UNIT

5

GREEN CHEMISTRY AND COMPOSITES

PART-A
SHORT QUESTIONS WITH SOLUTIONS

Q1. Explain the term 'Green Chemistry'.

Answer :

Green chemistry is a new branch of chemistry that deals with the production of more eco-friendly and efficient products. It makes use of maximum possible resources to reduce the production of hazardous substances during chemical synthesis of compounds.

Q2. Write notes on need of Green Chemistry.

Answer :

Now-a-days there is a huge development in science and technology which benefits the mankind in various aspects.

With the advent of scientific development chemistry (the products of chemical industry) has become a prominent part of our daily needs. The needs includes water treatment, waste disposal method, detergents, petroleum additives, polymers, material science, agricultural pesticides and fungicides etc. These chemical developments leads to new environmental problems and can cause harmful side effects and potential hazards. Hence, to overcome the above aspects there is a need of 'green chemistry' which deals with greener chemical products.

Green chemistry is not just the need, but also a demand keeping in view of the rise in global temperature due to global warming by following the benchmark set by the principles of green chemistry. It not only helps us to fight environmental pollution, but also undo the harm done to the environment throughout the ages by the mankind.

Q3. Write the principles of Green chemistry.

Answer :

The principles of Green Chemistry are,

(i) Prevention of Waste
(ii) Atom Economy
(iii) Safer Synthesis
(iv) Safer Chemicals
(v) Safe Solvents and Auxiliaries
(vi) Energy Efficiency
(vii) Renewable Feed Stock
(viii) Fewer Chemical Derivatives
(ix) Catalysis
(x) Design for Degradation
(xi) Real-time Analysis
(xii) Safer Chemistry for Accidental Prevention

Q4. Write notes on ionic liquids as green solvents for green synthesis.

Answer :

Ionic liquids are used as virtually green solvents in order to overcome the health and environmental problems caused by the solvents like DMF, CFC, methylene etc. These lead to ozone depletion, carcinogenic effects and are toxic in nature.

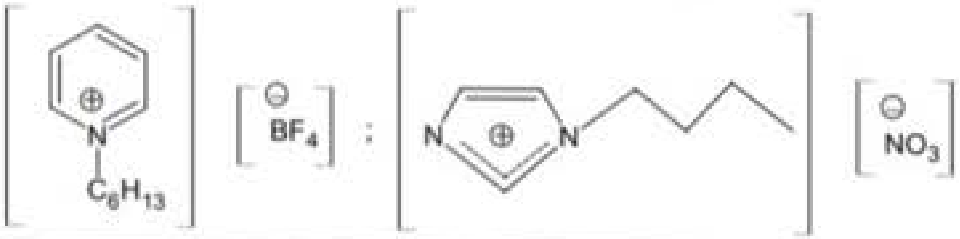
Ionic liquids are organic salts and have a melting point below 100°C. These are of two types,

(i) Simple ionic liquids

(ii) Binary liquids.

Example

Ethylammonium nitrate is a simple example of ionic liquid with melting point 12°C.



Q5. Write a short note on the following releting to green chemistry.

(i) Atom economy

(ii) Catalysis

Answer :

(i) Atom Economy

It is an important concept in the philosophy of green chemistry which encourages chemists to design synthetic methods by which maximum proportion of starting material can be incorporated into the final product. In simpler analogy, syntheses Atom economy is defined as,

$$\% \text{ Atom economy} = \frac{\text{Molecular weight of desired product} \times 100}{\text{Molecular weight of all reactants}}$$

(ii) Catalysis

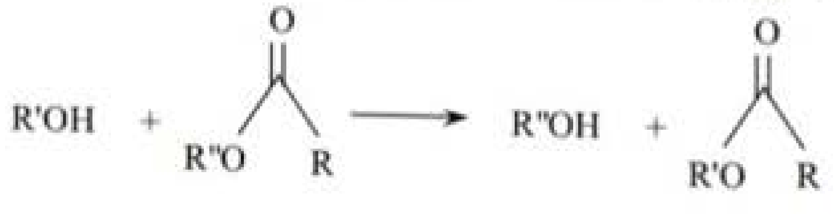
Waste generation must be minimized by using catalytic reagents and avoiding stoichiometric reagents. This is because catalysts are effective in small amounts and carry out a single reaction many times, whereas stoichiometric reagents are required in excess amounts and carry out reaction only once.

Q6. What is trans-esterification? Explain.

Answer :

Trans-esterification is a chemical reaction for conversion of vegetable oil to biodiesel. In this process, vegetable oil is chemically reacted with alcohol like methanol or ethanol in the preference of catalyst like lye. After the chemical reaction various components of vegetable oil break down to form new compounds.

The triglycerides are converted into alkyl esters, which is the chemical name of biodiesel. If methanol is used in the chemical reaction, methyl esters are formed while if ethanol is used than ethyl esters are formed. Both these compounds are biodiesel fuels with different chemical combination. In the chemical reaction alcohol replaces glycerin.



Alcohol + Ester ⟶ Different alcohol + Different ester

PART-B

ESSAY QUESTIONS WITH SOLUTIONS

5.1 GREEN CHEMISTRY

5.1.1 Concept, Principles of Green Chemistry – Atom Economy, Catalysis and Examples of Clean Technology

Q10. Explain the term green chemistry. What are its objectives?

Answer :

Green Chemistry

For answer refer Unit-5, Q1.

Objectives of Green Chemistry

The major objectives of green chemistry are,

(i) To minimize the generation of chemical waste by proper selection and design of chemical products.

(ii) To generate easy degradable products.

(iii) To obtain better atom economy through appropriate reduction of by-products formed during the processes.

(iv) To minimize the use of non-renewable resources.

(v) To enhance the use of renewable resources (like plant based raw materials).

Q11. Write short notes on 'Green house concept'.

Answer :

The concept of green house refers to a sustainable house which is used for the efficient growth of plants. This house is also known as 'Glass house'.

Green house can vary from small sized glass houses to large-sized houses. These include equipments such as screening installations, heating, cooling and lighting systems. The roofs and walls of a green house are generally constructed using glass and plastics, because of their heat absorbing capabilities.

Sun energy entering into the green house is absorbed by the plants and soil. This trapped heat maintains the green house warm. Proper ventilation during the construction helps to maintain desired temperatures in (of different sizes) sized green houses.

Q12. Explain the principles of green chemistry.

Answer : June-17, Q15(b)

In 1991 under the US Environmental Protection Agency's (EPA's) green chemistry program, the goal of green chemistry was identified as "the design of chemical product of processes that reduce or eliminate the use or generation of hazardous substances". To help achieve this goal. Anastas and Warner in 1998 gave the following twelve principles of green chemistry.

1. **Prevention of Waste**

   According to this principle, reducing the amount of waste generated at source is better than treating this waste after it has been formed.

2. **Atom Economy**

   It is an important concept in the philosophy of green chemistry which encourages chemists to design synthetic methods by which maximum proportion of starting material can be incorporated into the final product. In simpler analogy, syntheses Atom economy is defined as,

$$\% \text{ Atom economy} = \frac{\text{Molecular weight of desired product} \times 100}{\text{Molecular weight of all reactants}}$$

3. **Safer Synthesis**

   According to this principle, chemical processes that use and produce least hazardous chemical, substances must be designed.

4. **Safer Chemicals**

   Chemical substances that perform the desired function and possess little or no toxicity must be designed.

5. **Safe Solvents and Auxiliaries**

   Use of solvents, separation agents and other auxiliary chemicals must be avoided and if used, they must be render non-toxic.

6. **Energy Efficiency**

   The environmental and economic effect of use of energy in chemical synthesis must be identified and minimized. To achieve this, chemical reactions must be run at ambient temperature and pressure conditions whenever possible.

7. **Renewable Feed Stock**

   Stating materials that are renewable rather than depletable must be used whereever possible.

8. **Fewer Chemical Derivatives**

   Use of blocking or protecting groups or any temporary modifications of processes must be avoided, if possible to eliminate or minimize waste generation.

9. **Catalysis**

   Waste generation must be minimized by using catalytic reagents and avoiding stoichiometric reagents. This is because catalysts are effective in small amounts and carry out a single reaction many times, whereas stoichiometric reagents are required in excess amounts and carry out reaction only once.

10. **Design for Degradation**

    Chemical products that breakdown into non-toxic substances after use must be designed to avoid accumulation in the environment.

11. **Real-time Analysis**

    Analytical methods that provide in-process real time monitoring and control during synthesis must be developed and adopted to reduce or eliminate the formation of by-products.

12. **Safer Chemistry for Accidental Prevention**

    The potential for chemical accidents like explosions, fires incidents and release of toxic chemicals in to the environment must be minimized by using safer substances,

    Tang et. al beautifully condensed the above principles of green chemistry as PRODUCTIVELY.

P.	Prevent wastes
Q.	Renewal materials
O.	Omit derivatization steps
D.	Degradable chemical products
U.	Use safe synthetic methods
C.	Catalytic reagents
T.	Temperature and pressure ambient
I.	Inprocess monitoring
V.	Very few auxiliary substances
E.	E-factor, maximize feed in product
L.	Low toxicity of chemical products
Y.	Yes its safe.

Q13. Give a brief account on the 'methods of green synthesis, using green chemistry.

OR

Give any two examples of clean technology.

(Refer Only Two Methods)

Answer : Dec.-17, Q10

Methods of green synthesis employ principles and goals of 'Green Chemistry' to produce eco-friendly and efficient products. It maximizes the production of desired substances and reduces the hazardous by-products produced during the synthesis processes.

The major innovations made in green chemistry to enhance the overall synthesis process are,

(i) Alternative feedstocks or starting materials

(ii) Alternative reagents or transformation

(iii) Alternative reaction conditions or solvents

(iv) Alternative final products or target molecules.

(i) **Alternative Feedstocks or Starting Materials**

Use of eco-friendly feedstock (raw material used in industrial process) can minimize the risks to human health and environment. However, utilization of such feedstocks significantly increases the cost of the process. Thus, incorporating methods of green synthesis can make the process economical.

For instance, use of chlorinated aromatics (as feedstock) in the production of aromatic amines is very much hazardous to environment. This feedstock, if replaced with a green process of 'Nucleophilic substitution for hydrogen' can significantly minimize risks to environment.

(ii) **Alternative Reagents or Transformation**

Use of toxic reagents in the production or transformation of chemical substances can be replaced by green substances to achieve goals of green chemistry.

For instance, use of dimethyl sulphate in methylation of several chemicals can be highly toxic and crocinogenic (i.e., cancer causing agent). However, dimethyl/carbonate (a green substance) can significantly replace the toxic dimethyl sulphate to make the process environmentally clean. This green product can even eliminate the production of salt during the transformation processes.

(iii) Alternative Reaction Conditions or Alternative Solvents

Associated substances such as solvents can significantly contribute towards the pollution of environment during synthesis and formulation of products. These toxic solvents can be replaced by traditional solvents such as super-critical fluids, aqueous solvents, ionic liquids and reduced hazard organic solvents.

For instance, use of super-critical fluids offers an advantage of tunable properties, low cost and innocuous (harmless) products. Carbon dioxide (CO_2) is the most common super-critical fluid used in green chemistry.

Furthermore, aqueous solvents can replace organic solvents to enhance the efficiency of products.

(iv) Alternative Products and Target Molecules

The hazardous molecules present in certain chemical products can be removed to enhance the efficiency of the process.

For instance, involvement of isocyanates in the synthesis process of chemical substances can be replaced by eco-friendly acetylacetate esters.

Q14. Discuss the various applications of green chemistry.

Answer :

The important applications of green chemistry are,

(i) Green chemistry is extensively used in the production of various substances from natural materials. For instance, natural materials such as coconut, palm and palm seed serve as starting materials in green synthesis. These materials can inturn produce various substances that can be used in body care, food industries and pharmaceutical applications. Moreover, mineral oil used in the production of petrol and natural gas can be replaced by a green agent called palm oil.

(ii) Teflon can be easily produced using green solvents (such as supercritical CO_2) rather using organic substances (such as Trichlorotrifluoroethane). Nano-electronics also employ supercritical CO_2, because of its negligible impact on nanometric structures.

(iii) Ionic liquids are extensively used as 'Green Solvents' in green synthesis of products. Use of ionic liquids in the synthetic process yields higher production and provides easy recycling of products.

(iv) Green fuels and E-green propellants such as hydrogen peroxide (H_2O_2) is extensively replacing space engines, because of its hazardous-free decomposition.

(v) A metal-cleaning system which employs carbon dioxide and a surfactant is used in dry cleaning applications.

(vi) Green chemistry is increasingly used in organic and inorganic chemistry, biochemistry, analytical chemistry and in physical chemistry.

5.2 BIODIESEL

5.2.1 Sources, Concept of Trans-Esterification and Carbon Neutrality. Properties and Significance

Q15. Briefly explain about sources and significance of biodiesel.

Answer :

Sources of Biodiesel

Biodiesel is manufactured from the vegetable oils like soya, canola, jatropha, sunflower seed, algae and animal fats. The chemical name for biodiesel is fatty acid alkyl esters. There are a few methods for production of biodiesel, but the most commonly used method for production of biodiesel is called as trans-esterification. It is chemical conversion process of vegetable oil or animal fats to biodiesel.

Significance of Biodiesel

The importance of biodiesel is described below.

1. Biodiesel approach is easier to market than other alternative fuels by considering performance, infrastructure and other factors.
2. This can play a significant role in climate change policy and in measures to reduce GHG.
3. Due to important increase in production and use, this approach is supported by government policies.
4. This approach is largely agriculture driven (i.e., more than by energy concerns).
5. This technique has positive impacts for rural economy.
6. The usage of biodiesel brings potential to be commodity, increasing benefits and lowering costs.

Q16. Explain the different methods used in preparing the biodiesel and discuss its applications.

June-17, Q17(b)

OR

Explain the concept of trans-esterification and carbon neutrality.

Answer :

Trans-esterification

For answer refer Unit-5,Q6.

Glycerin that has been separated during trans-esterification process is released as the by-product of the chemical reaction. Glycerin will either sink to the bottom of reaction vessel or come to the surface depending on its phase. It can be easily separated by the centrifuges. This whole process is called as trans-esterification.

The biodiesel produced by process of trans-esterification has much lesser viscosity, which makes it capable to replace petroleum diesel in the diesel engines. The by-product of the trans-esterification chemical reaction is glycerin that originally formed bond between the chains of fatty acids. Glycerin can be used for various purposes. Thus, during trans-esterification process nothing goes wasted, all the products and by-products are utilized for various purposes.

Carbon neutrality

In earth's atmosphere, the proportion of carbondioxide (CO_2) is constantly increasing due to human activities which reslts in globalwarming.

Inorder to re-balance the CO_2 in the atmosphere, carbon based fuels are used to attain carbon neutrality. These fuels, when

burnt, neither increase nor decrease but prevents excess accumulation of the amount of CO_2 in the atmosphere.

In carbon neutrality, the amount of CO_2 released by human activities into the atmosphere is balanced by growing the

plants to absorb the same. However, plant growth keeps the planet warm. When plants absorb the released carbon, more gallons of carbon-neutral fuels can be produced, thus helping to reduce globalwarming.

Carbon neutrality can be achieved from various alternatives, i.e.,

- By changing the usage of finite fuels to renewable fuels.
- By growing more trees and reducing deforestation.
- By improving the efficiency of engines, etc.,

Q17. List out the properties of biodiesel.

Answer :

The following are the properties of Biodiesel

1. The calorific value of biodiesel is about 37.27 MJ/L, which is 9% lower than regular number 2 petrodiesel.
2. Variations in biodiesel energy density is more dependent on the feedstock used than the production process.
3. Biodiesel gives better lubricity and more complete combustion to obtain increased engine energy output.
4. Biodiesel is a liquid which varies in color (i.e., between gold and dark brown) depending on the production feedstock.
5. It is immiscible with water with high boiling point and low vapour pressure.
6. The flash point of biodiesel (> 130°C) is significantly higher than of petroleum diesel (64°C) or gasoline (–45°C).
7. Biodiesel has a density of $\cong 0.88$ g/cm^3, higher than petrodiesel ($\cong$ 0.85g/cm^3).
8. Biodiesel has an effect on copper-based materials (i.e., brass) and other materials zinc, tin, lead and cast iron

SPECTROSCOPY

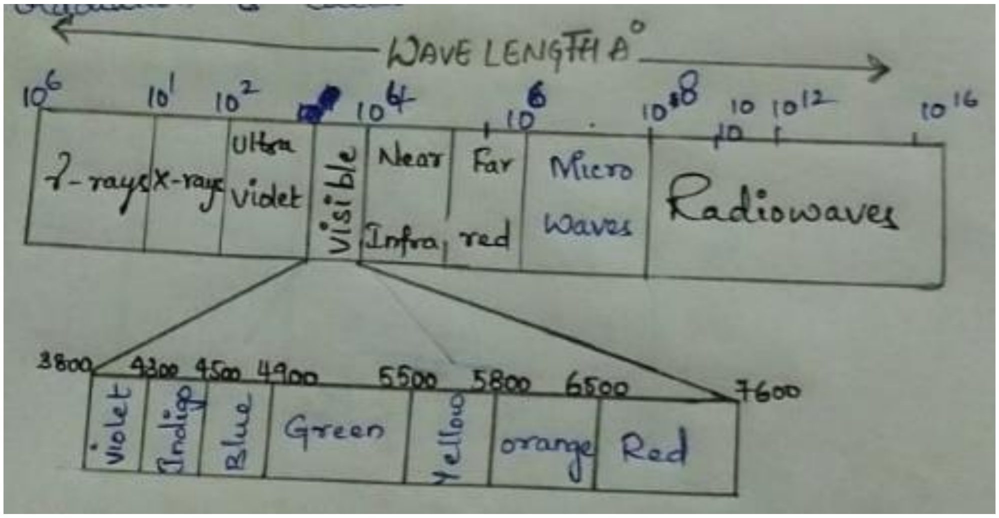
SAQ

1) What is spectroscopy?

ANS} It is a branch of science that deals with the study of interactions of matter with light (or) electromagnetic radiation. It is the most powerful tool available for the study of structures of atoms and molecules.

2) What is the electromagnetic spectrum for UV-visible spectra?

ANS} An electromagnetic spectrum is obtained when all the types of electromagnetic radiation are arranged in the order of increasing wavelength or decreasing frequencies. Visible light lies in the wavelength or range 3800-7600A°. If the wavelength range is less than 3800A°, the radiation is called ultraviolet radiation.



3) What is the electromagnetic spectrum for IR spectra?

ANS} An electromagnetic spectrum is obtained when all the types of electromagnetic radiation are arranged in order of increasing wavelength (or) decreasing frequencies. If electromagnetic radiation is greater than 7600A°, it is called infrared radiation. Both ultraviolet and IR radiation are not visible to Human eye.

Range of IR radiation = $7600*10^{4-6}$ m/s

= ($12500\ cm^{-1}$ - $50cm^{-1}$)

4) What is the electromagnetic spectrum for NMR spectra?

ANS} An electromagnetic spectrum is obtained when all the types of electromagnetic radiation are arranged in order of increasing wavelength (or) decreasing frequency. The electromagnetic spectrum ranges from 3MHz - 30,000MHz

5) Define UV-visible spectroscopy?

ANS} UV-visible spectroscopy is also called electronic spectroscopy as it involves the promotion of electrons [sigma, pi, n] from the ground state to higher energy state. Ultraviolet spectroscopy is used to measure the number of conjugated double bonds, differentiate between conjugated and non-conjugated systems. It also measures aromatic conjugation within the molecules.

6) Define IR spectrum?

ANS} Infrared spectroscopy is a very important tool for the determination of structure of a compound. It is also called vibrational spectroscopy at it involves the transition between energy levels. It is obtained when the frequency of molecular vibration corresponds to the frequency of the infrared radiation absorbed. Apart from vibrational changes, rotational changes also occur in the molecule, hence some fine structures are obtained on the vibrational bond.

7) Define NMR spectroscopy?

ANS} lite infrared and ultra-violet spectroscopy, nuclear magnetic resonance spectroscopy (NMR) is also a form of absorption spectroscopy. The sample absorbs electromagnetic radiation in the radio frequency region. It is a plot of the frequencies of absorption peaks versus peak intensities.

8) Define Absorption Spectrum.

Ans} When there is a transition from a lower energy state to a higher energy state, the energy absorbed will be equal to the energy difference ΔE. The spectrum thus obtained is called an absorption spectrum. Emission (or) absorption spectrum can be of two types:

(i) Atomic spectra (ii) Molecular spectra

9) Write the applications of UV-Visible Spectrum.

Ans)1. UV-visible absorption spectroscopy is useful in the structure elucidation of organic compounds, e.g., unsaturation or heteroatoms, etc.

2. Impurities present in organic compounds can be detected by UV-visible absorption spectroscopy.

3. The extent of conjugation in the polyenes can be detected with the help of UV spectroscopy.

4. An unknown compound can be identified with the help of UV spectroscopy.

5. It is used to detect the presence of certain functional groups present in compounds.

10) What are the applications of IR Spectroscopy?

Ans: Infrared spectroscopy is a very important tool used to determine the structure of organic compounds.

(a) Functional group region (4000–1500 cm^{-1})

Examples: -OH, NH_2, C=O

(b) The fingerprint region (1500–667 cm^{-1})

Examples: C–C, C–O, C–N

11) Mention some of the applications of NMR Spectroscopy?

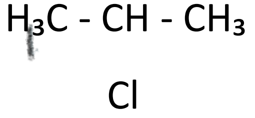
Ans) It is used to determine the structure of organic compounds. Number of signals gives the number of equivalent protons.

Example: CH3 [three-proton triplet]

$-CH_2O$ [two-proton triplet]

Splitting of signals specifies the number of neighboring protons.

Example:



$H_3C - \underset{Cl}{CH} - CH_3$

(a) Doublet (6H)

(b) Septet (1H) downfield

Position of the signals gives an insight into the functional groups, their position, presence (or) absence of hydrogen bonding, etc.

12) Write down the applications of MRI Spectroscopy?

Ans) Anomalies of the brain and spinal cord. Tumors, cysts, and other anomalies in various parts of the body. Certain types of heart problems. The evaluation of pelvic pain in women, with causes including fibroids and endometriosis. Breast cancer screening for women who face a high risk of breast cancer.

LAQ

1) What is the principle of UV spectroscopy? Explain, give any 5 applications.

A) Laws of absorption

Two fundamental laws govern the absorption of light by molecules. These are:

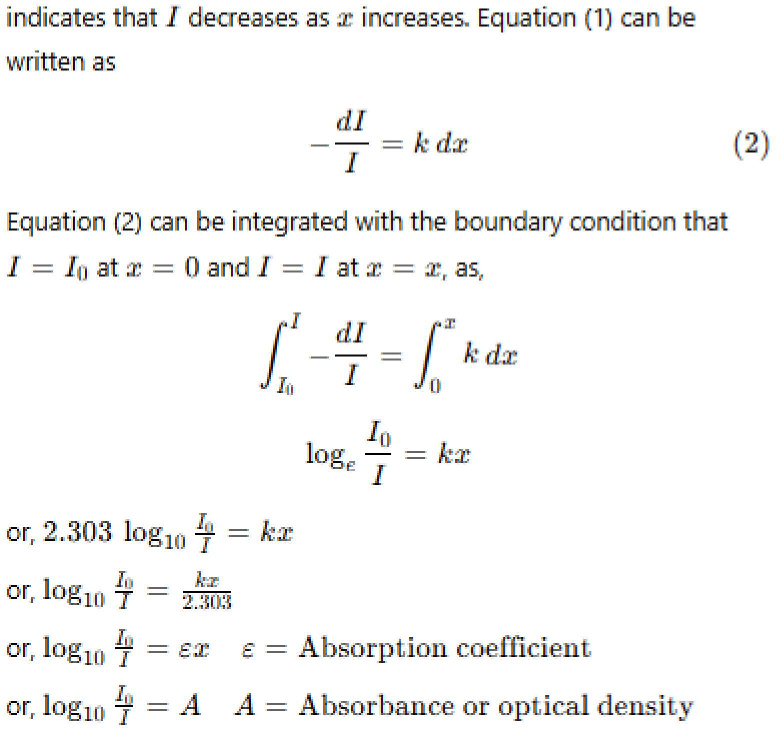
1) Lambert's law
2) Beer's law

Lambert's law

It states that when a beam of monochromatic light passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of the incident radiation. Mathematically,

$$-\frac{dI}{dx} \propto I \quad \text{or} \quad -\frac{dI}{dx} = kI$$

Where, k = proportionality constant
I = intensity of incident radiation
dI = infinitesimally small decrease in the intensity of radiation on passing through an infinitesimally small thickness, dx of the absorbing medium. The negative sign on the left-hand side indicates that I decreases as x increases.



indicates that I decreases as x increases. Equation (1) can be written as

$$-\frac{dI}{I} = k\,dx \qquad (2)$$

Equation (2) can be integrated with the boundary condition that $I = I_0$ at $x = 0$ and $I = I$ at $x = x$, as,

$$\int_{I_0}^{I} -\frac{dI}{I} = \int_0^x k\,dx$$

$$\log_e \frac{I_0}{I} = kx$$

or, $2.303\ \log_{10}\frac{I_0}{I} = kx$

or, $\log_{10}\frac{I_0}{I} = \frac{kx}{2.303}$

or, $\log_{10}\frac{I_0}{I} = \varepsilon x \quad \varepsilon = \text{Absorption coefficient}$

or, $\log_{10}\frac{I_0}{I} = A \quad A = \text{Absorbance or optical density}$

is the intensity of radiation before entering the absorbing medium (i.e., when x=0) and III is the intensity when the beam has travelled the thickness x of the absorbing material. The term $\log_{10}\frac{I_0}{I}$ is known as absorbance or optical density and is denoted by A.

Alternatively, Lambert's law can be stated as:
When a parallel beam of monochromatic light enters perpendicularly

into a homogeneous absorbing medium, the absorbance is directly proportional to the length of the path traversed by the beam.

Beer’s law

If the absorbing material is in the form of a solution, then the relationship between the intensities of incident and transmitted light is given by Beer’s law.

According to this law, when a parallel beam of monochromatic light enters perpendicularly into a dilute solution, the absorbance is directly proportional to the concentration of the solution. Mathematically,

$$A = \log_{10} \frac{I_0}{I} = k'c$$

where k is a constant and cc is the concentration of the solution.

Beer–Lambert law

It is the combined form of Beer’s law and Lambert’s law. According to it, when a beam of monochromatic light is passed through a solution, the decrease in intensity of radiation with thickness of the absorbing material is directly proportional to the intensity of incident radiation as well as to the concentration of the solution.

If a monochromatic light of intensity II passes through a solution of molar concentration cc and the length of the path is xx cm, then the mathematical form of Beer–Lambert’s law is

$$A = \log \frac{I_0}{I} = \varepsilon c x$$

where ε is a constant called the molar absorption coefficient or molar absorptivity. If c=1 and x = 1, then

Extinction A= ε

Thus, molar absorption coefficient (formally, the molar extinction coefficient) can be defined as the extinction due to a 1 cm thick layer of solution whose molar concentration is unity. It is characteristic of a compound provided the wavelength of light and temperature are kept constant.

Transmittance

If TT is the transmittance of a solution, then it is defined as

$$T = \log \frac{I}{I_0}$$

$$\text{or } T = -\varepsilon cb$$

Transmittance is the reciprocal of absorbance.

Extent of conjugation

Conjugation lowers the energy required for a π → π* transition. The greater the extent of conjugation, the longer is the absorption wavelength. For example, ethylene absorbs at 170 nm due to π → π* transitions whereas butadiene having two double bonds absorbs at 217 nm, and a polyene with 8 conjugated double bonds absorbs at about 290 nm, i.e., in the visible region and they appear coloured to the human eye. Similarly, lycopene with eleven conjugated double bonds absorbs at 454 nm and imparts red colour to tomatoes.

Determination of geometrical isomers

Effective π → π* transitions take place when the molecule is coplanar. The steric strain in cis-isomer prevents coplanarity. Thus, cis isomers absorb at a shorter wavelength when compared to the trans-isomer. For example, cis-stilbene absorbs at 280 nm and trans stilbene absorbs at 295 nm.

Identification of unknown compounds

Unknown compounds can be identified by comparing its spectra with the spectra of known compounds. Identical spectra reveal identical structure and if the spectra is different, then the structure is different.

Distinction between conjugated and non-conjugated compounds
Consider the following compounds: (a) $(CH_3)_2C=CH-C=OCH_3$
(b) $CH_2=CH-CH_2-C=CH_3$

Compound (a) has longer λ max values because C = O group is in conjugation with the double bond.

Detection of impurities
Ethanol contains benzene as an impurity. Since benzene is toxic in nature, it is essential to detect its presence. The presence of benzene can be detected through the UV spectrum of the sample at 280 nm (Fig. 15.13). Ethanol is transparent at this wavelength but benzene shows an absorption band with $\varepsilon_{\mathrm{max}} = 230$.

Detection of hydrogen bonding
Hydrogen bonding can be detected on the basis of the shift absorbed in polar solvents .

Quantitative analysis
This is based on Beer–Lambert's law

$A=\varepsilon*c*l$

where
A = absorbance at a particular wavelength
c = concentration of the sample
ε = constant termed as molar absorptivity or extinction coefficient.

The absorbance of the standard solution (A_1) and the unknown solution (A_2) are measured in a sample cell. If the concentration (c_1) of the standard solution is known, the concentration (c_2) of the sample can be determined as follows:

$A1/A2=c1/c2$

2) What is the principle of IR spectroscopy? Explain, give any 5 applications.

A)

Infrared spectrum

When a beam of IR radiation of varying frequency passes through a sample, it absorbs energy when the energy matches the difference between the vibrational energy levels of its bonds. Absorption bands are thus obtained. Infrared spectrum is usually plotted with the percentage transmittance rather than the absorbance as ordinate. This makes the absorption bands appear as dips or troughs rather than as maxima as in the case of ultraviolet and visible spectra. These dips or troughs are called bands and they represent absorption of infrared radiation at that frequency of the sample. The bands can be strong, medium, or weak depending upon the absorption.

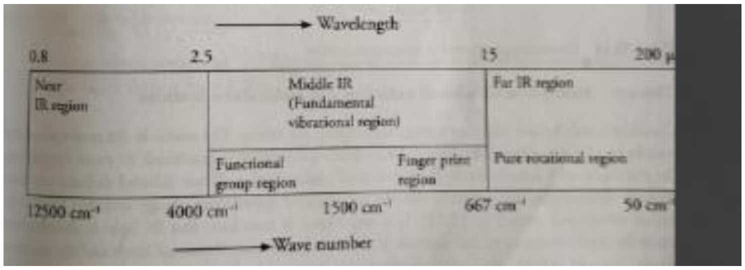
The position of the infrared absorption band is specified in frequency units expressed not in hertz but in wave numbers, cm^{-1} or by its wavelength (λ) measured in micrometers (µm, earlier called micron µ).

$$\bar{\nu} = \frac{1}{\lambda\ (\text{in cm})} \quad \text{or} \quad \bar{\nu} = \frac{10,000}{\lambda\ (\text{in } \mu\text{m})}$$

Band intensity is expressed either in terms of absorbance (A) or transmittance (T):

$$A = \log_{10}\left(\frac{1}{T}\right)$$

IR spectroscopy is divided into three regions:



- Near IR region: 12,500 cm^{-1} to 4,000 cm^{-1}
- Middle IR region: 4,000 cm^{-1} to 667 cm^{-1}
- Far IR region: 667 cm^{-1} to 50 cm^{-1}
- The near IR region extends from 12,500 cm^{-1} to 4,000 cm^{-1} wave number. It is of little significance as there are few absorptions in this range.
- The most important and useful region extends from 4000 cm^{-1} to 667 cm^{-1}. Most absorptions occur in this region.
- The far infrared region deals with the pure rotational motion of the molecule. Very few absorptions appear in this region. It extends from 667 cm^{-1} to 50 cm^{-1}.

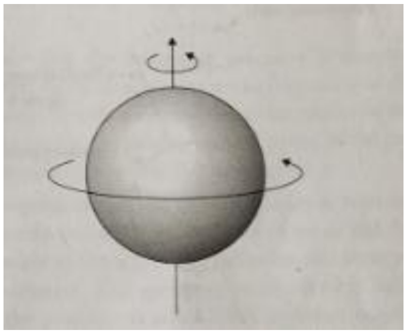
3) What is the principle of NMR spectroscopy? Explain, give any 5 applications.

A)

Magnetic properties of nuclei

(i)Nucleus – A tiny bar magnet

All nuclei carry a charge. These charged nuclei are considered to spin. The spinning nuclear charge generates a magnetic dipole along the axis so that these nuclei behave as tiny bar magnets having a magnetic moment μ.



Spinning charge in proton generates magnetic dipole

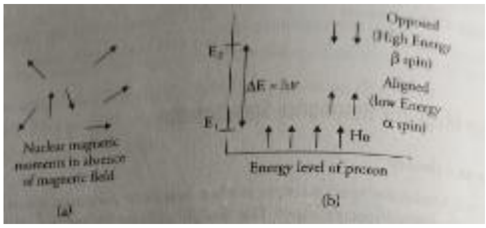
(ii) Effect of external magnetic field

In the absence of an external magnetic field, the magnetic moments are randomly oriented. If the nucleus is placed in an external magnetic field, it can be oriented in different ways. According to quantum mechanics, 2I + 1 orientations are possible where II is the spin quantum number of the nucleus. Hydrogen nucleus (proton) with the value of

$$I = \frac{1}{2}$$

can have 2I + 1, i.e., 2×(1/2)+1= 2 orientations with respect to the external magnetic field.

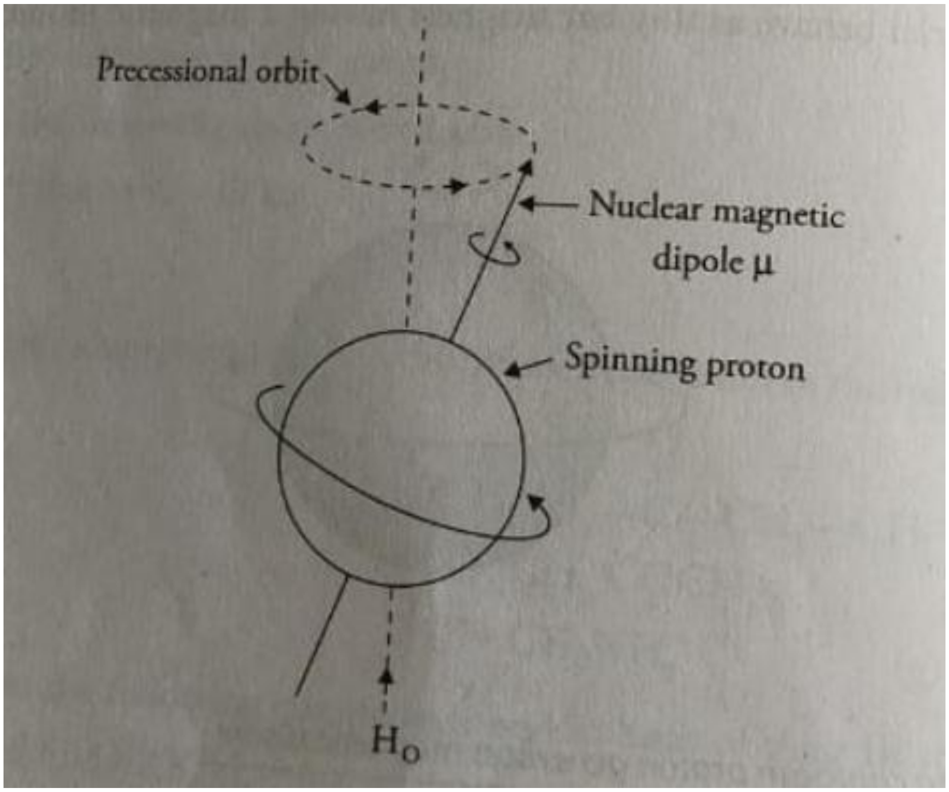
It can be aligned either
(i) Parallel to the field (α spin) or
(ii) Anti-parallel to the field (β spin)



(Figure 15.31) (a) Random orientation of magnetic moments in the absence of magnetic field
(b) Magnetic moments aligned in the presence of external magnetic field

(iii) Precessional motion

The movement of the nucleus is like that of a spinning top. The top spins and also moves around slowly. Similarly, the nucleus also performs a waltz-like motion; this waltz-like motion of the nucleus along the vertical axis is known as the precessional motion *(Fig. 15.32)*.



(Figure 15.32) Proton precessing in a magnetic field H_0

As the proton is a spinning magnet, it precesses along the axis of the magnetic field with its orientation either along the external magnetic field or opposite to it. The orientation along the field has low energy and is stable, whereas the anti-parallel orientation has high energy. This energy difference ΔE between the two states is given by

$\Delta E = 2\mu H_0$

Applying Bohr's relation

$\Delta E = h\nu$ ………………………… (ii)

Relating Eq. (i) and (ii), we have

$\nu = 2\mu H_0 / h$ ……………………….. (iii)

where:
ν = frequency of the electromagnetic radiation
μ = magnetic moment of the spinning nuclei
H_0 = external field in Gauss
h = Planck's constant

It is possible to induce transition between the two states. On absorbing energy, a proton precessing in the aligned orientation can pass into anti-parallel orientation. This transition of a proton from one orientation to another is called **flipping** of the proton. The proton can also return from a higher energy state (anti-parallel orientation β spin) to a lower energy state (α spin) by losing energy.

The energy required to flip the proton from one state to another depends upon the strength of the external field. Stronger the external field, greater will be the tendency of the proton to remain aligned with the field, and higher will be the frequency of radiation required to flip the proton to the higher energy state.

It is important to remember that the precessing proton will absorb energy only when the precessing frequency of the spinning nucleus is the same as the frequency of the radio frequency beam. When this occurs, the nucleus and the radiofrequency beam are said to be in resonance. For example, in the field of 14,092 Gauss, the energy required to cause flipping of the proton corresponds to the electromagnetic radiation of frequency 60 MHz (60 megahertz).

NMR spectrometers are designed so that the radiofrequency is kept constant and the strength of the magnetic field is constantly varied. Now, at some value of the field strength, the energy required to flip the proton matches the energy of the radiation, and absorption takes place. A signal is observed in the spectrophotometer. The spectrum so obtained is called the **NMR spectrum**. When the nucleus involved is the proton, it is called **PMR** or **proton magnetic resonance**.

Spin active nuclei

All nuclei do not exhibit NMR. Those nuclei which exhibit NMR phenomenon are called **spin active nuclei**. All nuclei possess spin angular momentum. Only those nuclei with spin quantum number **I** greater than zero will precess along the axis of rotation.

The spin quantum number **I** is associated with the mass number and atomic number of the nuclei (Table 15.13). It is the resultant of the spins of a proton and a neutron.

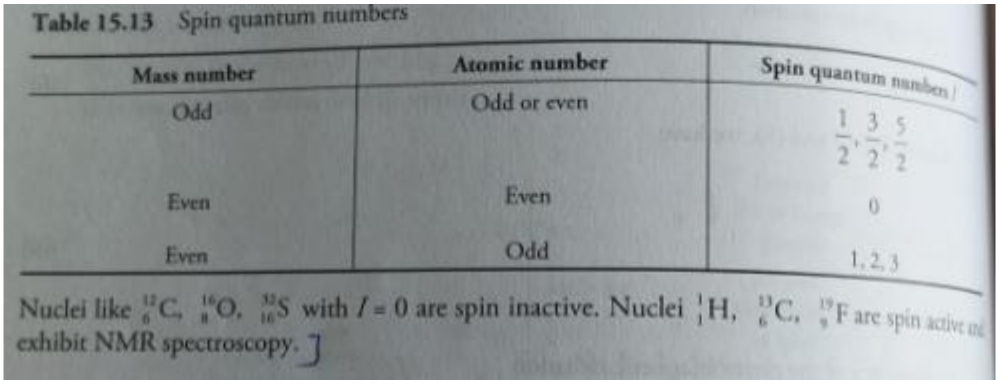


Table 15.13 Spin quantum numbers

Mass number	Atomic number	Spin quantum number I
Odd	Odd or even	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$
Even	Even	0
Even	Odd	1, 2, 3

Nuclei like $^{12}_{6}C$, $^{16}_{8}O$, $^{32}_{16}S$ with $I = 0$ are spin inactive. Nuclei $^{1}_{1}H$, $^{13}_{6}C$, $^{19}_{9}F$ are spin active
exhibit NMR spectroscopy.