identify the unknown samples.

2. Determination of molecular mass: Molecular mass of a compound is given *m/e* value of the molecular ion in the mass spectrum

$$M + e^- \longrightarrow \underset{\text{Molecular ion}}{M^+} + 2e^-$$

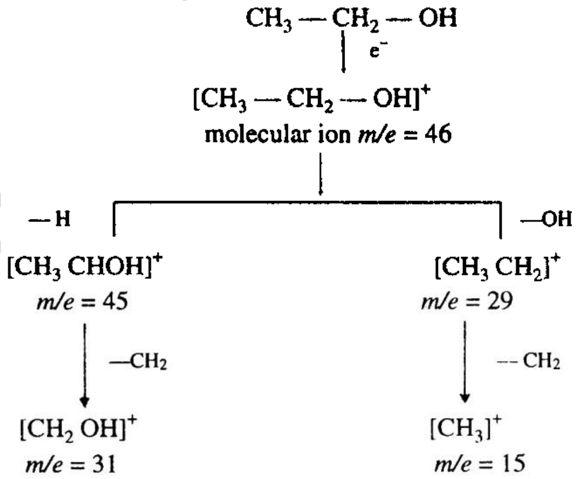
All that has to be done in interpreting the mass spectrum is to identify the M^+ peak (In most cases, it is the base peak). The molecular mass obtained in this way is the mass corresponding to common isotopes of the elements.

Once the molecular mass has been obtained, it is not difficult to arrive at the molecular formula.

3. Determination of molecular structure: Mass spectrum gives us various values of *m/e* which correspond to various fragments of the molecular ion. By establishing the nature of different fragments, we can know about the structure of the compound by joining those fragments together.

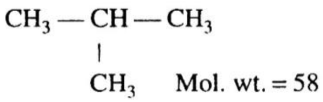
Q: Write down the different fragments with their *m/e* values obtained in the mass spectrum of ethanol.

Ans:



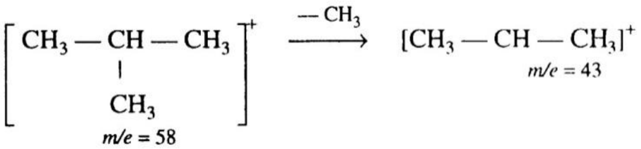
Q: Suggest molecular formulae for the fragment ions obtained from isobutene *m/e* 43, 28, 27.

Ans: The formula of isobutene is



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3 \quad \text{Mol. wt.} = 58$$

(*i*) Difference between the mol. Weights of isobutene and the first fragment is 58–43 = 15. It is equivalent to — CH_3. Hence



$$\left[CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3\right]^+_{m/e\,=\,58} \xrightarrow{-CH_3} \underset{m/e\,=\,43}{[CH_3-CH-CH_3]^+}$$

(*ii*) Difference between the molecular weights of the first and second fragments is 43–28 = 15. Again, it appears that —CH_3 is lost.

$$\underset{m/e\,=\,43}{[CH_3-CH-CH_3]^+} \xrightarrow{-CH_3} \underset{m/e\,=\,28}{[CH_3-CH]^+}$$

(*iii*) The difference between the masses of the second & third fragments is 28–27 = 1. Thus one hydrogen is lost.

$$\underset{m/e\,=\,28}{[CH_3-CH]^+} \xrightarrow{-H} \underset{m/e\,=\,27}{[CH_2-CH]^+}$$

EXERCISE

Q.1. A compound containing C,H and oxygen is found to contain C = 32% and Hydrogen = 4%. Its molecular weight is 150. Find its molecular formula.

Ans. Solution:

$$\%\text{age of C} = 32\%$$
$$\%\text{age of H} = 4\%$$
$$\%\text{age of O} = (100 - \%H + \%C)$$
$$= 100 - 36 = 64\%$$

Molecular mass = 150 g/mol

Molecular formula = ?

First to calculate empirical formula

$$\text{moles of C} = \frac{32}{12} = 2.6\text{moles}$$

$$\text{moles of H} = \frac{4}{1.01} = 3.96\text{moles}$$

$$\text{moles of O} = \frac{64}{16} = 4\text{moles}$$

molar ratio C : H : O

$$\frac{2.6}{2.6} : \frac{3.96}{2.6} : \frac{4}{2.6}$$

$$(1 : 1.5 : 1.5)$$

Multiply by 2 we get

$$\boxed{\begin{matrix} C & H & O \\ 2 & 3 & 3 \end{matrix}}$$

This is the empirical formula of compound.

Now Empirical formula weight =

$$= C_2H_3O_3 = 24 + 3 + 48 = 75g$$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

$$n = \frac{150}{75} = 2$$

$$\text{Molecular Formula} = n \times \text{Empirical formula}$$

$$= 2 \times C_2H_3O_3$$

$$\text{Molecular formula} = \boxed{C_4H_6O_6} \text{ Ans}$$

Q.2. Calculate the empirical formula of the compound that contains C = 27.3% and O = 72.7%.

Ans. Solution:

$$\%\text{age of } C = 27.3\%$$

$$\%\text{age of } O = 72.7\%$$

$$\text{Moles of } C = \frac{27.3}{12} = 2.27$$

$$\text{Moles of } O = \frac{72.7}{16} = 4.54$$

Molar Ratio C : O

$$\frac{2.27}{2.27} : \frac{4.54}{2.27}$$

$$1 : 2$$

$\boxed{CO_2}$ is the empirical formula of compound.

Q.3. What does EMR stand for?

Ans. EMR stands for electromagnetic radiations. Ans ESR stands for electron spin resonance spectroscopy.

Q.4. Write the range and unit of IR radiations.

Ans. The range of IR region is 5000–667cm^{-1}.

Unit is cm^{-1} or $\frac{1}{\text{cm}}$

Q.5. What is meant by stretching, bending vibrations.

Ans. Given in the theory.

Q.6. If a compound shows 100% transmittance, what do we infer from it?

Ans. If a compound shows 100% transmittance then it will have no absorbance..

Q.7. What does λ_{max} mean to you?

Ans. λ_{max} is that particular wavelength in UV-Vis spectroscopy at which a compound shows maximum absorption. Every compound has its own maximum wavelength for absorption and that wavelength must be kept throughout the experiment.

Q.8. Define and explain Bear-Lambert's Law.

Ans. Given in the theory.

Q.9. Why tetramethylsilane is used as a standard in NMR spectroscopy.

Ans. Given in the theory.

Q.10. Give units used in NMR spectroscopy.

Ans. The unit used in NMR spectroscopy is ppm.

Q.11. Explain the use of ionization chamber in mass spectrometer.

Ans. Given in the theory.

Q.12. Multiple Choice Questions.

(1) Which one of the following is quantitative chemical analysis?

(a) Salt analysis	(b)✓ Titration
(c) Flame test	(d) Borax Bead Test

(2) C_2H_6O is the molecular formula of?

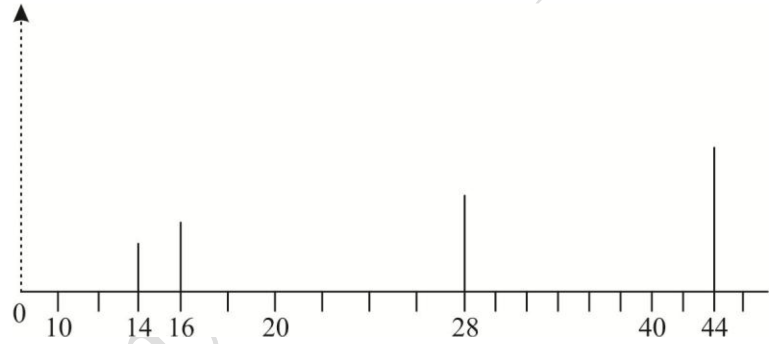
(i) Ethanol (ii) Methanol
(iii) Dimethyl ether (iv) diethyl ether
(a) (i) & (ii) (b) (ii) & (iii)
(c)✓ (i) & (iii) (d) (ii) & (iv)

(3) Which one of the following technique is used for determination of functional group is a compound?
(a)✓ IR Spectroscopy (b) NMR
(c) UV Spectroscopy (d) Mass spectroscopy

(4) Two different compounds will give different absorption peaks in ________ region of IR?
(a)✓ 600–1500cm^{-1} (b) 1500–4000cm^{-1}
(c) 3000–2500cm^{-1} (d) 2500–3500cm^{-1}

(5) Which one of the following methods would be best for finding the identify of an organic compound.
(a) Mass spectroscopy (b) NMR
(c)✓ IR (d) UV

(6) A mass spectrum is shown below.

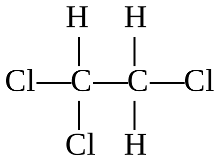


Which one of the following gives complete mass spectrum illustrated?
(a) CO_2 (b) N_2O
(c) C_3H_8 (d)✓ Mixture of CH_4 and N_2

(7) UV ranges from
(a) 400nm–800nm (b) 800–1200nm
(c) 1200–1600nm (d)✓ 10–400nm

(8) Which one of the following hydrocarbon produces an NMR spectrum with more than one peak.
(a) Methane (b) Ethane
(c)✓ Butane (d) Cyclobutane

(9) For the compound below, how many single peaks would you expect in its NMR spectrum?



$$Cl-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-Cl$$

(a)✓ 2 (b) 4
(c) 6 (d) 8

(10) How many types of “NMR” protons are there in butanoic acid?
(a) 8 (b) 2
(c) 6 (d)✓ 4

SHORT QUESTIONS

Q.11.Short Questions:

(i) Why magnesium perchlorate is used as H_2O absorber?

Ans. Magnesium perchlorate is an excellent oxidizing agent and superior drying agent used for the absorption of water. It is dried at a temperature of 180°C under vacuum to remove its water of hydration and to get anhydrous. It is hygroscopic, deliquescent and strongly absorb water but is does not absorb carbon dioxide so it is used as water absorber in combustion analysis method.

(ii) Acetic acid contains only C, H and O. 5gm sample of acetic acid was completely burnt. It gave 3.00gm of water and 7.33gm of CO_2 is produced. What is the mass percentage of each element in acetic acid. Also calculate the empirical formula of acetic acid.

Ans. Solution:

$$\text{mass of Acetic acid} = 5\text{gm}$$

$$\text{mass of } H_2O = 3\text{gm}$$

$$\text{mass of } CO_2 = 7.33\text{gm}$$

$$\text{\%age of elements} = ?$$

$$\text{Empirical formula} = ?$$

$$\text{\%age of C} = \frac{\text{mass of } CO_2}{\text{mass of comp}} \times \frac{12}{44} \times 100$$

$$\%C = \frac{7.33}{5} \times \frac{12}{44} \times 100 = 39.7\%$$

$$\text{\%age of H} = \frac{\text{mass of } H_2O}{\text{mass of comp}} \times \frac{2.02}{18} \times 100$$

$$= \frac{3g}{5} \times \frac{2.02}{18} \times 100$$

$$\%\text{age of H} = 0.6 \times 0.11 \times 100 = \boxed{6.6\%}$$

$$\%\text{age of O} = (100 - \%C + \%H)$$

$$\%\text{age of O} = 100 - 39.7 + 6.6$$

$$\boxed{\%O_2 = 53.7\%}$$

$$\text{Moles of C} = \frac{39.7}{12} = 3.30\text{moles}$$

$$\text{Moles of H} = \frac{6.6}{1.01} = 6.5$$

$$\text{Moles of } O_2 = \frac{53.7}{16} = 3.35$$

$$\begin{array}{lccccc} \text{Molar Ratio} & C & : & H & : & O \\ & \frac{3.30}{3.30} & : & \frac{6.5}{3.30} & : & \frac{3.35}{3.30} \\ & 1 & : & 1.95 & : & 1.01 \end{array}$$

As $1.96 \approx 2$ So

$$\begin{array}{ccc} C & H & O \\ 1 & 2 & 1 \end{array}$$

So empirical formula of acetic acid is $\boxed{CH_2O}$

(iii) Isoprene is a liquid compound that can be polymerized to form synthetic rubber. It is composed of 88.17% carbon and 11.83% hydrogen. Its molar mass is 68.11g/mole. What are its empirical and molecular formulae?

Ans. Solution:

$$\%\text{age of C} = 88.17\%$$

$$\%\text{age of H} = 11.83\%$$

$$\text{Molar mass} = 68.11\text{g / mole}$$

$$\text{Empirical formula} = ?$$

$$\text{Molecular formula} = ?$$

$$\text{Moles of C} = \frac{88.17}{12} = 7.34\text{mole}$$

$$\text{Moles of } H_2 = \frac{11.83}{1.01} = 11.83$$

$$\text{Molar Ratio} = \begin{array}{ccc} C & : & H \\ \dfrac{7.34}{7.34} & : & \dfrac{11.83}{7.34} \\ 1 & : & 1.61 \end{array}$$

Now multiply it with 5 to get the whole number ratio

$$\begin{array}{lccc} \text{Simple ratio} & C & : & H \\ 5 & (1 & : & 1.6) \end{array}$$

$$\boxed{C_5H_8}$$

Empirical formula of isoprene is C_5H_8.

Molecular formula of isoperene = n × E.F

But Empirical formula mass of isoprene $= C_5H_8$

$$= 60 + 8$$

$$= 68g$$

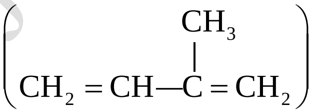
$$n = \frac{\text{M.Formula mass}}{\text{E.Formula mass}} = \frac{68}{68} = 1$$

$$\text{M.Formula} = n \times \text{Empirical formula}$$

$$= 1 \times C_5H_8$$

$$\text{M.formula} = \boxed{C_5H_8}$$

This shows that both empirical and molecular formulae of isoprene are the same.



$$\left(CH_2 = CH - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2 \right)$$

Structure of isoprene

(iv) Why modern method of analysis is superior over classical methods of analysis?

Ans. Given in the theory.

(v) Write down the main functions of IR, UV-visible and NMR spectroscopy?

Ans. Given in the theory.

(vi) What is meant by Beer-Lambert's Law? Explain.

Ans. Given in the theory.

(vii) Why it is necessary to use quartz cuvets in the U.V region, but less expensive glass or plastic cuvets are acceptable in the visible region.

Ans. The quartz cuvets are transparent in the UV region and do not absorb light below 380nm. While glass and plastic cuvets absorb light in the UV region. So glass and plastic cuvets can be used in visible region where these are transparent but not in the UV region. Analysis in the UV region can only be carried out by using quartz cuvets.

LONG QUESTIONS

Q.12.Long Questions:

(i) Define mass spectroscopy. Explain the construction and working of mass spectrometer.

Ans. Given in the theory.

(ii) Differentiate between Atomic emission and absorption spectra.

Ans. Given in the theory.

(iii) What is meant by NMR. Explain chemical shift in different cases.

Ans. Given in the theory.

(iv) Explain in detail spectroscopy. Write down its applications.

Ans. Given in the theory.

(v) Write notes on the following.

(a) IR spectroscopy **(b) UV visible spectroscopy**

Ans. Given in the theory.