

# MODERN METHODS OF CHEMICAL ANALYSIS

## Instrumentation

- Difference between instrumental and non-instrumental methods.
- Advantages of instrumental methods.



Chemistry



Analysis of ore or elements



Precipitation



Distillation

- The separated components can be identified by their colors, boiling or melting points, solubility's in a series of solvents, odors, optical activities or their refractive index.

- Physical properties of the analyte such as conductivity, electrode potential, light absorption or emission, mass-to-charge ratio, fluorescence etc., used for quantitative analysis.
- The techniques like distillation, extraction, and precipitation, etc. were replaced by **high efficient chromatography and electrophoretic techniques** for separation of components of complex mixtures.

## Volumetric analysis:-

In volumetric analysis, the **volume or mass of a standard reagent required to react completely with the analyte** will be determined by carrying out the titrations.

- Titrant (Known Concentration)
- Analyte (Unknown Concentration)
- Equivalence point
- End point

Types of titration:-

- (i) Acid-base
- (ii) Complexometric
- (iii) Precipitation
- (iv) Redox

# Volumetric analysis:-

In volumetric analysis method, an appropriate indicator is to be used.

Sl. No.	Type of volumetric method	Phenomena	Suitable Indicators	Examples
1	<b>Acid – Base titrations:</b>	<b>Neutralization</b>		
	strong acid vs strong base		Phenolphthalein	HCl vs. NaOH
	weak acid vs strong base		Phenolphthalein	CH <sub>3</sub> COOH vs NaOH
	strong acid vs weak base		Methyl orange	HCl vs. NH <sub>4</sub> OH
	weak acid vs weak base		No suitable indicator	CH <sub>3</sub> COOH vs NH <sub>4</sub> OH
2	Complexometric titrations	Complex formation	Eriochrome Black-T (EBT)	Zn (or Ca) vs. EDTA disodium salt
3	Precipitation titrations	Precipitation	Potassium chromate	Cl <sup>-</sup> vs. AgNO <sub>3</sub>
4	Redox titrations	Reduction and oxidation reactions	Diphenylamine	Fe <sup>2+</sup> vs. Cr <sup>6+</sup>

The essential conditions for any volumetric method of analysis are:

- The reaction must proceed to completion rapidly
- The reaction should not be complicated by additional or side reactions
- There should be a detectable change (such as a sharp change in color or formation of a precipitate) in the solution undergoing titration at the stoichiometric endpoint
- A suitable indicator must be available for detecting the endpoint.

## **Gravimetry:-**

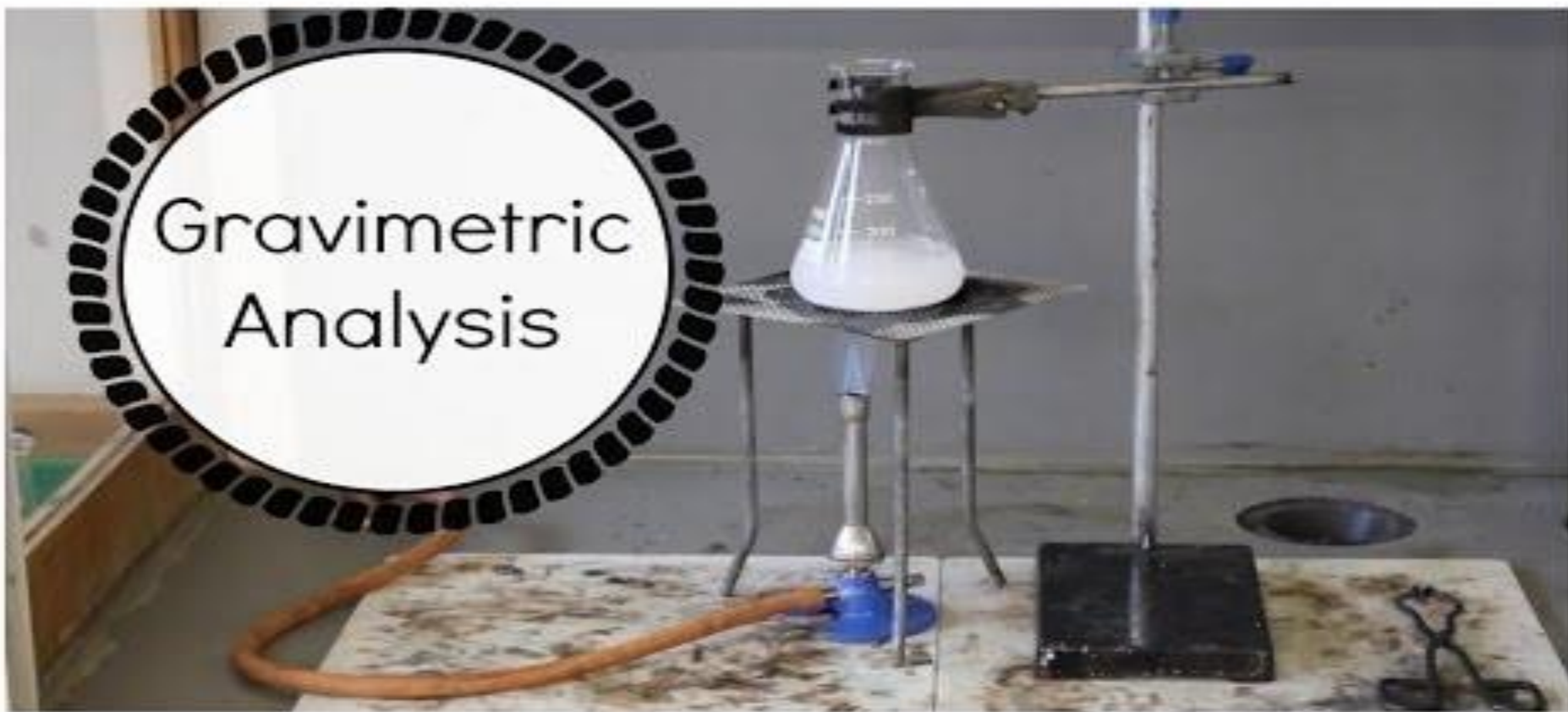
- In gravimetric analyses, the mass of the analyte or some compound produced from the analyte after treating it with appropriate reagent was determined.
- Its broadly classified as volatilization methods and precipitation methods.
- Volatilization methods involve the drying or heating of a sample to determine by weight of the content of volatile and or non-volatile components.
- Precipitation methods involve the formation of a precipitate through an appropriate reaction and weighing the precipitate.

The precipitation methods generally proceed through four steps:

- **Precipitation:** conversion of analyte into a precipitate by an appropriate chemical using a selective reagent
- **Digestion:** allow the precipitate to be in contact with its mother liquor and heat it on a steam bath during which recrystallization occurs, and pure crystals/product is formed.
- **Filtration:** the digested precipitate will be filtered using appropriate Whatman filter papers or sintered glass crucibles, which are to be selected based on the type of precipitate and the residue forming.
- **Washing, drying and weighing:** the filtered precipitate is to be washed with a very dilute solution of its mother liquor then ignited followed by weighing and drying until it gives a constant weight.



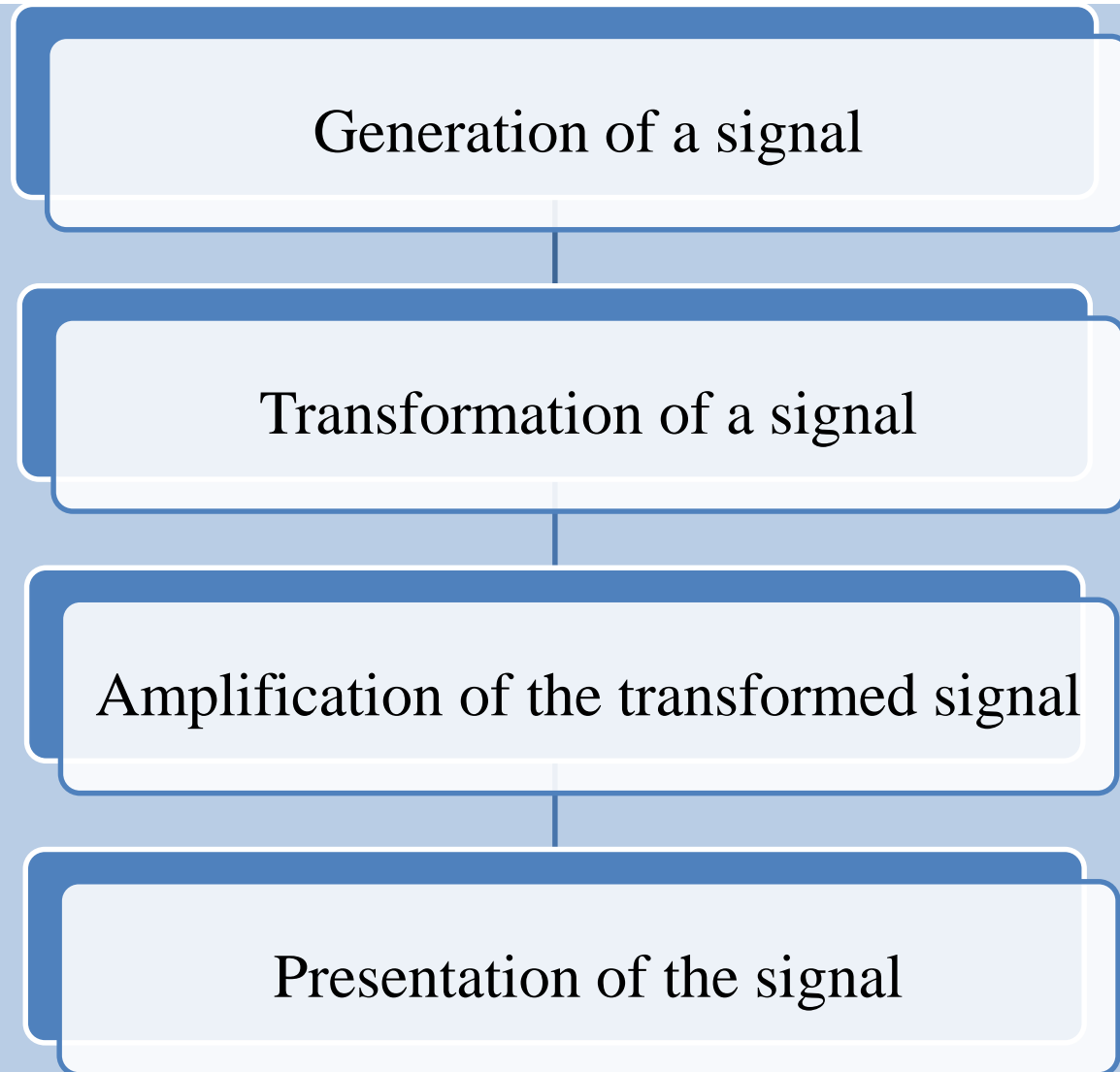
# Gravimetric Analysis



## Function of instruments

- Signal is produced which reflects the chemical or physical property of a chemical system.
- The resulting signal may be used directly or transformed to one of a different nature, amplified and read on some device.

# Flow diagram of Instruments



# Instrumental analysis

```
graph TD; A[Instrumental analysis] --> B[Destructive methods  
(Sample is destroyed)]; A --> C[Non-destructive methods  
(Sample remains unchanged)];
```

Destructive methods  
(Sample is destroyed)

Non-destructive methods  
(Sample remains  
unchanged)

Physical property measured	Instrumental methods based on measurement of property
Absorption of radiation	Spectrophotometry (X-ray, UV, Visible, IR, colorimetry, atomic absorption, NMR and ESR)
Emission of radiation	Emission spectroscopy (X-ray, UV, Visible, flame photometry, fluorescence, radio chemical methods)
Scattering of radiation	Turbidimetry, nephelometry, Raman
Refraction of radiation	Refractometry, interferometry
Diffraction of radiation	X-ray, Electron diffraction methods
Rotation of radiation	Polarimetry, Optical rotatory dispersion, Circular dichroism
Electrical potential	Potentiometry, Chronopotentiometry
Electrical conductance	Conductivity
Electrical current	Polarography, Amperometric titrations
Thermal properties	Thermal conductivity and enthalpy methods
Kinetic methods	Rate of Reaction

- There is a group of instrumental procedures that are adopted for **separation and resolution of closely related compounds**.
- Most of these procedures are based on chromatography, solvent extraction or electrophoresis.

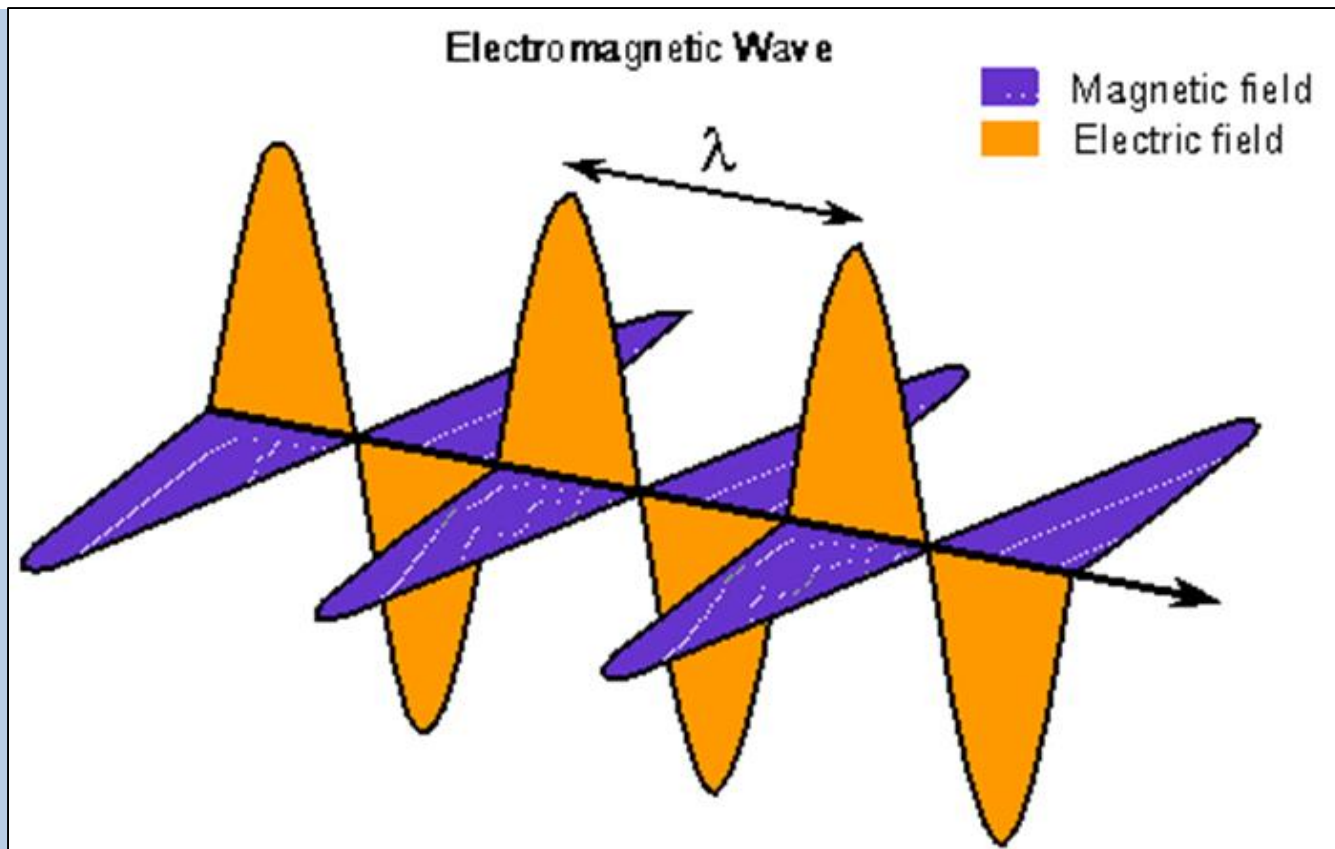
**Spectroscopy:-** It's the branch of science dealing with the study of interaction of electro magnetic radiation with matter.

- Energy is absorbed or emitted by the matter in discrete amount called quanta.

# Electromagnetic radiation

- Electromagnetic radiation is a form of energy that is transmitted through space at an enormous velocity.
  - It doesn't require supporting medium.
  - It is said to have a dual nature, exhibiting both wave and particle characteristics.

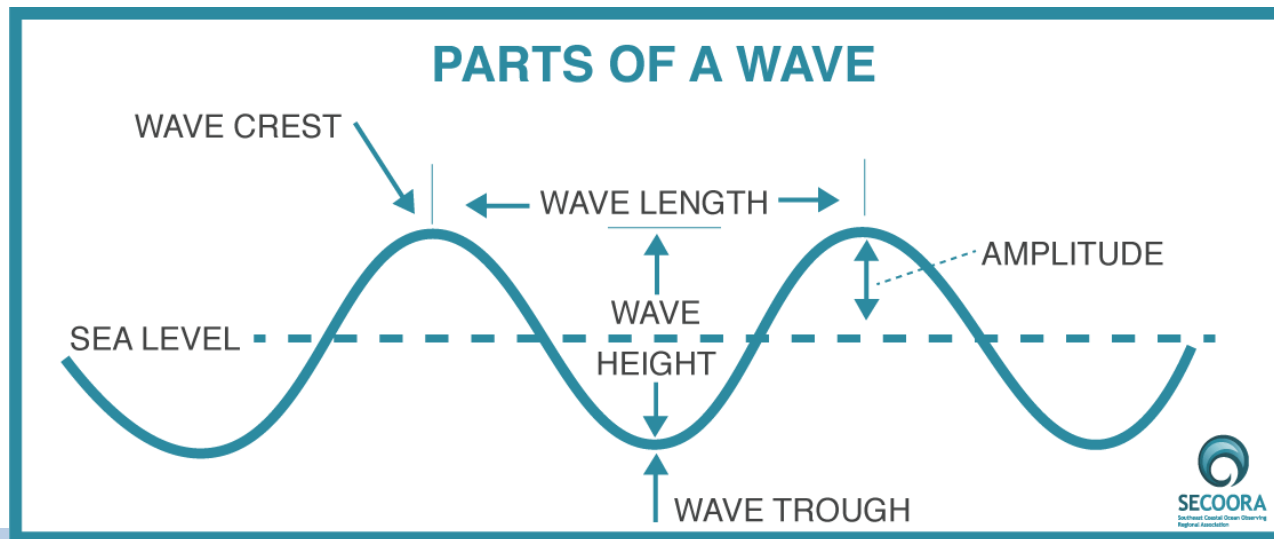
- Electromagnetic radiation is an alternating electrical and magnetic force field in space.
- The two components oscillate in planes perpendicular to each other and perpendicular to the direction of propagation of the radiation.





**Amplitude:-** It is an vector quantity that provides a measure of the electric or magnetic field strength at a maximum point in the wave.

**Period:-** The time required for the passage of successive maxima or minima through a fixed point in space is called a period ( $p$ ) of the radiation.



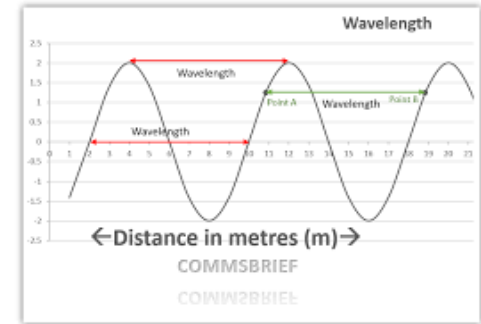
- **Frequency ( $\gamma$ ):** Frequency of an electromagnetic wave is the number of oscillations that occur in 1 second.
- Frequency has units of reciprocal time. Its generally expressed in cycles per Seconds or in Hertz (Hz).
- $1 \text{ Hz} = 1 \text{ cycle s}^{-1}$
- $\gamma = 1/p$  (  $P = \text{Period}$  )
- Depends on **source**

**Wavelength ( $\lambda$ ):-** It is the distance between two equivalent points on successive electromagnetic wave.

$$1\lambda\text{m} = 10^{-4}\text{ cm} = 10^{-3}\text{ cm} = 10^{-6}\text{ m}.$$

**Wavenumber ( $\bar{\gamma}$ ) :-** Frequency as the wave number which is defined as the number of waves per centimeter in vacuum.

$$\bar{\gamma} = \frac{1}{\lambda}$$



**Velocity(c):-** The velocity is dependent upon the **medium** through which radiation is passing. It has the unit  $\text{cm s}^{-1}$ .

**wavelength** x frequency = velocity

$$\lambda \times \gamma = v \text{ (c)}$$

# Relation between Frequency, velocity and wavenumber

$$\bar{\gamma} = \frac{1}{\lambda} \dots\dots\dots (a)$$

$$\text{but } \gamma = \frac{C}{\lambda} \dots\dots\dots (1) \quad [\text{since } c = \gamma \times \lambda]$$

$$\frac{1}{\lambda} = \frac{\gamma}{C} \dots\dots\dots (2)$$

$$\lambda = \frac{C}{\gamma} \dots\dots\dots (3)$$

Equation (a) and (2) are equal

$$\bar{\gamma} = \frac{\gamma}{C} \text{ (or) } \gamma = C\bar{\gamma} \quad [C = 3 \times 10^8 \text{ ms}^{-1}]$$

# Particle properties of electromagnetic radiation

- Wave nature of electromagnetic radiation fails to explain many phenomena like **photoelectric effect**.
- To explain that, it's assumed that the electromagnetic radiation consists of a stream of discrete packets (particles) of pure energy, called photons or quanta.

$$E = h\gamma \dots\dots(1)$$

$$\gamma = \frac{C}{\lambda} \dots\dots(2)$$

$$E = \frac{hC}{\lambda} \dots\dots(3)$$

$$E = hC\bar{\gamma} \dots\dots(4)$$

Give a brief **Introduction** to **Spectroscopy**.

Interaction of Electromagnetic Waves with Matter

Absorption

Emission

Spectroscopy



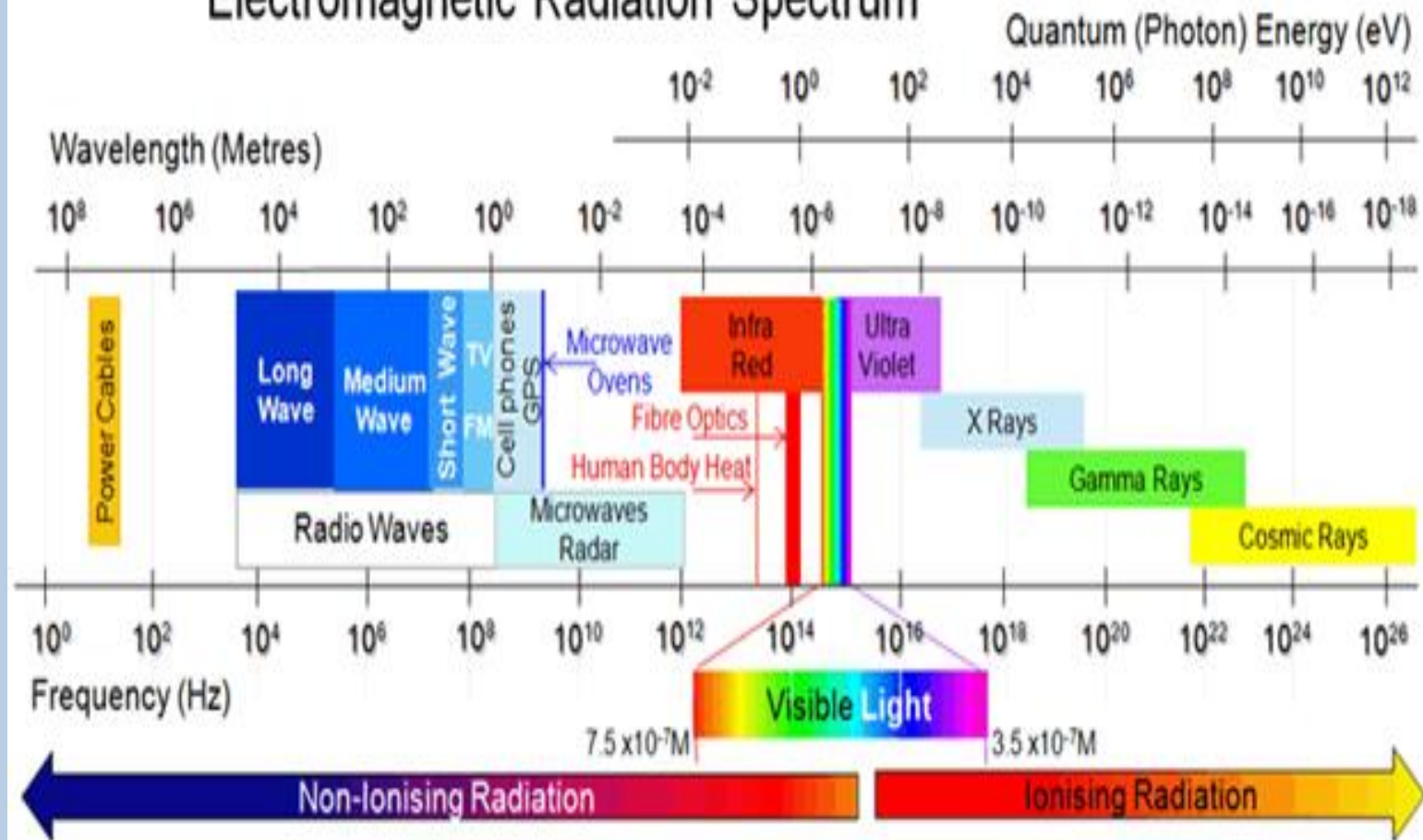
Particle

**Keywords**

- *Interaction*
- *Electromagnetic Radiation*
- *Matter*

**SPECTROSCOPY** is the **Study** of *Interaction* of *Electromagnetic Radiation* with *Matter*.

# Electromagnetic Radiation Spectrum



# Types of spectroscopy

## (i) $\gamma$ -ray region:-

$$\nu = 3 \text{ EHz to } 300 \text{ EHz (1 exa Hz} = 10^{18} \text{ Hz)}$$

$$\lambda = 100 \text{ pm to } 1 \text{ pm}$$

- $\gamma$  rays have sufficient energy to bring about nuclear transformation.
- The  $\gamma$ -ray resonance spectroscopy is known as Mossbauer Spectroscopy.

## (ii) X-ray region:-

$$\nu = 30 \text{ PHz to } 3 \text{ EHz}$$

$$\lambda = 10 \text{ nm to } 100 \text{ pm}$$

- The energy of X-rays is sufficient to cause the transitions of core electrons of atoms and molecules.
- X-ray spectroscopy and X-ray photoelectron spectroscopy (XPS) is associated with the X-ray region.



- ***Visible and Ultraviolet region:*** These are further made up of the following regions.

*Vacuum ultraviolet: 1 – 800 nm*

*Ultraviolet: 180 – 400 nm*

*Visible: 400 – 750 nm*

- ***Infrared region:*** This region has been further divided into the following sub-regions.

*Infrared (near) : 0.7 – 2.5  $\mu$*

*Infrared: 2.5 – 15  $\mu$*

*Far infrared: 15 – 200  $\mu$*

***Microwave region:*** (0.1 mm to 1 cm wavelength) This region corresponds to changes in the rotation of molecules. Separations between the rotational levels of molecules are of the order of hundreds of joules per mole.

**Radiofrequency region:**

(10 m – 1 cm wavelength) The energy change involved in this region arises due to the reversal of a spin of nucleus or electron. This is of the order 0.001 – 10 J/mole.

## **INTERACTION OF EMR WITH MATTER**

- When EMR passes through matter, a variety of phenomena may occur.
- If the photons of radiation possess the appropriate energies, they may be absorbed by the matter and result in electronic transitions, vibrational changes or rotational changes or combination of these.
- After absorption, atoms or molecules become excited. They give out energy quickly either by losing energy in the form of heat or by re-emitting EMR.

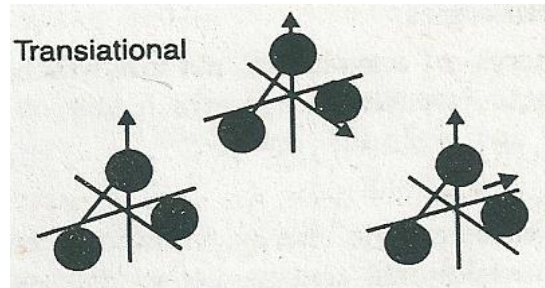
## **INTERACTION OF EMR WITH MATTER**

- The portion of EMR which passes into the matter, instead of being absorbed, may undergo scattering or reflection or may be re-emitted at the same wavelength or a different wavelength.
- When EMR is neither absorbed nor scattered, it may change orientation or polarization.
- In some cases, the molecules after absorbing radiation become excited, but they do not lose energy very quickly but with some delay.
- In such cases, the energy is re-emitted as radiation usually of longer wavelength than was initially absorbed. This phenomenon is called as fluorescence.
- If in some cases, there is a detectable time delay in re-emission, the phenomena are termed as phosphorescence.

# Molecular Spectroscopy

A molecule may possess internal energy which can be subdivided into three classes.

$$E_{\text{Total}} = E_{\text{Trans}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{ele}}$$



## Translational energy:-

- Energy is associated with the uniform velocity of a molecule.
- This is generally described with respect to the centre of mass of molecule.

$$E_t = \frac{1}{2} mv^2$$

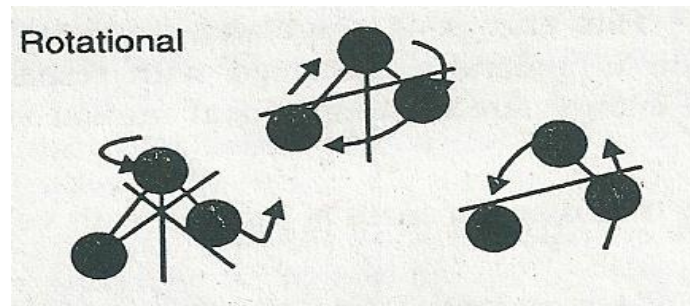
Due to translational motion, the molecule is free to move in the three perpendicular directions x,y and z.

**Rotational energy:-** This type of energy is associated with the overall rotation of the molecule with the atoms considered as fixed point masses.

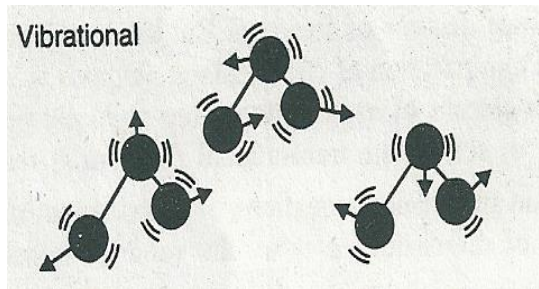
$$E_{\text{rot}} = \frac{1}{2} I \omega^2$$

$I$  = Moment of Inertia

$\omega$  = Angular velocity



**Vibrational energy:** This type of energy is associated with the oscillation of atoms which are considered as point masses about equilibrium positions.



#### **(d) Electronic energy:-**

- The energy required to move the electron from the ground state to an excited state varies with the type of molecular bond in which the electron exists.
- Further, the vibrational and rotational energies of the molecules are added to the electronic energies.

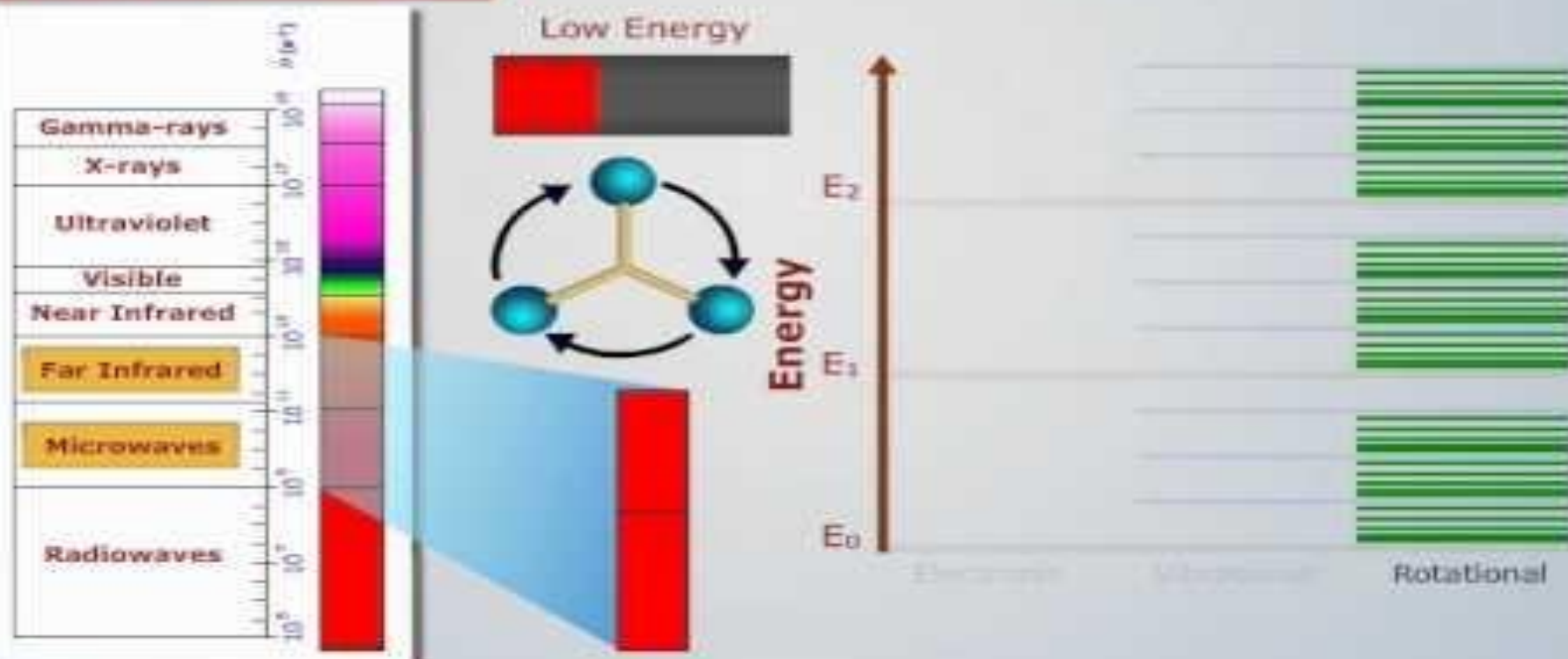
$$E_{\text{electronic}} \gg E_{\text{vibrational}} \gg E_{\text{rotational}} \gg E_{\text{translational}}$$

Since the translational energy is negligibly small, we can write the Born-Oppenheimer approximation as

$$E_{\text{total}} = E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{electronic}}$$

# What are **Different Types** of **Molecular Spectra**

## ROTATIONAL SPECTRA





# Interaction of Electromagnetic radiation with matter

- If the photons of radiation absorbed or emitted by matter may result in electronic, vibrational, rotational changes or combination of these.

Portion of electromagnetic radiation = being absorbed

Portion of electromagnetic radiation = being reemitted.

- When electromagnetic radiation is neither absorbed not scattered, it may undergo changes .

Reemitted radiation = Fluorescence.

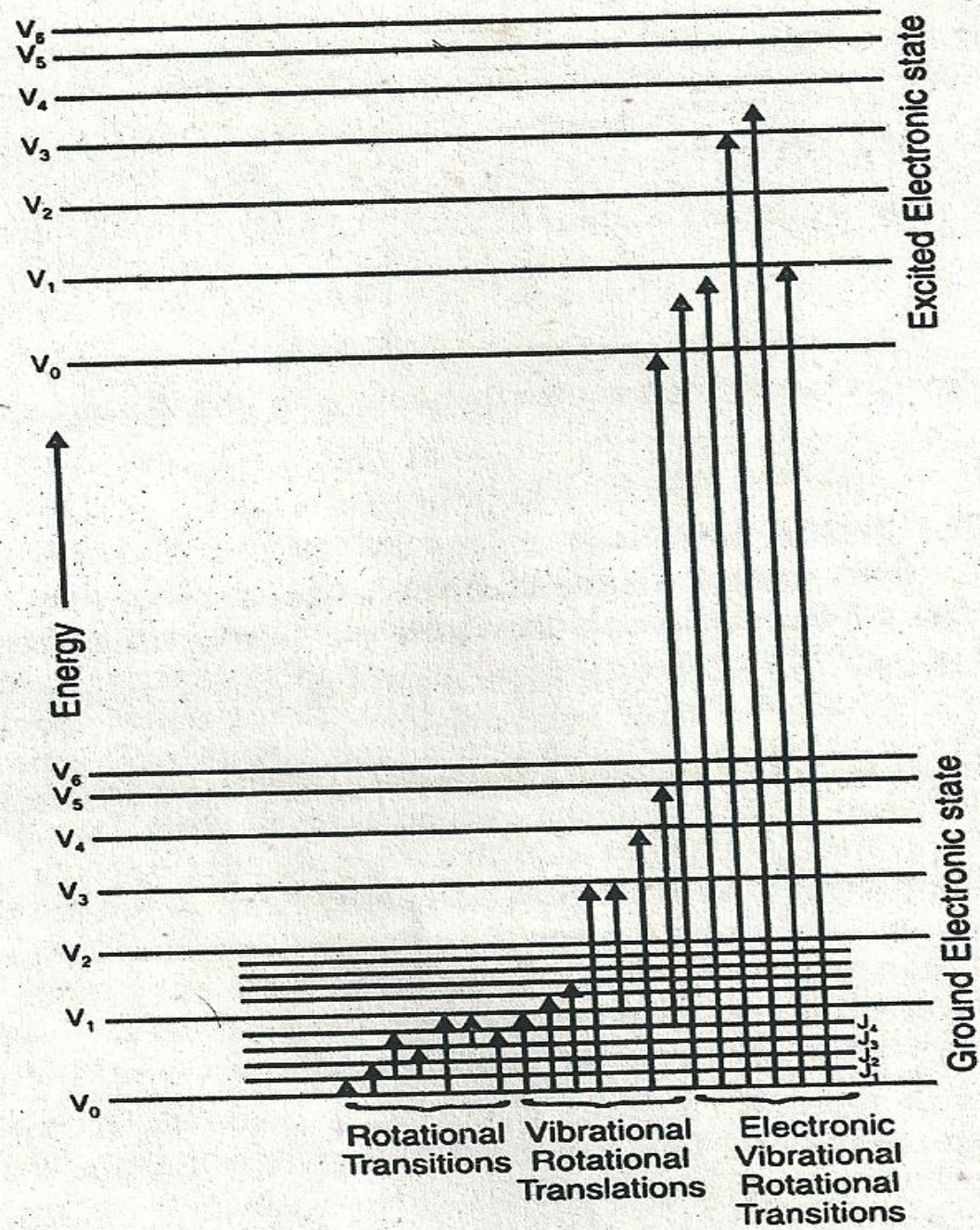
Delayed emission = Phosphorescence.

- **Rotational (Microwave) spectra:** These spectra result from transitions between the rotational energy levels of a gaseous molecule on the absorption of radiations falling in the microwave region.
- These spectra are shown by the molecules which possess a permanent dipole moment, e.g., HCl, CO, H<sub>2</sub>O vapor, NO, etc.
- Homonuclear diatomic molecules like H<sub>2</sub>, Cl<sub>2</sub>, etc., and linear polyatomic molecules such as CO<sub>2</sub> which do not possess a dipole moment, do not show microwave spectra.
- Microwave spectra occur in the spectral range of 1 – 100 cm<sup>-1</sup>

- **Vibrational and vibration-rotation (Infrared) spectra:**
- These spectra originate from transitions induced between the vibrational energy levels of a molecule on the absorption of radiations belonging to the infrared region.
- IR spectra are shown by molecules when vibrational motion is accompanied by a change in the dipole moment of the molecule.
- These spectra occur in the spectral range of  $400 - 4000 \text{ cm}^{-1}$ .

## Electronic spectra:

- Electronic spectra arise from an electronic transition in a molecule by absorption of radiations falling in the visible and ultraviolet regions.
- While electronic spectra in the visible region span  $12,500 - 25,000 \text{ cm}^{-1}$ , those in the ultraviolet region span  $25,000 - 70,000 \text{ cm}^{-1}$ .
- Since vibrational and rotational transitions invariably accompany electronic transitions in a molecule, the electronic spectra of molecules are highly complex.



Two Electronic Levels are Shown

## **Spectrophotometry:**

- When a monochromatic light of initial intensity  $I_0$  passes through a solution in a transparent vessel, some of the light is absorbed so that the intensity of the transmitted light  $I$  is less than  $I_0$ .
- There is some loss of light intensity from scattering by particles in the solution and reflection at the interfaces, but mainly from absorption by the solution.
- The relationship between  $I$  and  $I_0$  depends on the path length of the absorbing medium,  $b$  and the concentration of the absorbing solution,  $c$ .



### **Lambert's law:-**

When a ray of monochromatic light passes through an absorbing medium, its intensity decreases exponentially as the length of the medium absorbing increases.

### **Beer's law:-**

When a monochromatic light passes through an absorbing medium, its intensity decreases exponentially as the concentration of the medium absorbing increases.

### **Transmittance:-**

The ratio of intensities is known as the transmittance (T), and this is usually expressed as the percentage.

The probability that the photons of a beam of intensity **I** will be absorbed by the sample is directly proportional to the concentration and thickness of the absorbing solution, and it can be expressed as

$$dI/I = -\alpha c dx \dots\dots\dots (2)$$

Where  $dI$  = Change in intensity produced by absorption of radiation

$dx$  = Thickness of the medium

$C$  = Concentration of solution

$\alpha$  = Proportionality constant

$-$  = reduction in intensity

Integration of Eq 2. between limits  $I = I_0$  at  $x = 0$  and  $I = I$  &  $x = b$  gives,



$$\ln (I/I_0) = 2.303 \log (I/I_0) = - \alpha bc \dots\dots\dots (3)$$

According to equation 3, the intensity of a beam of monochromatic radiation decreases exponentially with an increase in the thickness  $x$  and the concentration  $c$  of the medium. This is **Beer-Lambert law**.

➤ Putting  $\alpha/2.303 = \varepsilon$  and defining  $\log (I_0/I)$  as absorbance,  $A$  of the solution, we get

$$A = \log (I_0/I) = \varepsilon bc \dots\dots\dots (4)$$

Where  $\varepsilon$  = Extinction coefficient of the medium

It is the characteristic of the solute and depends on the nature of the solvent, temperature, and wavelength of the radiation employed.

When the concentration is expressed in  $\text{mol dm}^{-3}$  and the path length in cm, then  $\epsilon$  is expressed in  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  is referred as molar absorption coefficient or molar extinction coefficient.

## Limitations of the Beer-Lambert law:

- Chemical and instrumental factors limit the linearity of the Beer-Lambert law. The probable causes of nonlinearity are:
- Deviations in absorptivity coefficients at *high concentrations* ( $>0.01M$ ) due to electrostatic interactions between molecules nearby
- Scattering of light due to particulates in the sample
- Fluorescence or phosphorescence of the sample
- Changes in refractive index at a high analyte concentration
- Shifts in chemical equilibria as a function of concentration
- Non-monochromatic radiation, deviations can be minimized by using a relatively flat part of the absorption spectrum such as the maximum of an absorption band
- Stray light

### **Numerical:**

- The molar extinction coefficient of phenanthroline complex of iron (II) is  $1200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , and the minimum detectable absorbance is 0.01. Calculate the minimum concentration of the complex that can be detected in the experiment if the path length is 1.00 cm.

$$A = \epsilon bc$$

$$c = A/\epsilon b = 0.01 / 1.00 * 1200$$
$$= 8.33 \times 10^{-6} \text{ M}$$

# PROBLEMS

(1) Calculate the energy in Joule per quantum calories per mole, and electron volts on photons of wavelength  $3000 \text{ \AA}$ .

$$E = h\nu$$

$$E = \frac{hc}{\lambda}$$

$$h = 6.62 \times 10^{-34} \text{ Joule.Sec} \quad c = 3 \times 10^8 \text{ ms}^{-1}$$

$$\lambda = 3000 \text{ \AA} = 3000 \times 10^{-8} \text{ cm}$$

$$E = 6.62 \times 10^{-19} \text{ Joule}$$

$$E = Nh \gamma$$

$N$  = Avogadro's number

$$\text{Energy per mole} = x/4.184 \text{ Joule cal}^{-1}$$

$$= x/23060 \text{ cal mol}^{-1}\text{eV}^{-1}$$

(2) Calculate  $\bar{\gamma}$ ,  $\gamma$  and E for typical ultraviolet radiation of wavelength  $2000 \text{ \AA}$ . Express the value of E in ergs

$$E = h\gamma = \frac{hc}{\lambda} = hc \bar{\gamma}$$

$$E = h \gamma = 6.62 \times 10^{-27} \text{ erg}\cdot\text{sec} \times 1.5 \times 10^{15} \gamma \text{cycles sec}^{-1} \\ = \text{erg.}$$

(3) Calculate the wave number of radiation whose wavelength is  $4\text{ }\mu\text{m}$

$$1\text{ }\mu\text{m} = 10^{-4}\text{ cm}$$

$$4\text{ }\mu\text{m} = 4 \times 10^{-4}\text{ cm}$$

$$\text{Wavenumber } \bar{\gamma} = 1/\lambda = 1/4 \times 10^{-4}\text{ cm} = 2500\text{ cm}^{-1}$$



(4) Calculate the frequency of radiation whose wavelength is 400 nm. Express this wavelength in wavenumber

$$\text{Wavelength } \lambda = 400 \text{ nm} = 400 \times 10 \text{ \AA} = 400 \times 10 \times 10^{-8} \text{ cm} = 4 \times 10^{-5} \text{ cm}$$

$$\text{Frequency, } \gamma = C/\lambda = 3 \times 10^{10} \text{ cm s}^{-1} / 4 \times 10^{-5} \text{ cm} \\ = 7.5 \times 10^{-4} \text{ Hz}$$

$$\text{Wavenumber, } \bar{\gamma} = 1/\lambda = 1/4 \times 10^{-5} \text{ cm} = 25000 \text{ cm}$$

(5) Calculate the frequency of the radiation in Hertz of wavelength 350 nm.

$$\gamma = c/\lambda, c = 3 \times 10^{10} \text{ cm sec}^{-1}, \lambda = 3500 \times 10^{-8} \text{ cm}$$

$$\gamma = 3 \times 10^{10} / 3500 \times 10^{-8}$$

$$= 8.57 \times 10^{14} \text{ Hertz}$$

(6) What is the wavenumber of the lines of frequency  $4 \times 10^{14}$  Hertz?

$$\bar{\gamma} = \gamma / \lambda, = 4 \times 10^{14} / 3.0 \times 10^{10} = 1.33 \times 10^4 \text{ cm}^{-1}$$

(7) Calculate the wavenumber of the radiation if the frequency is  $2.06 \times 10^{14}$  Hertz.

$$\gamma = C/\lambda$$

$$\text{But } \bar{\gamma} = 1/\lambda$$

$$\begin{aligned}\text{Therefore } \bar{\gamma} &= \gamma/C = 2.06 \times 10^{14} / 3.0 \times 10^{10} \\ &= 6866 \text{ cm}^{-1}\end{aligned}$$

(8) Calculate quantum of energy, E in joules, J mol<sup>-1</sup>

$$E = hc/\lambda$$

$$E = 6.626 \times 10^{-34} \text{ Js} \times 3.0 \times 10^8 \text{ ms}^{-1} / \lambda \times 10^{-9} \text{ m}$$

$$E(\text{J}) = 1.9878 \times 10^{-16} / \lambda (\text{nm}) \text{ J}$$

$$\begin{aligned} E (\text{J mol}^{-1}) &= 1.9878 \times 10^{-16} \text{ J} / \lambda (\text{nm}) \times 6.023 \times 10^{23} \text{ mol}^{-1} \\ &= 1.2 \times 10^8 / \lambda (\text{nm}) \text{ J mol}^{-1} \end{aligned}$$

## Online address for you tube videos

- <https://www.youtube.com/watch?v=cxhA2p0dB-I>
- <https://www.youtube.com/watch?v=dkARLSQWHH8>
- <https://www.youtube.com/watch?v=vt3WO2rf9Qs>

## References

- (1) SPECTROSCOPY (ATOMIC AND MOLECULAR) :- GURDEEP R. CHATWAL, SHAM K. ANAND
- (2) INSTRUMENTAL METHODS OF CHEMICAL ANALYSIS :- GURDEEP R. CHATWAL, SHAM K. ANAND
- (3) FUNDAMENTALS OF MOLECULAR SPECTROSCOPY :- COLIN N. BANWELL AND ELAINE E. McCASH
- (4) FUNDAMENTALS OF ANALYTICAL CHEMISTRY:- SKOOG, WEST, HOLLER, CROUCH
- (5) ELEMENTARY ORGANIC SPECTROSCOPY:- Y.R. SHARMA