4^{TH} SEM COMPLEMENTARY CHEMISTRY

CALICUT UNIVERSITY

PHYSICAL AND APPLIED CHEMISTRY

2019 ADMISSION ONWARDS

Prepared by

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SEMESTER IV
Course Code: CHE4C04
Complementary Course IV: PHYSICAL AND APPLIED CHEMISTRY

Total Hours: 48; Credits: 2; Hours/Week: 3; Total Marks 75 (Internal 15 & External 60)

Objective (s): To provide the students a thorough knowledge about colloidal chemistry, nanochemistry and the importance of chemistry in daily life. It also imparts the idea of green processes with an importance for environment.

Module I: Colloidal Chemistry (6 hrs)

True solution, colloidal solution and suspension. Classification of colloids: Lyophilic, lyophobic, macromolecular, multimolecular and associated colloids with examples. Purification of colloids by electrodialysis and ultrafiltration. Properties of colloids: Brownian movement – Tyndall effect – Electrophoresis. Origin of charge and stability of colloids – Applications of colloids: Delta formation, medicines, emulsification, cleaning action of Coagulation - Hardy Schulze rule – Protective colloids - Gold number. Emulsions,detergents and soaps.

References

1. B. R. Puri, L. R. Sharma, M. S. Pathania, *Principles of Physical Chemistry*, 46th Edition, Vishal Publishing Company, New Delhi, 2013.
2. F. Daniels, R. A. Alberty, *Physical Chemistry*, 5th Edn., John Wiley and Sons, Canada, 1980.

Module II: New Vistas in Chemistry (6 hrs)

Nanochemistry: Introduction – classification of nanomaterials (0D, 1D, 2D) - size dependence of material properties (optical, electrical and catalytic) - surface to volume ratio and its significance, - application of nanomaterials in electronics, optics, catalysis and medicine(detailed discussion not expected).

Green Chemistry: Definition and need of green chemistry- principles (detailed discussion not expected) - atom economy- green solvents- green synthesis of Ibuprofen.

References

1. M. A. Shah, Tokeer Ahmad, *Principles of Nanoscience and Nanotechnology*, Narosa Publishing House, New Delhi, 2010.
2. T. Pradeep, *A Textbook of Nanoscience and Nanotechnology*, McGrawhill, New Delhi, 2012.
3. V. K. Ahluwaliya, *Green Chemistry*, Narosa Publishing House, New Delhi, 2011.

Module III: Chromatography (6 hrs)

Chromatography- Introduction - Adsorption and partition chromatography - Principle and applications of column, thin layer, paper and gas chromatography - Rf value – Relative merits of different techniques.

References

1. R. A. Day Junior, A. L. Underwood, *Quantitative Analysis*, 5th Edn., Prentice Hall of India Pvt. Ltd. New Delhi, 1988.
2. J. Mendham, R. C. Denney, J. D. Barnes, M. Thomas, *Vogel's Text Book of Quantitative Chemical Analysis*, 6th Edn., Pearson Education, 2003.
3. R. Gopalan, *Analytical Chemistry*, S. Chand and Co., New Delhi.

Module IV: Spectroscopy (10 hrs)

Origin of spectra - Interaction of electromagnetic radiation with matter. Different types of energy levels in molecules: Rotational, vibrational and electronic levels. Statement of Born-Oppenheimer approximation - Fundamental laws of spectroscopy and selection rules (derivations not required).

IR Spectroscopy: Introduction - Group frequency concept - Characteristic stretching frequencies of O-H, N-H, C-H, C=C, C=N and C=O functional groups - Fingerprint region in IR spectra.

UV-Visible Spectroscopy: Introduction - Beer-Lambert's law - Electronic transitions in molecules ($\sigma\rightarrow\sigma^*$, $n\rightarrow\sigma^*$, $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$) - Chromophore and auxochrome - Red shift and blue shift.

NMR Spectroscopy: Introduction - Chemical shift and spin-spin coupling - Application in elucidating the structure of ethanol, dimethyl ether, propanal and acetone (detailed study not required).

References

1. P. S. Kalsi, *Applications of Spectroscopic Techniques in Organic Chemistry*, 6th Edn., New Age International (P) Ltd., New Delhi, 2004.

2. C. N. Banwell, E. M. Mc Cash, *Fundamentals* of *Molecular Spectroscopy*, 4th Edn., McGraw–Hill publishing Company Limited, New Delhi, 2002.

Module V: Polymers (4 hrs)

Classification of polymers - Addition and condensation polymers – Thermoplastics and thermosetting plastics - Structure and applications of synthetic rubbers (Buna-S, Buna-N and neoprene), synthetic fibres(Nylon 66, Nylon 6 and dacron), thermoplastics (polyethene, polystyrene, PVC and teflon) and thermosetting plastics (bakelite and melmac). Uses of kevlar, nomex and lexan – Biodegradable polymers (PGA, PLA and PHBV) and their applications.

References

1. V. R. Gowarikar, *Polymer Chemistry*, New Age International Pvt. Ltd., New Delhi, 2010.
2. Fred. W. Billmeyer, *Textbook of Polymer Science*, 3rd Edn., Wiley India, Delhi, 2008.

Module VI: Environmental Pollution (6 hrs)

Definition – Types of pollution.

Air pollution: Pollution by oxides of nitrogen, carbon and sulphur. Effects of air pollution: Depletion ofozone, green house effect and acid rain.

Water pollution: Pollution due to sewage, industrial effluents, soaps, detergents, pesticides, fertilizers and heavy metals – Eutrophication - Biological magnification and bioaccumulation - Effects of water pollution. Water quality parameters – DO, BOD and COD (elementary idea only).

Soil pollution – Pollution due to plastics.

Thermal pollution and radioactive pollution: Sources, effects and control measures.

References

1. A. K. De, *Environmental Chemistry*, 6th Edn., New Age International Pvt. Ltd., New Delhi, 2006.
2. A. K. Ahluwalia, *Environmental Chemistry*, Ane Books India, New Delhi, 2008.

Module VII: Chemistry in Daily Life (10 hrs)

Petrochemicals: Name, carbon range and uses of fractions of petroleum distillation – Octane number - Cetane number – Flash point. LPG and CNG: Composition and uses.

Pharmaceuticals: Drug - Chemical name, generic name and trade names with examples. Antipyretics, analgesics, antibiotics, antacids, antiseptics (definition and examples, structure not expected).
Dyes: Definition – Requirements of a dye - Theories of colour and chemical constitution – Structure and applications of martius yellow, indigo and alizarin.
Food: Food additives: Food preservatives, artificial sweeteners and antioxidants (definition and examples, structures not required) Commonly used permitted and non-permitted food colours (structures not required).
Cement: Manufacture, composition and setting.
Glass: Types of glasses and uses.

References

1. Gurdeep R. Chatwal, *Synthetic Drugs*, Himalaya Publishing House, Bombay, 1995.
2. Jayashree Ghosh, *A Textbook of Pharmaceutical Chemistry*, 3rd Edn., S. Chand and Company Ltd., New Delhi, 1999.
3. B. Sivasankar, *Food processing and preservation*, Prentice – Hall of India Pvt. Ltd. New Delhi, 2002.
4. Srinivasan Damodaran, Kirk L. Parkin, Owen R. Fennema, *Food Chemistry*.

MODULE: 1- COLLOIDAL CHEMISTRY

True solution:

- Homogeneous system in which particles of the solute are of molecular size.
- Diameter range of particles is 0.1-1nm.
- Particle are not visible to the naked eye or even under powerful microscope.
- Diffuse rapidly.
- Do not settle down on standing.
- Particles cannot be retained on filter paper.
- Eg: sugar solution, NaCl solution

Suspension:

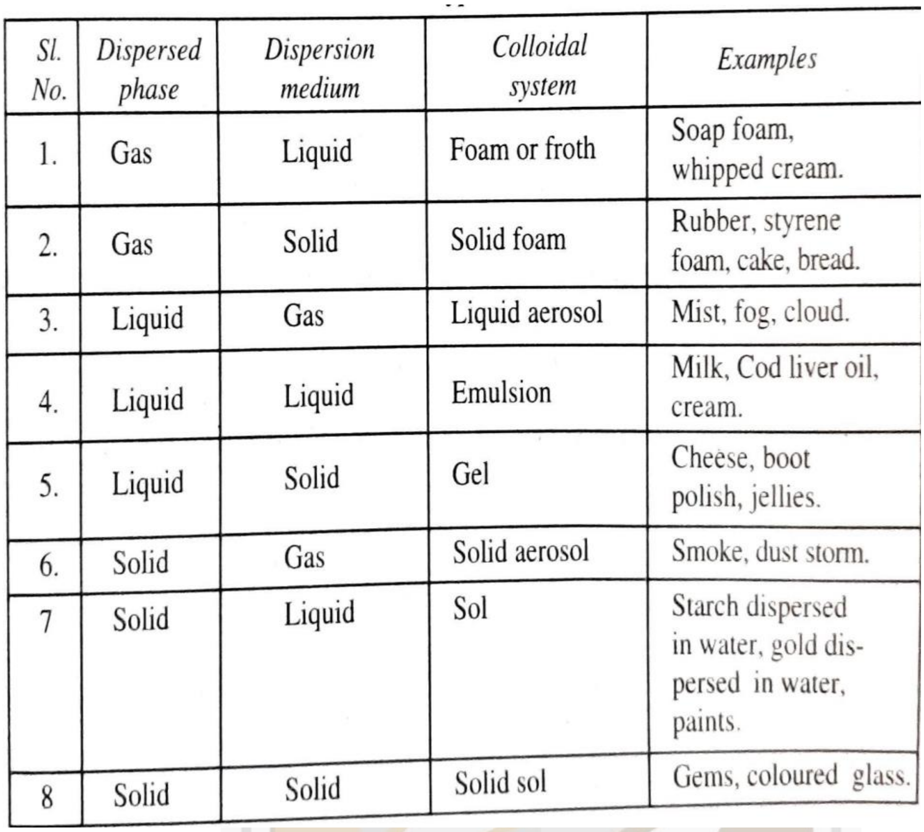
- Heterogenous system containing large particles.
- Diameter range greater than 1000nm.
- Particles are visible to the naked eye or under microscope.
- Do not show diffusion.
- Particles settle readily under gravity.
- Can be retained on filter paper.
- Eg: sand in water. $BaSO_4$ in water.

Colloidal solutions:

- Intermediate between true solutions and suspensions.
- Heterogeneous system in which dispersed particles are larger than molecules but not large enough to seen under microscope.
- Diameter range is 1-1000nm.
- Have lower rate of diffusion.
- They do not settle down on standing.
- Cannot be retained on filter paper.
- Eg: Dispersion of starch, ferric hydroxide in water.
- Colloidal solution consist of two phases-dispersed phase and dispersion medium.
- Dispersed phase consist of colloidal particles having diameters in the range 1-1000nm. Dispersion medium consist of the solvent or medium in which colloidal particles are dispersed.

Classification of colloidal systems

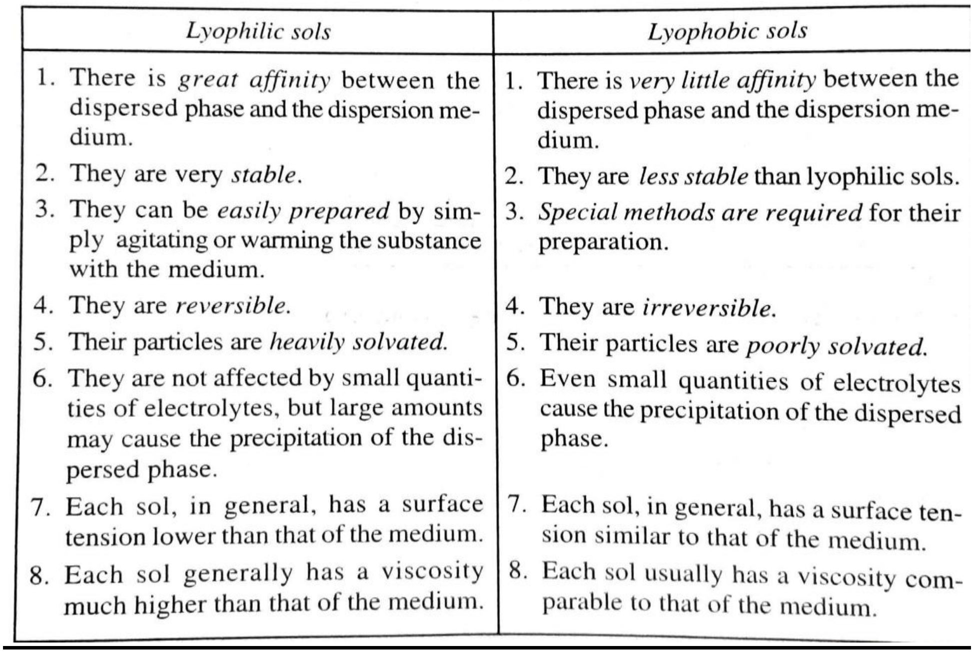
a) Classification based on the states of aggregation of the two phases



Sl. No.	Dispersed phase	Dispersion medium	Colloidal system	Examples
1.	Gas	Liquid	Foam or froth	Soap foam, whipped cream.
2.	Gas	Solid	Solid foam	Rubber, styrene foam, cake, bread.
3.	Liquid	Gas	Liquid aerosol	Mist, fog, cloud.
4.	Liquid	Liquid	Emulsion	Milk, Cod liver oil, cream.
5.	Liquid	Solid	Gel	Cheese, boot polish, jellies.
6.	Solid	Gas	Solid aerosol	Smoke, dust storm.
7	Solid	Liquid	Sol	Starch dispersed in water, gold dispersed in water, paints.
8	Solid	Solid	Solid sol	Gems, coloured glass.

b) Classification based on affinity between the two phases

- Classified into two- lyophilic and lyophobic colloids.
- If the dispersed phase is solid and dispersion medium is liquid, the colloidal system is called sol. Sols are classified into lyophilic and lyophobic sols.



Lyophilic sols	*Lyophobic sols*
1. There is *great affinity* between the dispersed phase and the dispersion medium.	1. There is *very little affinity* between the dispersed phase and the dispersion medium.
2. They are very *stable*.	2. They are *less stable* than lyophilic sols.
3. They can be *easily prepared* by simply agitating or warming the substance with the medium.	3. *Special methods are required* for their preparation.
4. They are *reversible*.	4. They are *irreversible*.
5. Their particles are *heavily solvated*.	5. Their particles are *poorly solvated*.
6. They are not affected by small quantities of electrolytes, but large amounts may cause the precipitation of the dispersed phase.	6. Even small quantities of electrolytes cause the precipitation of the dispersed phase.
7. Each sol, in general, has a surface tension lower than that of the medium.	7. Each sol, in general, has a surface tension similar to that of the medium.
8. Each sol generally has a viscosity much higher than that of the medium.	8. Each sol usually has a viscosity comparable to that of the medium.

c) Classification into macromolecular, multimolecular and associated colloids

Macromolecular colloids:

- Colloidal dispersions of macromolecular substances are called macromolecular colloids.
- Strong chemical bonds are present between macromolecular particles.
- Most of these systems show lyophilic behaviour.

Eg: Sols of starch, gelatin , proteins,rubber etc

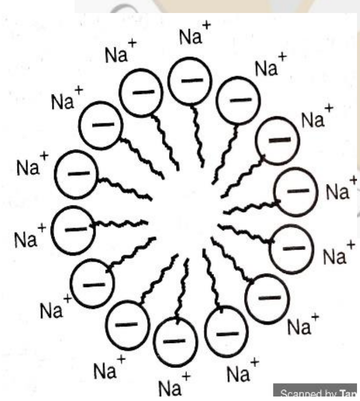
Multimolecular colloids:

- Colloidal particles are aggregate of atoms or molecules having diameter less than 1 nm.
- Weak vandewaal's force are present between particles.
- These systems generally show lyophobic behaviour.
- Eg: Aqueous sulphur sol, Aqueous Gold sol

Associated colloids:

- Certain substance behave as normal electrolytes at low concentrations and show colloidal properties at high concentration due to the formation of aggregated particles called micelles. Such colloidal systems are called associated colloids.
- Eg: soaps and detergents

  In soaps, micelles are formed above critical micelle concentration(CMC).



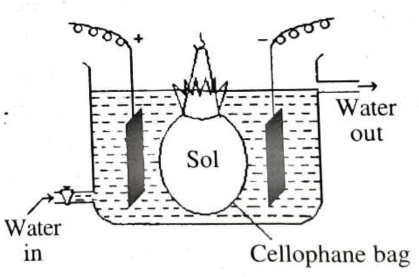
Purification of sols

- The excess amount of electrolytes or other soluble impurities destabilize the sols. It is therefore, necessary to purify them. Purification methods generally adopted are

i) Electrodialysis:

- Dialysis is the process of removing soluble impurities from a colloidal system by allowing them through a porous membrane such as parchment or cellophane. These membranes are permeable to solvent molecules and impurities but not to colloidal particles.

- The apparatus used for dialysis is called dialyser. A bag made from parchment membrane is filled with impure sol. This is suspended in water taken in a large dish. The soluble impurities diffuse leaving the pure sol behind. To speed up the process, electric field is applied. Two electrodes are dipped in water outside the bag and electric field applied. The ions present in the colloidal solution migrate out to oppositely charged electrodes. This modified form of dialysis is called electrodialysis.



ii) Ultrafiltration:

- Ultrafiltration is the process of removing soluble impurities from the colloidal system by allowing them to diffuse through an ultrafilter.
- The ultrafilter will allow solvent and impurities to pass , but not the colloidal particles.
- Ultrafilter are made from cellophane. It can also be prepared from ordinary filterpaper by impregnating them with gelatin or collodion.
- To speed up the process, pressure or suction is used to force the impurity solution out of the sol.

PROPERTIES OF SOLS

Kinetic property

a) Brownian movement:

- The ceaseless,erratic, zig-zag motion exhibited by the colloidal particles is called Brownian movement.
- It is due to the unequal bombardment of colloidal particles by constantly moving particles of dispersion medium. The molecules of the medium impart momentum to the colloidal particles.
- Brownian movement counteracts the force of gravity acting on colloidal particles, it is responsible for the stability of colloids.

Optical property

b) Tyndall effect

- When a beam of light is passed through a colloidal solution and is then viewed at right angles to it, the path of beam becomes visible as a bright streak. This is called Tyndall effect. The path is called Tyndall beam or Tyndall cone.
- Waves of shorter wavelength will be more intense in the scattered light .Hence colourless solutions have bluish Tyndall beam.
- Tyndall effect arises due to scattering of light by colloidal particles.

- Intense Tyndall effect is observed only when (i) the diameter of the dispersed phase is not much smaller than the wavelength of light used. (ii) there is a large difference in the refractive indices of the dispersed phase and dispersion medium

- Lyophilic sols generally show weak Tyndall effect as the difference between refractive indices of dispersed phase and dispersion medium is small. This is due to the presence of heavy sheath of solvent around sol particles.

- Tyndall effect is not observed for true solutions because the solute particles are too small to scatter light. Thus, it can be used as a method to distinguish between true solutions and colloidal solutions.

- Tyndall effect is made use of in ultramicroscope to study about colloidal solutions. The light from the source is condensed by a series of slits and lenses and passed through the sol. The scattered light (Tyndall beam) is viewed through a microscope placed at right angles to the beam. The colloidal particles are as bright spots of light moving irregularly against dark background.

ELECTRICAL PROPERTIES

- Colloidal particles carry electrical charge, either positive or negative.

- Charge on colloidal particles is due to preferential adsorption of ions on the particles.

  Ferric hydroxide [$(Fe(OH)_3$] sol contains positively charged particles due to the selective adsorption of Fe^{3+} ions.

  Arsenious sulphide (AS_2S_3) sol contains negatively charged particles due to the selective adsorption of S^{2-} produced from the dissociation of H_2S.

- Charge also arises due to self-dissociation and formation of ionic micelles.

  In aq. Dispersion of soap (RCOONa), $RCOO^-$ aggregate together to form negatively charged ionic micelles.

- Sol particles also become charged by electron capture during electro-dispersion or by frictional electrification.

Electrical double layer and zeta potential

- The stability and electrical properties of colloids can be explained by the existence of an electrical double layer at the interface between dispersed phase and dispersion medium.

- The electrical double layer consist of a fixed layer and a diffuse (mobile) layer of equal and opposite charges.

- Fixed layer consist of either positive or negative ions held firmly on solid. The diffuse layer consist of mobile layer of ions extending to some distance into the liquid phase. It contains both positive and negative ions . Their distribution is such that the net charge is equal and opposite to that on fixed layer. The ion which is found excess in mobile layer is called counter ions.

- The distribution of ions is not uniform in the diffuse layer. Close to the fixed layer, there will more ions of opposite sign due to preferential attraction.

- The difference in potential between the position of closest approach of the ions to the fixed layer at the surface and the electroneutral region of bulk liquid across the diffuse layer is called zeta potential.

  Zeta potential, $\zeta=4\pi ed/D$

Electrophoresis

- When a colloidal solution is placed in an electrical field, the electrically charged colloidal particles migrate towards the oppositely charged electrode. This phenomenon is called electrophoresis.
- Electrophoresis occurs due to the formation of electrical double layer. When an emf is applied, the oppositely charged fixed and diffuse layers are displaced with respect to each other. The charged sol particles are now free to move, they move towards oppositely charged electrode.

Isoelectric point

- The pH at which the sol particles of an ampholytic substance become electrically neutral and exhibit no movement in an electric field is called isoelectric point.

  Eg: The isoelectric point of albumin is 4.9

Stability of sols

- In lyophobic and lyophilic colloids, the sol particles carry similar electrical charges. Repulsion between them holds the particles apart. Hence, they do not coalesce into non colloidal aggregates.
- In lyophilic colloids, a heavy sheath of solvent, resulting from extensive solvation, acts as a barrier to their aggregation. Hence they are more stable than lyophobic colloids.
- Brownian movement is also responsible for the stability of sols.

Coagulation of sols

- The precipitation of the dispersed phase of a colloidal solution through the induced aggregation of its particles is known as coagulation or flocculation.
- Coagulation can be done by neutralizing the charges on the sol particles. This can be done
  1. By causing persistent electrophoresis
  2. By the addition of an oppositely charged colloid.
  3. By persistent dialysis to remove the adsorbed ions.
  4. By the addition of electrolytes.

     On addition of electrolytes, the colloidal particles take up oppositely charged ions from the electrolyte and gets neutralized.

     Eg: The negatively charged As_2S_3 sol can be coagulated on adding some $BaCl_2$ solution.

Hardy- schulze rule

- The law states that “greater the valency of the ion bearing a charge opposite to that on sol particles, the greater is its power to cause coagulation”.

  Eg: The power of Na^+, Ba^{2+}, and Al^{3+} to cause coagulation of negatively charged sol like As_2S_3 sol is in the order $Na^+ < Ba^{2+} < Al^{3+}$.

  The coagulating power of some ions in coagulating a positively charged sol like $Fe(OH)_3$ sol is $Cl^- < SO_4^{2-} < PO_4^{3-} < [Fe(CN)_6]^{4-}$.

Flocculation value

- The minimum concentration of an electrolyte required to cause coagulation of a sol is called flocculation value.
- It is expressed in terms of millimoles of electrolyte per litre of the sol.
- The flocculation values of $NaCl$, $BaCl_2$ and $AlCl_3$ for the negatively charged As_2S_3 sol are respectively 52, 0.69 and 0.093.

Protective colloids

- A lyophilic substance that offers protection to a lyophobic sol from the precipitating effect of electrolytes are called protective colloids.
- Eg: Gelatin can protect a gold sol.
- The lyophilic substances differ in their protective powers. It is usually expressed in terms of Gold numbers.
- Gold number of a protective colloid is the weight in milligrams of dry protective colloid that just prevents the coagulation of 10 ml of a standard gold sol on adding 1ml of 10% sodium chloride solution.
- Smaller the gold number of a lyophilic colloid, greater is its protective action.

Applications of coagulation

- Rubber latex is a colloidal solution of negatively charged rubber particles dispersed in water. It is coagulated using formic acid or acetic acid to yield rubber.
- Smoke, which is a colloidal solution of carbon particles in air, is precipitated and removed by electrophoresis in Cottrel smoke precipitator.
- Sewage water contains particles of dust, dirt, mud and garbage of colloidal size. They are removed by electrophoresis. The colloidal particles move towards the oppositely charged electrodes, get coagulated and settle down.

Emulsions

- A colloidal system in which both the dispersed phase and dispersion medium are liquids is known as emulsion.
- One of the phase is water and the other is a liquid immiscible with it, usually known as oil.
- There are two types of emulsions-

  i) Oil-in-water emulsions: oil is the dispersed phase and water is the dispersion medium. Eg: milk, vanishing cream,emulsified drugs etc.

ii) Water-in- oil emulsions: water is the dispersed phase and oil is the dispersion medium. Eg: Cod liver oil, butter, ice-cream etc.

- **Emulsification-**The process of making an emulsion is termed as emulsification. It is made by shaking together the two immiscible component liquids. Such emulsions have properties similar to lyophobic colloids and are unstable due to large interfacial tension between dispersed phase and dispersion medium.
- Stable emulsions are prepared by adding emulsifiers or emulsifying agents. They are capable of lowering the interfacial tension between oil and water and thereby preventing the aggregation of droplets. They have properties similar to lyophilic colloids. Eg of emulsifiers- soaps and detergents, proteins, gums etc.
- The breaking up of an emulsion is called demulsification. This can be brought by adding electrolytes, by destroying the emulsifier or by physical methods such as freezing, boiling, centrifugation.

Applications of emulsions and emulsification

- Milk and cream which are emulsions of fat in water are used as constituents of our diet.
- Large number of drugs in the form of emulsions are used in the body.
- An emulsion of asphalt is used in making roads.
- Several Cosmetics are used in the form of emulsions.
- Several high quality paints are emulsions.
- Froth floatation process used in the concentration of sulphide ores make use of emulsification.
- Cleansing action of soaps and detergents is based on their emulsifier properties. Their cleansing action is ascribed to their ability to emulsify grease with water. The hydrocarbon chain of the soap or detergent gets attached to the oil (grease) and its polar head gets attached to water. It forms an interfacial film, lowers the interfacial tension between grease and water and promotes emulsification. Most of the dirt sticks to the grease and is released from the cloth during rubbing.
- A number of medicines are used in the form of sols, emulsions and gels for easy and effective absorption and assimilation by body tissues.

  Eg: Colloidal sulphur is applied as germ killer.

  Oozing of blood from minor cuts is stopped using coagulants like alum.

  Sols of gold, calcium and iron are taken orally and through injections for raising the vitality of human system.

  Argyrol and protargol are sols of silver used in ophthalmic lotions.

  Several antacids, antibiotic syrups, cough syrups, antiseptic lotions, antifungal creams etc are colloidal in nature.

MODULE-2- NEW VISTAS IN CHEMISTRY

PART 1: NANOCHEMISTRY

Nanochemistry

- The nanochemistry is explained as the study of the synthesis of materials and properties of materials in the range of nanoscale.

  Therefore, 1nm = 10^{-7} cm OR 1nm = 10^{-9} m

Some basic terms

a) Nanoscale

- It usually refers to structures with a length scale applicable to nanotechnology, usually cited as 1-100nm

b) Nanoparticles

- Particles can be regarded as nanoparticles if one of their dimensions is less than 100 nm across

- Examples: DNA - 2.5nm, haemoglobin – 6.5nm, viruses – 10-100nm

c) Nanomaterials

- Those which contain nanostructures as their component building blocks

d) Nanotechnology

- It is the deliberate design, construction, characterization and utilization of functional structures, devices and systems through the control of matter at the nanometer-length dimensions i.e., at the atomic and molecular scale.

e) Quantum size effect

i. Quantum structures

- At nano level, particles become electronically comparable to atoms and molecules.

- At these quantum mechanical length scales, there occurs a modification of the properties of each system.
- The quantum sized nano structures are referred to as quantum structures

ii. *Quantum size effects*

- Confined electrons have higher energy than those in bulk crystal, and it depends on dot size.

iii. *Quantum dots*

- Nano particles that are small enough and are thus capable to exhibit characteristic quantum behavior in electronic and optical properties are called quantum dots.

Classification of nanomaterials:

- Types of Nanomaterials based on number of dimensions which lie outside the nanoscale
- Zero dimensional (0D) – In this all dimensions are reduced to nm range, movement of electron is restricted all three x, y, z directions.

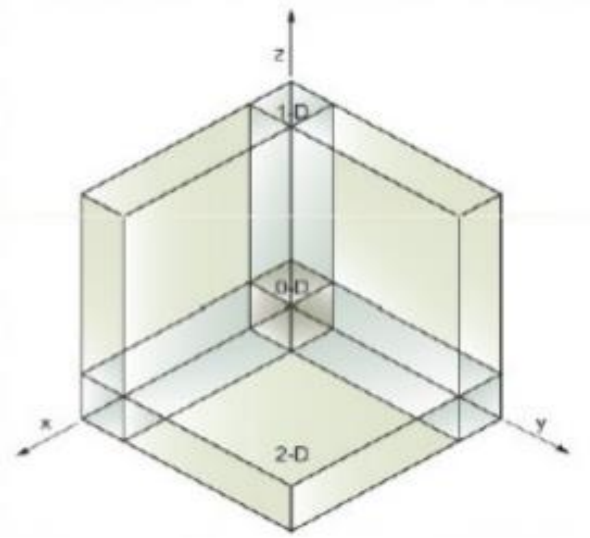
  E.g: Quantum dots, nanoparticles.

- One dimensional (1D) - In this two dimensions are reduced to nm range and one dimension remains large and electron is allowed to move along this dimension.

  E.g: Nanowires, Nanorods.

- Two dimensional (2D) - In this one dimension is confined to nm range and two dimensions remain large and electron is allowed to move along these two directions.

  E.g: Nanowells, Nanofilms, Nanocoatings.



Size dependence of material properties

a) Optical properties:

- Colour of gold nanoparticles change from blue to deep red upon decreasing sizes.
- It is due to surface plasmon resonance.
- A surface plasmon is a neutral oscillation of the electron gas inside a given nanosphere.
- When the sphere is small compared to wavelength of incident light and the light has a frequency close to the oscillation frequency of the surface plasmon, absorption of energy occurs, causing the size - dependant colour.
- In the case of quantum dots, electrons are spatially confined within the dimensions of the quantum dots into quantized energy states. This phenomenon is called quantum confinement, which is responsible for their optical properties.

b) Electrical properties:

- In a metal electrical conductivity is associated with electron mobility in the metal and also to the mean free path
- In metallic nanomaterials, the electronic movement is restricted to the inside of the nanoparticles and most of the electrons are tightly bound.

- In this situation of quantum confinement, a metallic material chosen does not exhibit bulk metallic behavior.
- When nanoscale is reached, the bulk metal may become a semiconductor or insulator.
- CNTs cannot conduct electricity. But the conductivity varies with the diameter and helicity of the tube lattice. i.e, it becomes semiconducting as these parameters changes.

c) Catalytic property

- The smaller the particles of a catalyst greater would be surface area per unit volume, more will be number of active sites and greater efficiency
- Example: nano Pt supported on alumina have greater catalytic efficiency than macro Pt in the oxidation of CO to CO_2.

Surface to volume ratio and its significance

- The ratio of surface area (S m^2) to its volume (V m^3) is called surface to volume ratio (S/V)
- Unit is m^{-1}
- When a given amount of a material in bulk state is divided into particles of smaller dimensions, there occurs an increase in surface area but total volume remains the same.

Significance:

- In the bulk state most of the atoms are in interior rather than in surface
- If bulk material is divided into particles of nanoscale, there occurs an increase in surface area to volume ratio.
- Hence the numbers of active sites for interaction will also increases.
- Thus at nanoscale given material maximizes the surface area and there by maximizes its reactivity.

Applications of nanomaterials:

a) In electronics

- Miniaturization of present day semiconductor microelectronics to the nano level, controlled by nanosystems

CNTs –

- ❖ Semiconductor chips, sensors, and high resolution display devices.
- ❖ Due to high heat conductance capacities, they are used for the production of quantum wires capable of carrying electricity thousands of miles with no energy loss, and in a fast rate

Semiconductor quantum dots –

- ❖ Single electron transistors, computer chips, bioimaging devices, solar cells etc.,

- Nano materials are used as surface coatings in electrical and electronic goods (antimicrobial properties) including refrigerators, vacuum cleaners, washing machines, mobile phones and computer peripherals

b) Optics

- Examples: metallic nanoparticles, quantum dots, oxide nanaoparticles, polymer nanoparticles etc.
- Used in energy efficient circuits, LEDs, solar cells, UV absorbing sunscreen lotions etc.
- Gold and CdSe nanoparticles are used to impart different colouration to glass.
- Fluorescent nanaoparticles like semiconductor quantum dots, fluorescent silica nanoparticles, silica coated fluorescent polymer particles, dye loaded latex nanobeads etc. are used for imaging applications.
- Novel nano particles that can be employed for the colour imaging process in photography have been synthesized.

c) Catalysis

- Nano catalysts include materials like various forms of carbon (carbon black, carbon nanotubes, fullerenes etc.), inorganic nanotubes (W, BN, etc.), metals (Al, Fe, Co, Ni, Ag, Au, Pt etc.), and oxides (Al_2O_3, Fe_2O_3, ZnO, CeO_2, In_2O_3 etc.)
- They have importance in industries and research.
- Their catalytic activity is due to large surface to volume ratio and hence they have large number of active sites. (e.g.: nano Pd has greater catalytic efficiency than macro Pd in hydrogenation of alkene)
- Nano catalysts have greater selectivity. (e.g. nanaogold shows selectivity in partial oxidation reactions like propylene to propylene oxide, but its bulk counterpart not)

d) In medicine

- Nanomaterials are designed for specific diagnostic or therapeutic medical uses
- Example: CdSe -ZnS quantum dots in targeting and imaging cancer cells
- Nanodrugs: nano particles used for drug delivery
- Nano particles are used in wound dressings, catheters etc
- They are also used for water disinfection, food packaging etc.
- Another application is in non viral gene therapy, tissue culture engineering, fabrication of artificial blood vessels and artificial organs.

PART 2: GREEN CHEMISTRY

- Green chemistry is the utilization of a set of principles that reduces or eliminates the use and generation of hazardous substances in the design, manufacture and application of chemical products so that any adverse impact on environment is prevented or at least reduced.

The twelve principles of green chemistry

By Anastas and Warner

1. WASTE PREVENTION

Prioritize the prevention of waste, rather than cleaning up and treating waste after it has been created. Plan ahead to minimize waste at every step.

2. ATOM ECONOMY

Reduce waste at the molecular level by maximizing the number of atoms from all reagents that are incorporated into the final product. Use atom economy to evaluate reaction efficiency.

3. LESS HAZARDOUS CHEMICAL SYNTHESIS

Design chemical reactions and synthetic routes to be as safe as possible. Consider the hazards of all substances handled during the reaction, including waste.

4. DESIGNING SAFER CHEMICALS

Minimize toxicity directly by molecular design. Predict and evaluate aspects such as physical properties, toxicity, and environmental fate throughout the design process.

5. SAFER SOLVENTS & AUXILIARIES

Choose the safest solvent available for any given step. Minimize the total amount of solvents and auxiliary substances used, as these make up a large percentage of the total waste created.

6. DESIGN FOR ENERGY EFFICIENCY

Choose the least energy-intensive chemical route. Avoid heating and cooling, as well as pressurized and vacuum conditions (i.e. ambient temperature & pressure are optimal).

7. USE OF RENEWABLE FEEDSTOCKS

Use chemicals which are made from renewable (i.e. plant-based) sources, rather than other, equivalent chemicals originating from petrochemical sources.

8. REDUCE DERIVATIVES

Minimize the use of temporary derivatives such as protecting groups. Avoid derivatives to reduce reaction steps, resources required, and waste created.

9. CATALYSIS

Use catalytic instead of stoichiometric reagents in reactions. Choose catalysts to help increase selectivity, minimize waste, and reduce reaction times and energy demands.

10. DESIGN FOR DEGRADATION

Design chemicals that degrade and can be discarded easily. Ensure that both chemicals and their degradation products are not toxic, bioaccumulative, or environmentally persistent.

11. REAL-TIME POLLUTION PREVENTION

Monitor chemical reactions in real-time as they occur to prevent the formation and release of any potentially hazardous and polluting substances.

12. SAFER CHEMISTRY FOR ACCIDENT PREVENTION

Choose and develop chemical procedures that are safer and inherently minimize the risk of accidents. Know the possible risks and assess them beforehand.

Green synthesis

- A green synthesis is one in which the use and/or generation of hazardous substances, utilization or wastage of energy, and production of wastes are reduced to an optimum minimum
- Designing a green synthesis involve choosing environment friendly starting materials that can be converted to useful and environmental friendly end products in an environmental friendly media with a very high percentage yield under optimum temperature, pressure and catalytic conditions

Atom economy

- It evaluates how much of the reactants of a reaction gets incorporated into the final desired product.

$$\% \text{ atom economy} = \frac{\text{Relative molecular mass of desired product}}{\text{Total of the relative molecular masses of the reactants}} \times 100$$

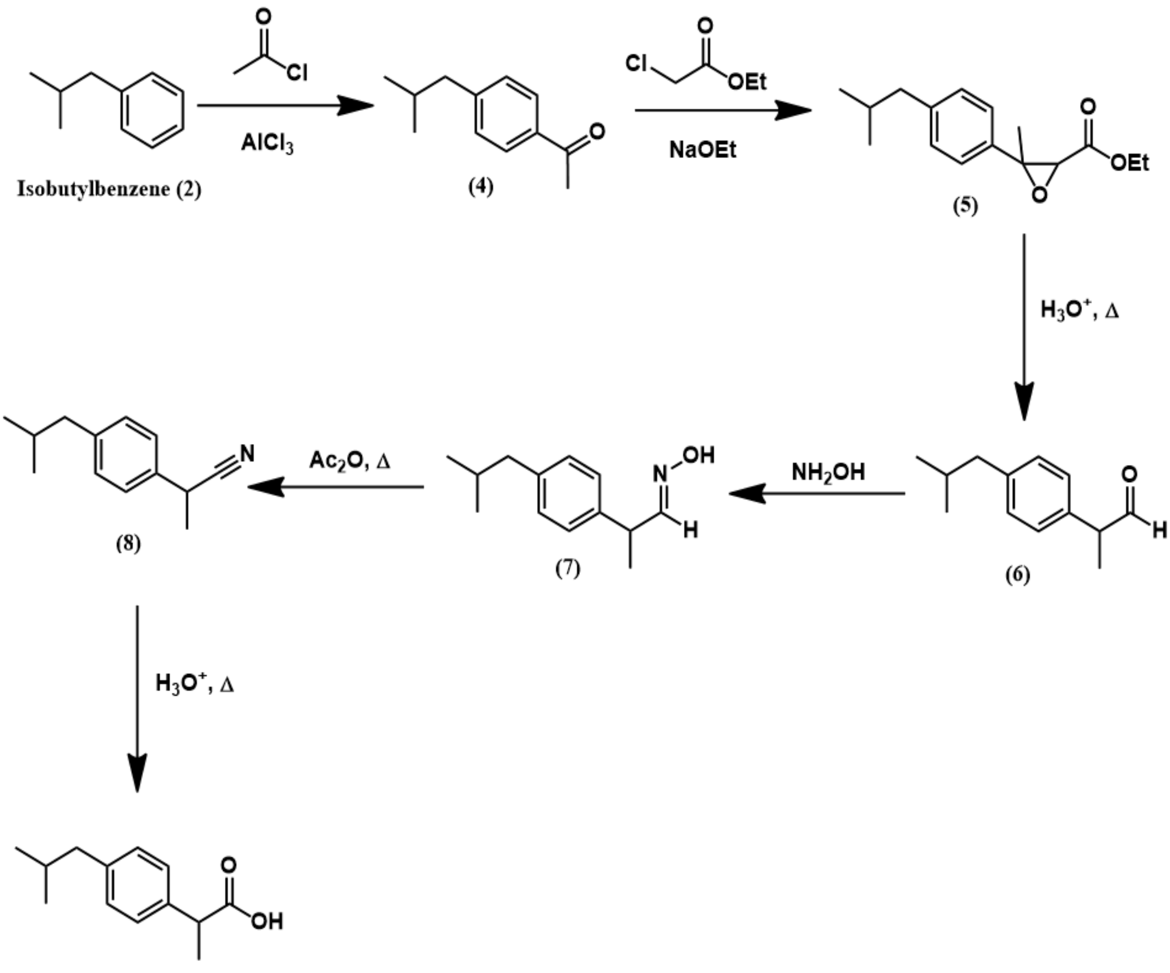
- The greater the percentage of atom economy, the lower the amount of wastes produced and the greener the synthesis would be.

Green solvents

- A Green solvent is one by the use of which adverse environmental impact during its whole life-cycle is the least
- Examples: Water, supercritical CO_2, ionic liquids, and some polymerized solvents
- The greener the solvent used the greener the synthesis is

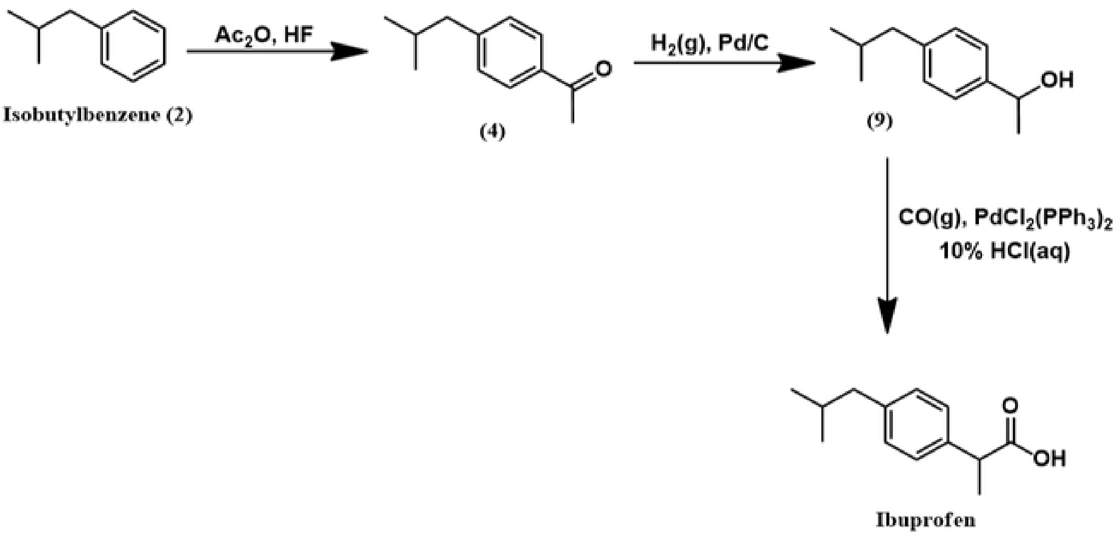
Green synthesis of ibuprofen

- Ibuprofen is a non steroidal anti-inflamatory drug (NSAID) used for relief of arthritis and also uesd as an antipyretic and analgesic.
- The original Boots synthesis of ibuprofen consisted of 6 steps starting from Friedel-Crafts acylation of isobutylbenzene.



Ibuprofen

- This synthesis results in large quantities of unwanted waste chemical byproducts that must be disposed.
- Atom economy is only 40% and hence it is not a green method.
- An improved synthesis by BHC Company requires only 3 steps.
- This synthesis produces less waste and high atom economy.
- The synthesis starts with acetylation of isobutylbenzene.
- The product is then hydrogenated in presence of Raney nickel to get corresponding alcohol.
- It is then subjected to Pd catalysed carbonylation to get ibuprofen


Isobutylbenzene (2)
Ac$_2$O, HF
O
(4)
H$_2$(g), Pd/C
OH
(9)
CO(g), PdCl$_2$(PPh$_3$)$_2$
10% HCl(aq)
O
OH
Ibuprofen

MODULE-3 –CHROMATOGRAPHY

- Chromatography is an analytical technique used for separation, purification and identification of chemical components in mixtures.
- It is a simple and inexpensive technique.

Basic principle of chromatography

- Principle- The differential distribution of the sample components between two mutually immiscible phases.
- Stationary phase- remain fixed, and they tend to retard the movement of mobile phase.
- Mobile phase- they percolates through the interstices or over the surface of stationary phase, and carries the components along the column of the stationary phase.
- Stronger the interaction of a component with the stationary phase, the more retarded is its movements.
- Stationary phase may be solid or liquid. Mobile phase is liquid or gas.

Classification of chromatographic technique

- Classification based on types of phases-
  i. Liquid- solid chromatography(LSC)- mobile phase is liquid and stationary phase is solid adsorbent
  ii. Liquid- liquid chromatography(LLC)- Mobile phase and stationary phases are liquids.
  iii. Gas- liquid chromatography(GLC)- Mobile phase is gas and stationary phase is liquid.
  iv. Gas- solid chromatography(GSC)- Mobile phase is a gas and stationary phase is a solid adsorbant.
- Classification based on mechanism of phase distribution
  i. Adsorption chromatography- based on the selective adsorption of sample components on a solid adsorbant. Eg: LSC, GSC
  ii. Partition chromatography- It is based on partiotioning of sample components between liquid stationary phase and a mobile gas / liquid phase. Eg: LLC, GLC
- Classification based on operational technique-
  i. Column chromatography- it involves a column of solid adsorbant as the stationary phase.
  ii. Plane Chromatography-it involves a flat, thin layer of material which acts as stationary phase. Mobile phase is the liquid that move through the solid phase by capillary action.

  They are of two types-

    a) Paper chromatography(PC)

b) Thin- layer chromatography(TLC)

COLUMN CHROMATOGRAPHY

Adsorption column chromatography (liquid- solid chromatography)

Principle-

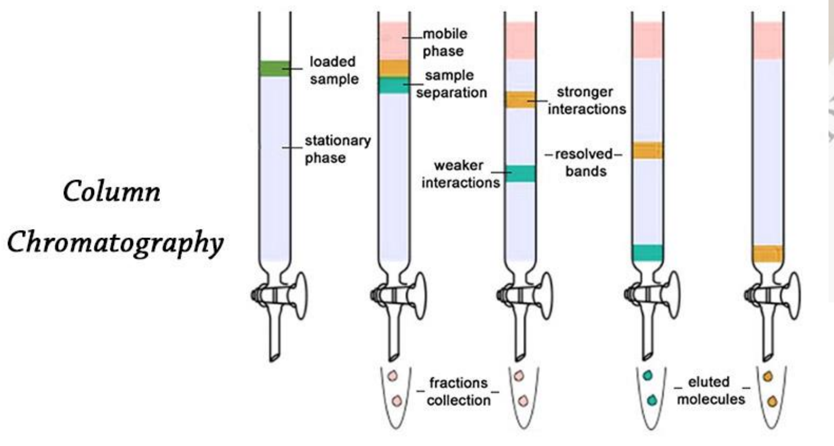
- Based on selective adsorption of sample components on an adsorbent column.
- The stationary phase is the packed adsorbent column with silica gel, alumina or cellulose.
- The mobile phase consist of solvent like acetone, benzene etc.
- The differential migration of components along the column results in separation.

Process-

- Adsorbent column is a long glass tube packed with a suitable adsorbent. A solution of mixture of components is introduced at the top of column. As it moves down the column, different components are adsorbed at different rates.
- The components are extracted from the adsorbent column by passing suitable solvent.
- The weakly adsorbed component emerges first while strongly adsorbed one comes out last.
- The solvent is removed by suitable methods.

Elution- the process of dissolving out the components from the adsorbent using suitable solvent is called elution. The solvent used is called eluent.

Chromatogram- The column or strip of material containing constituents of a mixture separated by chromatography is called chromatogram.



Applications-

- Effective method for the separation of two or more similar organic components from the mixture.
- Purification of organic substances from contaminants.
- Identification, separation and purification of natural products.
- Can be used for the concentration of solutes from dilute solutions.
- Useful for the identification of various industrial products.

PARTITION COLUMN CHROMATOGRAPHY (LIQUID- LIQUID PARTITION CHROMATOGRAPHY)

Principle-

- Stationary phase consist of a thin layer of liquid held on the surface of porous inert solid support like cellulose, silica gel, starch, calcite etc.
- Mobile phase is another liquid immiscible with stationary phase.
- The process is based on the principle that different components have different partition coefficients in the stationary and mobile phases. Thus, they move at different rates and result in separation.

Partition Coefficient, $K = Cs/Cm$

Cs=Concentration in stationary phase.
Cm=Concentration in mobile phase

- The component with least 'K' travels more quickly by mobile phase.
- The component with highest 'K' is retarded most by stationary phase.

Process-

- The stationary phase is a column of finely divided solid adsorbent holding firmly a thin layer of polar liquid.
- The mobile phase is a Non–polar liquid.
- The mobile phase is introduced at the top of column.
- Components which is having high partition coefficient phase moves slowly and are held by stationary phase. And those having least partition coefficient moves to the mobile phase.
- The components in stationary phase are eluted using suitable solvent.
- Eg: A mixture of Co and Ni ions can be separated by using (water + cellulose) as stationary phase and (acetone+ HCl) as mobile phase.

Applications-

- Quantitative separation of a mixture of organic or inorganic substances.
- Purification of products.
- Identification of organic and inorganic products of a mixture.

Chromatogram-

- A detector detects the solute concentration when placed at the column outlet. The plot obtained when signal is plotted as function of time is called chromatogram.

Retention time-

- The time taken by a particular analyte peak to reach detector after introduction of sample is called retention time (t_R).
- The lower the retention time, weaker is its interaction with stationary phase.
- The position of the peak helps to identify the components and the areas under the curve gives the concentration of each component.

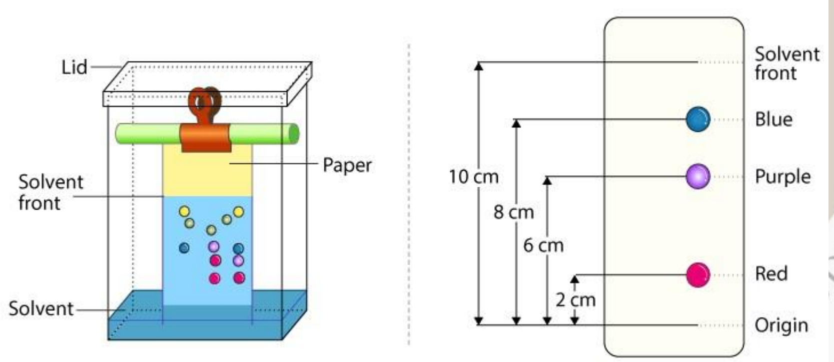
PLANAR CHROMATOGRAPHY

- Planar chromatography is a chromatography on a plane surface. They include paper chromatography (PC) and Thin-layer chromatography (TLC).

Paper chromatography

- It is a special case of liquid- liquid partition chromatography.
- The stationary phase is a film of liquid adsorbed on a paper made of cellulose.
- The mobile phase is another liquid moving over it.
- The principle involved is the partitioning of components between the two liquid phases. The separation arises due to differential migration of components.

Process-



- The apparatus consist of a paper held on a support, a solvent trough and an air-tight glass cylinder.
- The sample solution is spotted near the lower edge of the paper strip. The paper is suspended in a glass cylinder with its lower end dipping in solvent taken as mobile phase.
- As the solvent moves up through the paper by capillary action, the components are differentially distributed in the two immiscible liquids and results in separation.
- The paper strip is removed. The solvent front is marked on it and dried. The coloured components will appear as coloured spots. The position of the colourless components may be determined by spraying the paper with suitable reagent.
- A comparison of Rf values helps in identification of the component.

Applications

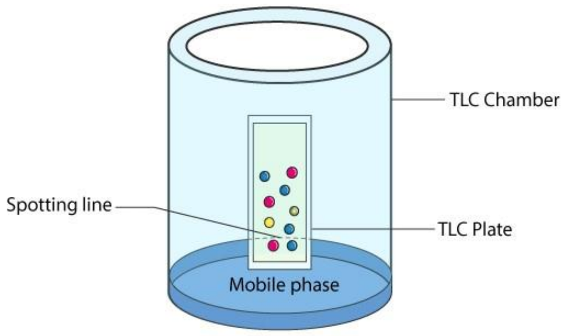
- Suitable for separation and identification of sample components present in trace quantities.
- Used in laboratories and industries for checking purity of organic chemicals.
- Used in separation of components which are chemically similar.
- Used in determination of metals in ores.
- Used to detect drugs and dopes in animals and humans.
- Resolution of isomeric metal complexes.

THIN-LAYER CHROMATOGRAPHY

Principle-

- The stationary phase is a film of liquid adsorbed on a uniform thin layer of an adsorbent like silica gel alumina etc. coated on a glass plate.
- The mobile phase is a suitable solvent immiscible with stationary phase.
- The basic principle is the differential distribution of the components between two immiscible phases which brings about a difference in the rates resulting in separation.

Process-



- A slurry is prepared by mixing adsorbent and liquid. The slurry is then spread on a flat and uniform glass plate. This is called chromoplate.
- The solution containing the components is spotted near the edge of chromoplate. The plate is placed in a slanting manner in a glass tank containing the solvents, which act as mobile phase.
- The plate is kept in such a way that the spots are just above the solvent. The tank is closed with a lid.
- The solvent moves up by capillary action carrying the components. The components are carried at different rates and results in separation.
- The plate is then taken out, solvent front is marked and Rf value is determined.

Applications-

- They can be used for separation, purification and identification of components present in minute quantities.
- Used for the analysis of complex organic mixtures.
- Used for identification and separation of drugs and alkaloids.
- Used in checking purity of samples.
- Useful in separation and isolation of biochemical preparations.
- Used for the detection of contaminants and adulterants in chemicals samples.

Rf value

- The ratio of distance travelled by a particular component to the distance travelled by the solvent front during the same time is called Rf value.
- Rf value depends on solvent, quantity of medium of separation, temperature and nature of substance.

GAS CHROMATOGRAPHY

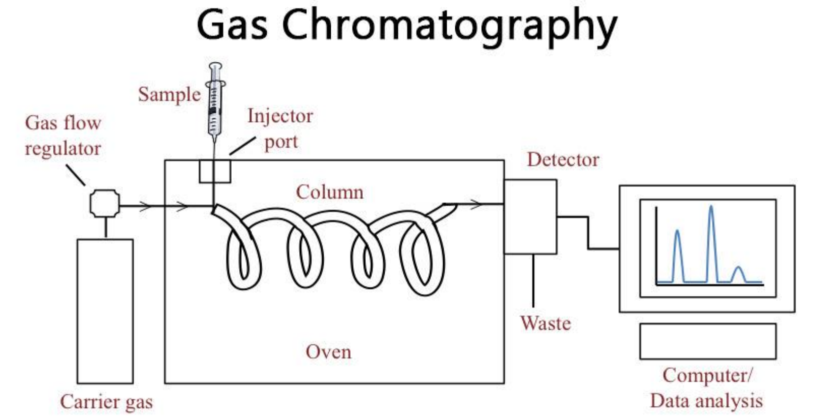
- Two types- Gas-liquid chromatography(GLC) and Gas- Solid chromatography(GSC)

Gas- liquid chromatography-

Principle-

- Stationary phase consist of non- volatile liquid like polyethylene glycol held on a porous solid solid.
- Mobile phase is a gas called carrier gas.
- The components are differentially partitioned between the mobile gas phase and stationary liquid phase.
- After the components of mixture are separated, they are detected with the help of detector.

Process-



- The carrier gas is an inert gas like helium, argon, nitrogen or $C0_2$. It is supplied into the apparatus from a cylinder.
- Sample is injected into the heated chamber by means of a syringe. From here, the sample in the form of vapour state is carried into the column by carrier gas.
- The column consist of coiled tube made of heat resistant material like stainless steel, modified glass or Teflon. The column is placed at high temperature.
- As the carrier gas carry the vapourized sample through the column, separation of components takes place. The less volatile molecule interacts with the stationary phase inside the column and moves slowly. The more volatile molecules interacts more with the mobile phase and moves fast down the column.
- After the separation, detection is done with the help of detectors. Flame ionization detector(FID) and thermal conductivity detectors can be used. The detector response is sent to a recorder. The recorder yields a plot of signal intensity as a function of time.

Analysis of peak-

- The number of peaks gives the number of components in the sample.
- The area under each peak gives the relative concentration of that component in the sample.
- On comparison with the standard information, the retention time can be used to identify each component.

Merits of GLC-

- Most versatile separation technique.
- Used for separation of benzene and cyclohexane, which is impossible by conventional distillation techniques.

Applications of GLC

- Used for separation of component in complex organic and biochemical system.
- Used for identification of natural products.

- Gas chromatograms are used to check purity of organic compounds.
- Used as an analytical technique in petroleum industry, petrochemical industry, biomedical analysis, manufacture of medicines etc.
- GLC are often combined with mass spectrometry, IR spectroscopy and NMR spectroscopy in various qualitative and quantitative analysis.

MODULE: 4-SPECTROSCOPY

INTRODUCTION

- Spectroscopy deals with the interaction of electromagnetic radiation with matter.
- It measure and interpret the absorption or emission of electromagnetic radiation that occurs when the molecules, atoms or ions undergo transition from one energy level to another.

ELECTROMAGNETIC RADIATION

- Electromagnetic radiation is the radiant energy that is propagated through free space or through a material medium.

Characteristics:

- They show wave particle dual nature.
- They are associated with oscillating electric and magnetic fields perpendicular to each other and also to the direction of propagation of energy.
- All kinds of electromagnetic radiation travel with the same velocity(c) in vacuum, 3×10^{8}m/s.
- The frequency(υ) of a wave is related to wavelength(λ) and velocity(c) of light by

  $\upsilon=c/\lambda$

- Energy of radiation (E) is related to its frequency, wavelength, wave number($\bar{\upsilon}$) by the equations

  $E=h\upsilon$

  $=hc/\lambda$

  $=hc\bar{\upsilon}$ $\quad$ $h=6.626\times10^{-34}$ Js

ELECTROMAGNETIC SPECTRUM

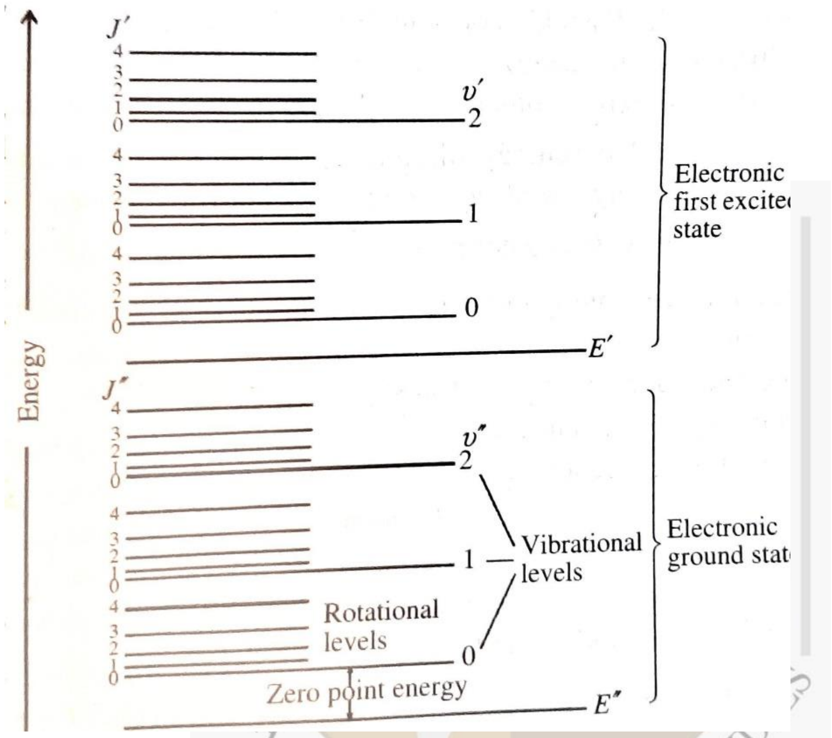
- The orderly distribution of electromagnetic waves according to their frequencies (or wavelengths) into different regions is called electromagnetic spectrum.

General features of spectroscopy

Energy levels in molecules

- The total energy of a molecule is the sum of translational, vibrational, rotational and electronic energies. Out of these rotational, vibrational and electronic energies are quantized.
- Rotational energy is the energy possessed by the molecule by virtue of rotation about an axis passing through its centre of gravity. Rotational energy states are designated by quantum number J. J=0, 1, 2, 3,…..
- Vibrational energy is the energy associated with the periodic displacement of the atoms from their equilibrium positions. Vibrational energy states are designated by quantum number υ. $\upsilon = 0, 1, 2\ldots$

- Electronic energy is the energy associated with the distribution of the electrons of the molecule in its various energy states. Electronic energy levels are designated by quantum no. 'n'. n=1, 2, 3,…
- Within each electronic state there are a number of vibrational energy states and within vibrational energy states there rotational energy levels.
- The order of energy difference ΔE is electronic> vibrational> rotational.
- The electronic, vibrational and rotational levels of a molecule are collectively called molecular energy levels.



Interaction of electromagnetic radiation with matter

- When a sample is irradiated, either the electric field component or magnetic field component of radiation can interact with molecular system. This will result in absorption of radiation of a particular frequency by the system.
- For absorption to occur, the energy of photon ($h\upsilon$) must match the energy difference (ΔE) between the quantized energy levels E_1 and E_2.

  $\Delta E = E_2 - E_1 = h\upsilon$

  OR

  A molecule can absorb a particular frequency only if there exist within the molecule an energy transition of magnitude $\Delta E = h\upsilon$

  This is called Bohr condition for spectral transitions.

- When a beam is made to fall on sample, there will be a decrease in intensity corresponding to that particular frequency being absorbed. The record of the particular frequency or wavelength can be made with an instrument called spectrometer and the resulting spectrum is called absorption spectrum.

- Molecule excite to higher energy states on absorbing radiation and when these return to lower levels, they emit radiations of particular frequency satisfying Bohr condition. The record of particular frequency emitted is made by using spectrometer and the resulting spectrum is called emission spectrum.
- The absorption and emission spectrum are complementary to each other and provides the same kind of information regarding molecular structure.
- The spectrum is a plot of some parameters like intensity or absorbance or % transmittance against another parameters like wave length or wave number of light.

Born- Oppenheimer approximation

- According to Born- Oppenheimer approximation, the motion of the nuclei is so slow compared to the speed of electrons. Therefore, motion of nuclei and electrons in a molecule can be treated separately.
- In molecular spectroscopy, Born- Oppenheimer approximation means the electronic, vibrational, and rotational energies are completely independent of each other such that Total energy $E_{total} = E\,(elec) + E(vib) + E\,(rot)$
- Change in total energy of a molecule $\Delta E_{total} = \Delta E(elec) + \Delta E(\,vib) + \Delta E(rot)$

IR SPECTROSCOPY(VIBRATIONAL SPECTROSCOPY)

- Two types of fundamental vibrations are

i) Stretching vibrations – Movement along the bond axis such that interatomic distance is increasing or decreasing.

ii) Bending vibrations- There occurs a change in bond angle.

- Absorption of quantum of radiation in the infra-red region having a frequency equal to the characteristic frequency of vibration increases the amplitude of vibration and raises the molecule to higher vibrational level. The spectra from such absorptions causing vibrational transitions are called vibrational spectra or infrared spectra.

Selection Rules

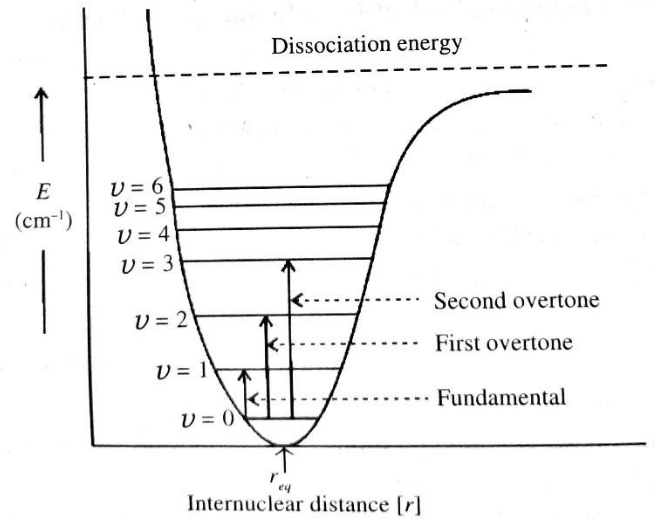
- For a particular vibration to result in absorption if infrared radiation, the displacement of atoms during that vibration must cause a change in dipole moment of the molecule.
- Symmetric diatomic molecules like H_2,Cl_2 etc are IR inactive molecules because the bond stretching vibrations in them do not result in any change in dipole moment.
- Heteronuclear diatomic molecules like HCl and polyatomic molecules like H_2O, CO_2, NH_3, CH_4 etc are IR active molecules because these molecules have vibrational modes which are capable of changing dipole moment.
- As per the simple harmonic oscillator model, according to quantum mechanical principles, the selection rule for vibrational transitions is “Only those vibrational transitions are allowed in which the vibrational quantum number v changes by one unit”.

  For an allowed transition, $\Delta\upsilon = \pm 1$, $\Delta\upsilon = +1$ for absorption and $\Delta\upsilon = -1$ for emission

- For anharmonic oscillators, the selection rule is $\Delta\upsilon = \pm 1, \pm 2, \pm 3, \ldots$

Fundamental bands and overtones

- The transition of one vibrational mode of a molecule between ground state($\upsilon=0$) and first excited state ($\upsilon=1$) involving absorption of one quantum of energy is called fundamental transition. The frequency corresponding to fundamental transition is called fundamental frequency and the corresponding signal in the spectrum is called fundamental band.
- In addition to fundamental band in the IR spectrum, presence of signal at higher frequencies can occur, these are called overtones.
- The transition $\upsilon=0$ to $\upsilon=2$ occurs at frequency about twice that of fundamental transitions and are called first overtones. The transition $\upsilon=0$ to $\upsilon=3$ occurs at frequency about three times that of fundamental and are called second overtones.
- The intensity of signals are of the order fundamental> first overtone> second overton



NORMAL MODES OF VIBRATION OF MOLECULES

- A molecular vibration in which all atoms vibrate with the same frequency and pass through their equilibrium positions simultaneously is called normal mode.
- A linear molecule has (3n-5) and non-linear molecule has (3n-6) normal modes of vibration, where n = no. of atoms in the molecule.
- Different normal modes of vibration having same frequency is called degenerate.

CO_2

- Linear triatomic molecule. There are (3n-5)=4 normal modes of vibration.

a) Symmetric stretching- It involves no dipole moment change. Hence IR inactive.

b) Asymmetric stretching- IR active ,$\upsilon=2350cm^{-1}$.

c) In- plane bending- IR active.

d) Out-of plane bending- IR active

- Bending vibrations are degenerate and $\upsilon=667cm^{-1}$.

H_2O

- Non-linear triatomic molecule. There are(3n-6)= 3 normal modes of vibration.

a) Symmetric stretching- IR active, $\upsilon=3652\text{cm}^{-1}$.

b) Asymmetric stretching- IR active, $\upsilon= 2530\ \text{cm}^{-1}$.

c) Symmetric bending- IR active, $\upsilon=1596\ \text{cm}^{-1}$.

Concept of group frequencies

- Bonds in a chemical group vibrate with frequencies which are independent on remaining portion of the molecule. They show a characteristic frequency irrespective of the molecule. Recording the spectra of a large number of organic compounds gives data on characteristic absorptions of most functional groups. Such data can be used in the identification of various groups present in an unknown organic compound.
- Eg: **O-H**

    Free -3650-3600cm^{-1}

    H-bonded- 3500- 3200cm^{-1}

    Carboxylic acids- 3400-2400cm^{-1}

  N-H- Primary and secondary amines and amides

    Stretch-3500-3100cm^{-1}

    Bend- 1640- 1550cm^{-1}

  C-H

  Alkanes- Stretch-3000-2850cm^{-1}

  Alkenes- Stretch- 3100-3000cm^{-1}

  Alkynes- Stretch- 3300cm^{-1}

  C=C

  Alkene- 1680-1600cm^{-1}

  Aromatic- 1600 and 1475cm^{-1}

  C=N Nitriles 2260-2240cm^{-1}

  C=O Ketones 1725-1705cm^{-1}

    Aldehydes 1740- 1720cm^{-1}

Fingerprint region

- The region 700-1400 cm^{-1} of IR spectrum is called fingerprint region. The pattern of vibrations in this region is unique characteristic of each molecule.
- The frequencies of some of the stretching vibrations and most of the bending vibrations fall in the fingerprint region. Similar molecules may show similar spectra

outside the fingerprint region, but the band pattern is different in the fingerprint region.

- Very helpful in establishing the identity of an unknown compound by comparing with IR spectra of known compound.

Applications:

- **Elucidation of structure-**

  If the IR spectrum of a compound shows an absorption band at a frequency which is characteristic of a particular group, it indicates the presence of that group in that compound.

- **Detection of H- bonding-**

  The O-H group generally absorbs around 3600cm^{-1}. The presence of H-bonding , lengthens the bond, weakens it and lower the vibrational frequency.

UV-VISIBLE SPECTROSCOPY (ELECTRONIC SPECTROSCOPY)

- Electronic spectroscopy involves the study of electronic transitions from lower to higher quantized energy levels by absorbing energy in UV and visible regions.

Beer- Lambert's law-

- When a beam of monochromatic radiation passes through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the solution is directly proportional to the intensity of radiation and also to the concentration of solution.

  $-dI/dx \ \alpha \ Ic$

  I is the intensity of radiation and c the molar concentration of the solution

  $-dI/dx = kIc$

  $dI/I = -kcdx$

  If I_o is the intensity of incident radiation and I_x the intensity of emergent radiation, x is the thickness of medium, then on integration within the limits I_x and I_o

  $\int dI/I = -kc\int dx$

  $\ln I_x/I_o = -kcx$

  $\log I_x/I_o = -kcx/2.303$

  $\log I_o/I_x = kcx/2.303$

  $\log I_o/I_x = \varepsilon cx$

  where $k/2.303 = \varepsilon$, called molar absorption coefficient or molar extinction coefficient.

  $\log I_o/I_x = A$, known as absorbance or optical density of the solution.

  When $I_x = (1/10)I_o$ and $c = 1$ mol L^{-1}, then

  $\varepsilon = 1/x$

- Molar absorption coefficient is defined as the reciprocal of the thickness of 1 molar solution which reduces the intensity of radiation to 1/10 th of its initial value.
- The ratio of the emergent intensity(I_x) to the incident intensity(I_o) is called transmittance(T).

  $T=I_x/I_o$
- $A= -\log T$

Electronic spectra in polyatomic molecules

- Electrons are filled up in molecular orbitals in the increasing order of energy. The Lowest energy electronic transition is caused by absorption of radiation from HOMO to LUMO. In most of the organic and inorganic molecules, the HOMO is bonding(σ or π) or non- bonding(n) where as LUMO is an antibonding (σ* or π*) .Electronic transition by absorption of UV or visible radiation involves excitation of an electron from bonding or non- bonding MO into one of the antibonding MOs.
- Six kinds of transitions are possible and the decreasing order of energy of excitation are

$$\sigma \rightarrow \sigma^* > \sigma \rightarrow \pi^* \approx \pi \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

- The last three transitions occur in the near UV and visible region and are generally applicable in electronic spectroscopy.
- Saturated hydrocarbons which contain only single bonds and no lone pairs do not show absorption in near UV and visible region. Compounds containing non- bonding electrons show absorption in near- UV and visible region.

Terms of importance

a) λmax : The wavelength at which maximum absorption occurs.

b) Absorbance: $A=\log I_o/I_x$

c) Molar absorption coefficient(ε): $A=\varepsilon cx$. It is a measure of the intensity of absorption for maximum absorption. The magnitude of ε is directly proportional to the probability of a particular transition. The ε value at λmax is εmax.

d) Transmittance:

$T=I_x/I_o$

Nature of the spectrum

- Absorption of UV- Visible radiation induces electronic transitions as well as vibrational and rotational transitions. Thus, an electronic transition produces a number of bands which corresponds to vibrational and rotational transitions.
- Vibrational transitions produces coarse structure and rotational transitions produce fine structure on the electronic spectra. This structure is visible for gaseous samples.

- In liquid or solid, the lines merge together and form a broad band.

Chromophores

- Chromophores are isolated functional groups which exhibits a characteristic peak in the UV or visible region.
- They are generally groups having unsaturated centres or hetero atoms or both.
- Eg: -C=C-, -C≡C-, -C=O, -COOH,-NO_2, -N=N, -C≡N etc.

Auxochromes

- Auxochromes are functional groups that does not show absorbtion above 200nm, but when present along chromophore, shift absorption to longer wavelength and increase the intensity of absorption peak.
- Eg: -OH, -NH_2, -OR, -NHR, -NR_2,-SH,-SR etc

Shifts in absorption maximum and peak intensity

Four types of shifts are

a) **Bathochromic shift(Red shift):**

Shift of absorption maximum(λmax) to longer wavelength.

Eg: benzene shows a λmax of 255nm. Aniline($C_6H_5NH_2$) shows λmax of 280nm.

b) **Hypsochromic shift(Blue shift):**

Shift of absorption maximum to shorter wave length.

Eg: aniline shows λmax of 280nm. Addition of acid to aniline gives anilinium ion which shows λmax of 254nm.

c) **Hyperchromic shift:**

Shift of molar absorption coefficient (ε_{max}) to a higher value, showing an increase in the intensity of absorption band. Bathochromic shift is often accompanied by hyperchromic shift,

Eg: conversion of phenol to phenoxide ion shifts εmax from 6200cm^{-1} to 9200cm^{-1}.

d) **Hypochromic shift:**

Shift of molar absorption coefficient (εmax) to a lower value, showing a decrease in intensity of absorption band. Hypsochromic shift is accompanied by hypochromic shift.

Eg: conversion of benzoic acid to benzoate ion shift εmax from 11600cm^{-1} to 8700cm^{-1}.

APPLICATIONS OF ELECTRONIC SPECTROSCOPY

1. **Organic chemistry:**
    a) Identification of compounds:

The spectrum of each compound is the unique characteristics of its structure. Comparison of spectrum of an unknown compound with the spectra of known compound, make it possible to identify the compound.

b) Detection of functional groups:

Functional group containing unsaturated centres or heteroatoms show characteristic absorption maximum in the UV- Visible spectroscopy. Chromophores in unknown compound can be detected by comparison of its spectrum with the known compounds.

c) Identification of geometrical isomers:

Trans isomers have generally higher λmax and εmax as compared to cis compounds.

d) Study of conjugation:

Presence of conjugation shifts λmax to higher values. Greater the conjugation, the higher will be the λmax.

2. **Inorganic chemistry:**

   - Several co-ordination complexes show peaks in the UV-Visible region arising from d-d transitions, charge transfer (CT) transitions etc.
   - Electronic spectra provides information regarding nature and types of metal ions and ligand present and also the types of interaction present in co-ordination compounds.

3. **Organic and inorganic qualitative analysis**.

The expression for Beer- Lambert law is

$\log I_o/I_x = \varepsilon c x$

$A = \varepsilon c x$

If we plot a graph between A and c we get a straight line which pass through the origin.

To estimate the concentration of unknown solution, we prepare a series of standard dilute solutions. Their absorbances (A) are measured using spectrophotometer. Then we plot a graph between A and c. we get a linear plot which passes through the origin. This curve is known as calibration curve. Then, the absorbance of unknown solution is measured. The concentration corresponding to the measured absorbance of the unknown solution is obtained from calibration curve.

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (NMR)

- NMR is a spectroscopic technique based on the absorption of electromagnetic radiation in the radiofrequency region by nucleus of non- zero spin quantum number I.

- Energies of certain nuclei get splitted in the presence of magnetic field. Absorption of radiofrequency radiation cause transition between these magnetically induced energy levels.

Basic principles

- The nuclei of many isotopes have spin angular momentum ($\vec{I}$) characterized by spin quantum number I.
- The spin quantum number can be determined from mass number and atomic number.

Mass no.	Atomic no.	Spin quantum no. I
Odd	Odd or even	Half integer
Even	Even	zero
Even	Odd	Integer

- Nuclei with non- zero spin quantum number can give NMR spectra.
- The spinning of such nuclei produces a magnetic field. It act as magnetic dipole.
- In the presence of an external MF, the degenerate spin states split into (2I+1) different energy levels. The allowed spin states is given by magnetic quantum no. mI. mI= -I, (-I+1),….., (I-1), I.
- The magnitude of the magnetic dipole is expressed in terms of nuclear magnetic moment $\vec{\mu}$. It is proportional to spin angular momentum.

$\vec{\mu}=\gamma\vec{I}$

γ is the gyromagnetic ratio of the nucleus.

$\gamma=gN(e/2mp)$

gN is the nuclear g- factor. e is the charge of proton. Mp is the mass of proton.

Therefore, $\vec{\mu}= gN(e/2mp)\vec{I}$

Nuclear magnetic resonance

- In an external field B_0, the magnetic moment interacts with the field. The energy of the nucleus is given by

$E= -\gamma B_0 M_I h/2\pi$

Substituting the value of γ and putting $eh/4\pi mp = \beta_N$,nuclear magneton.

$E= -g_N \beta_N B_0 M_I$

The separation between the energy levels is given by

$|\Delta E| = |gN|\beta_N B_0|\Delta M_I|$

When $\Delta M_I=1$

$\Delta E = |gN|\beta_N B_0$

- Absorption of radio frequency energy results in transition between nuclear magnetic energy levels that corresponds with the separation between energy levels. This phenomenon is called NMR resonance.

- The selection rule is $\Delta M_I = \pm 1$
- The frequency of radiation that corresponds to the transition is called resonance frequency.

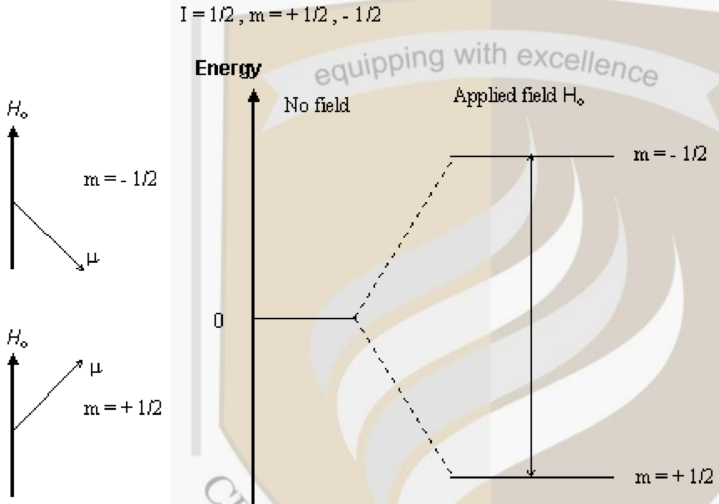
  $$\upsilon = \Delta E/h = \frac{|g_N|\beta_N B_0}{h}$$

- The frequency of radiation depends on strength of applied magnetic field.

PROTON NMR SPECTROSCOPY

- Proton has I value=1/2

  There are (2I+1) = 2 allowed spin states. The magnetic moment are aligned either parallel (M_I=+1/2, lower energy) or anti- parallel (M_I= -1/2, higher energy) with the applied field.



- When frequency of radiation become equal to frequency of separation of the two spin states, absorption takes place and a NMR signal is obtained.
- In NMR experiments, the magnetic field (B_0) is kept constant and frequency is varied (frequency sweep method) or frequency is maintained constant and magnetic field is varied (field sweep method).

CHEMICAL SHIFT

Electron Shielding and de-shielding

- When a compound is placed in a MF, the surrounding electrons also generate a MF called induced MF or secondary MF.
- The induced MF may reinforce or oppose the applied MF.
- If induced MF opposes the applied field, then effective field experienced by the proton decreases. Thus, protons are said to be shielded. Greater MF is required by protons for flipping to higher state. Thus, proton absorbs upfield.

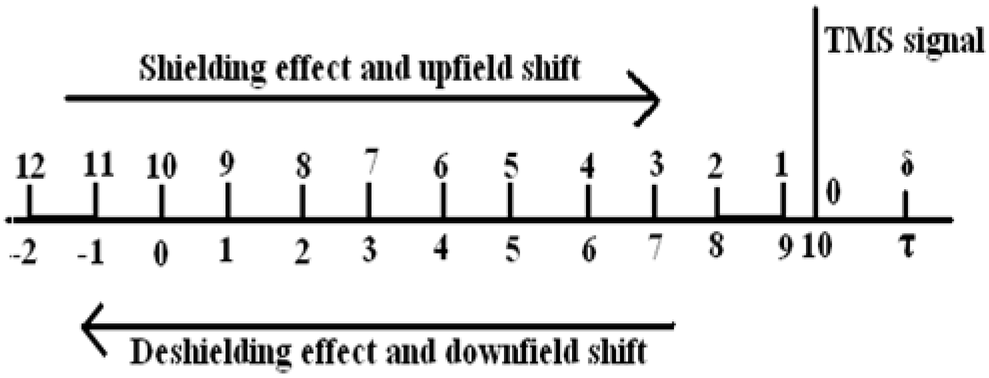
- If induced MF supports the applied MF, the effective field experienced by the proton increases. Thus, protons are said to be deshielded. Deshielded protons absorbs downfield. They require smaller field to flip.
- Protons in different chemical environments have different shielding and deshielding effects.
- Protons in the identical chemical environment are said to be chemically equivalent and they will produce only one peak in NMR spectra.
- The difference in the absorption position of a particular proton from that of a reference proton is called chemical shift of that proton.
- The most commonly used reference compound is Tetramethyl silane (TMS). Its protons are more shielded than almost all organic protons. It give a sharp intense peak.
- Chemical shift value on δ- scale is given by

  $$\delta = \frac{B_{Ref} - B_{sample}}{B_{ref}} \times 10^6 \qquad \text{(field sweep)}$$

  Frequency sweep:

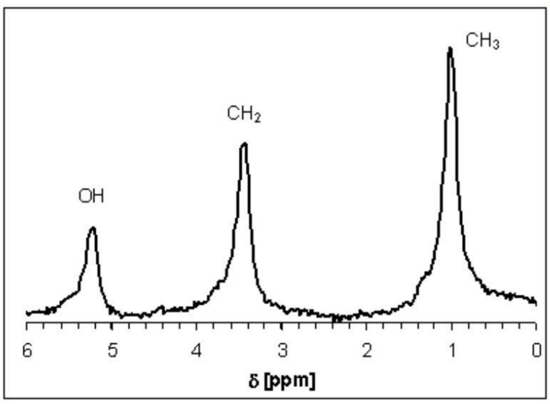
  $$\delta_{sample} = \left(\frac{v_{sample} - v_{reference}}{v_{reference}}\right) \times 10^6$$

- For protons of most compounds the chemical shift varies from 0 to 10 ppm. The chemical shift of TMS proton is take as zero.



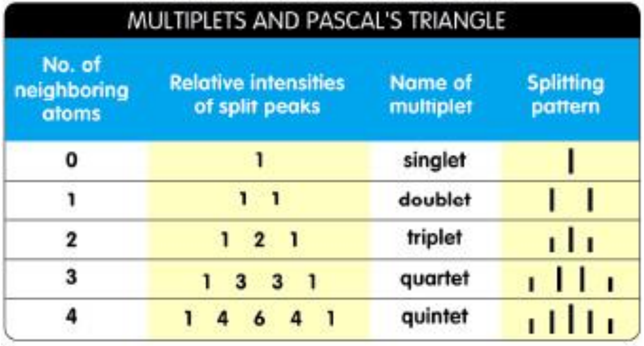
- Protons in the same chemical environment absorbs at the same field strength.
- Eg: NMR Spectrum of ethanol (CH_3- CH_2- OH) under low resolution.

  There are three peaks corresponding to three groups of protons. Proton of –OH , -CH_2 and -CH_3 group. The –OH proton is shielded to lesser extend due to high electronegativity of O atom. So, OH proton absorbs at low field strength. Number of signals is equal to number of types of equivalent protons.


Low resolution NMR spectrum ethanol

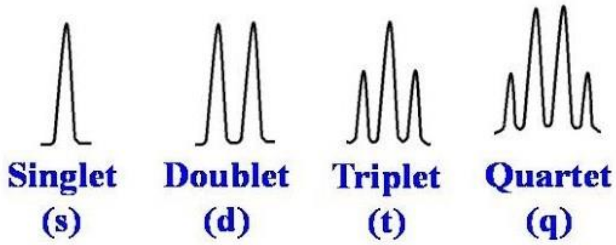
SPIN-SPIN COUPLING

- When NMR experiment is carried out at high resolution, the signals may get splitted into multiplet, ie, doublet, triplet, quartet etc.
- This is due to the interaction of spins of one set of protons with another set through the bonding electrons.
- General rules for determining spectra-
  - Equivalent protons do not give rise to observable splitting.
  - If the number of neighbouring protons is n, then the signal is splitted into (n+1) lines. This is called (n+1) rule.
  - If nA and nX are number of equivalent protons of set A and X, and if their spin couple with another set M containing nM protons , then the signal of M split into (nA+1)(nX +1) lines. This is the advanced (n+1) rule.
  - The relative intensities of peaks is given by coefficient of binomial expansion $(1+x)^n$. The coefficients are given by pascal's triangle.



MULTIPLETS AND PASCAL'S TRIANGLE

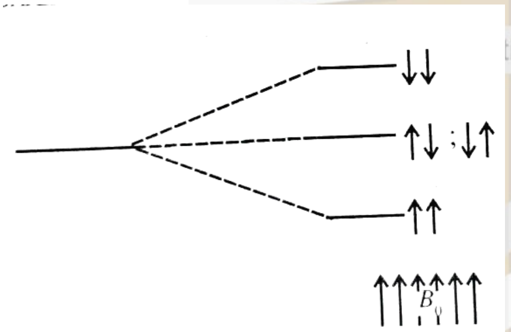
No. of neighboring atoms	Relative intensities of split peaks	Name of multiplet	Splitting pattern
0	1	singlet	❙
1	1 1	doublet	❙ ❙
2	1 2 1	triplet	ı ❙ ı
3	1 3 3 1	quartet	ı ❙ ❙ ı
4	1 4 6 4 1	quintet	ı ❙ ❙ ❙ ı



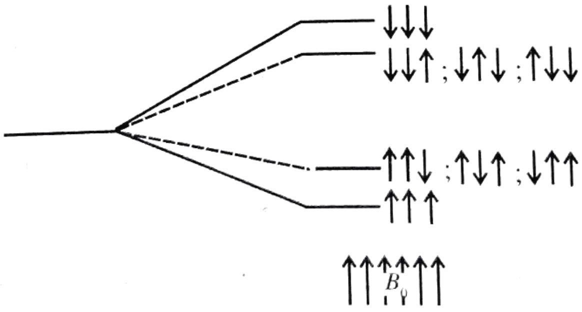
- The midpoint of the multiplet represent the chemical shift.

NMR spectrum of ethyl bromide(CH_3-CH_2-Br)

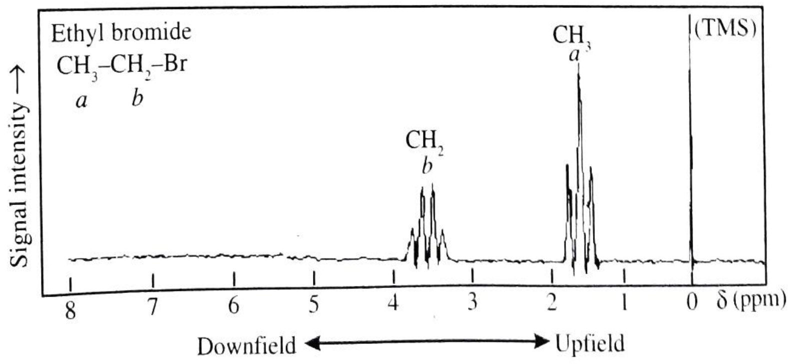
- There are two sets of protons- CH_3(methyl) and -CH_2(methylene).
- For methylene (CH_2) protons there are four equal probable combinations of spin orientations of which two are equivalent.



- The combination which is aligned with the field causes deshielding of methyl protons and the combination aligned opposite to the field causes shielding of methyl protons. The two equivalent combinations at the centre do not affect the methyl protons. Thus CH_3 signal is split into triplet of intensity 1:2:1
- For methyl (CH_3)protons there are eight equally probable orientations of spin orientations which include 2 sets of three equivalent combinations.



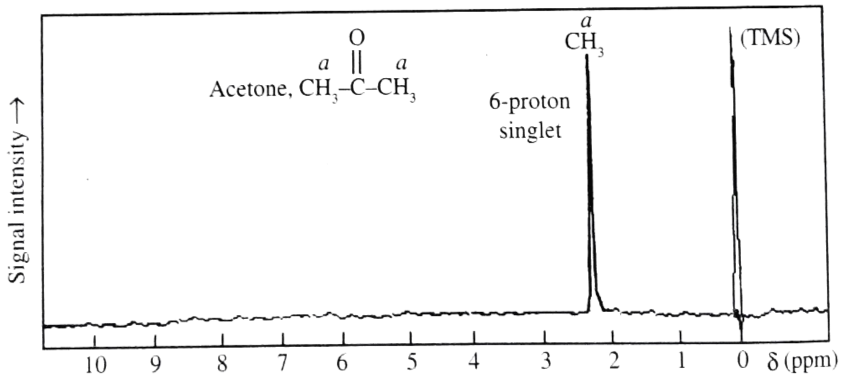
- These spin orientations of CH_3 have similar effect on proton of CH_2 group. The CH_2 group split into a quartet with intensity 1:3:3:1.



NMR SPECTRA OF SOME SIMPLE COMPOUNDS

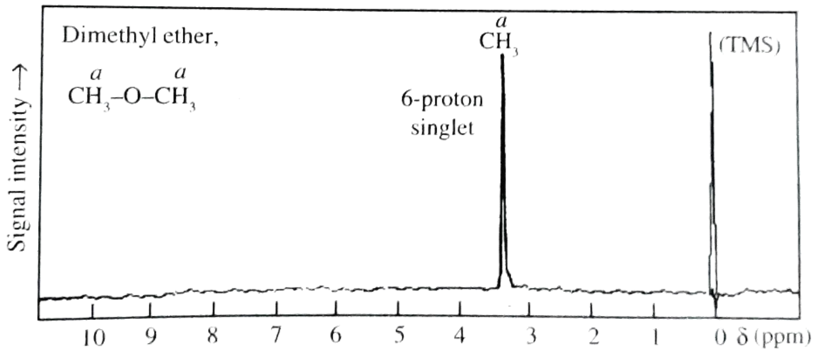
1. Acetone or propanone(CH_3-CO-CH_3)

- The six protons have identical chemical environments. They are chemically equivalent and show the same chemical shift.
- A single peak around δ=2.1 ppm is obtained.



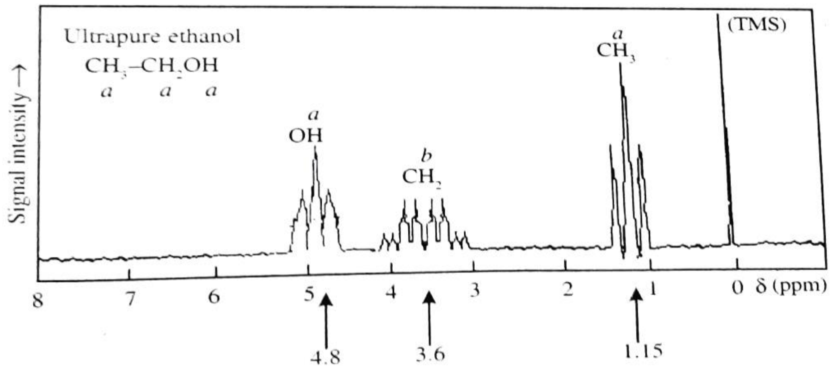
2. Dimethyl ether or methoxymethane (CH_3-O-CH_3)

- The six protons have identical chemical environments. They are chemically equivalent and show same chemical shift.
- A single peak around δ= 3.2 ppm is obtained.



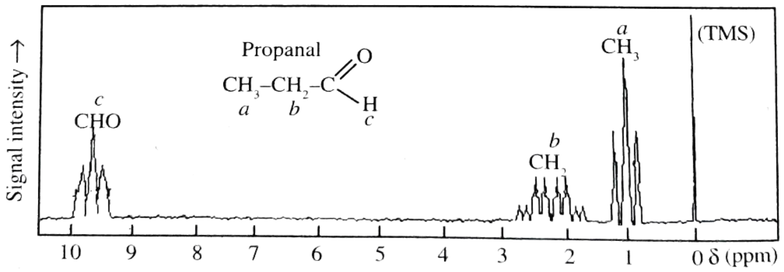
3. Ethanol (CH_3-CH_2-OH)

- Extra pure alcohol under high resolution show three sets of signals.
- A triplet at δ=1.15 for methyl protons due to their coupling with -CH_2 protons.
- A quartet of doublet at 3.6 δ for CH_2 protons due to their coupling with methyl (CH_3) protons and the hydroxyl (OH)proton.
- A triplet for the hydroxyl protons at 4.8 δ due to the coupling with CH_2 protons.



4. **Propanal (CH_3- CH_2- CHO)**

- Under high resolution, propanal shows three sets of signals.
- A triplet at 1.0 δ for CH_3 protons due to their coupling with CH_2 protons.
- A quartet of doublets at 2.2 δ for CH_2 protons due to their coupling with CH_3 and CHO protons.
- A triplet for CHO proton around 9.8 δ due to their coupling with CH_2 protons.



MODULE -5: POLYMERS

- Polymer is a substance of high molecular mass, composed of many repeating units called monomers.
- The process in which a polymer is formed from its monomer units is called polymerisation.

CLASSIFICATION OF POLYMERS

1. ON THE BASIS OF ORIGIN

i) ***Natural polymers***- Polymers of natural origin. Eg: Starch, Cellulose, proteins etc.

ii) ***Synthetic polymers***- Man- made polymers. Eg: Polythene, PVC, Terylene etc.

2. ON THE BASIS OF STRUCTURE

i) ***Linear polymers***- Polymers in which monomer units are joined together to form long chains , which are stacked one above the other to form a well- packed structure.

Eg: high density polythene, nylon

ii) ***Branched- chain polymers-*** Monomer units are joined together to form long chains with branches along them.

Eg: Low density polythene, glycogen.

iii) ***Cross-linked polymers***- Monomer units are joined together to form 3-D network structure.

Eg: Bakelites, melamine- formaldehyde resin.

3. ON THE BASIS OF MODE OF FORMATION

i) ***Addition polymers***- The polymers formed by addition polymerisation are called addition polymers as chain- growth polymers.

Eg: polythene, PVC

- The process in which monomer units add on to each other to form a polymer is called addition polymerisation or chain- growth polymerisation.

ii) ***Condensation polymers***- The polymers formed by condensation polymerisation are called condensation polymers or Step- growth polymers.

Eg; Nylon66, Terylene, Glyptal

- The process in which monomer units condense with the elimination of small molecules like H_2O, HCl, NH_3, CO_2. is called condensation polymerisation or step- Growth polymerisation

4. BASED ON KIND OF MONOMER UNITS

i) **Homopolymers**- Polymers formed from one kind of monomer units.

Eg: polythene, polystyrene, P.V.C.

ii) **Copolymers**- Polymers formed from different kinds of monomer units.

Eg: Nylon66, Glyptal, Buna-S

5. **ON THE BASIS OF MOLECULAR FORCES**.

i) **Elastomers-** polymers having weak intermolecular forces between the polymer chains. They possess high elasticity, softness, stretchability and toughness. They have cross-links between the chains, which help them to regain their original shape.

Eg; natural rubber, synthetic rubber like Buna-S, Buna-N, neoprene.

ii) **Fibres-** polymers having strong intermolecular forces between the polymer chains. They possess high tensile strength, are tough, stiff and abrasion- resistant, retain their properties over wide range of temperature.

Eg: nylon66, terylene

iii) **Thermoplastics-** polymers which soften on heating and become rigid on cooling. The properties of polymers are not affected on heating and cooling. They can be easily moulded and remoulded. Their intermolecular forces are in between elastomers and fibres. There is no cross- linking between chains.

Eg: Polythene, PVC, Teflon.

iv) **Thermosetting polymers-** Polymers when heated, undergo permanent change to give hard infusible and insoluble products. They cannot be remelted and remoulded. They get highly cross-linked. They attain permanent rigidity on heating.

Eg: Bakelites, urea- formaldehyde polymer.

STRUCTURES AND APPLICATIONS OF SOME COMMERCIALLY IMPORTANT SYNTHETIC POLYMERS

1)SYNTHETIC RUBBERS

i) Buna-S:

- Obtained by addition copolymerisation of buta-1,3-diene and styrene in the presence of sodium or H_2O_2 and $FeSO_4$.
- They can be vulcanized by using sulphur.
- They have high mechanical strength and is superior to natural rubber.
- They are abrasion- resistant.
- They are widely used in tyre industry
- Used as soles and components of shoes.
- Used for insulating wires and as adhesives and lining for vessels.

iv) Buna-N:

- Obtained by addition copolymerisation of buta-1,3-diene and vinyl cyanide in the presence of sodium or H_2O_2 and $FeSO_4$.
- They can be vulcanized by using sulphur.

- They are resistant to oils and solvents.
- They are abrasion resistant.
- They are superior to natural rubber and are resistant to ageing.
- They are used as oil-seals.
- Used to manufacture automobile and aircraft parts, conveyer belts and adhesives.

v) **Neoprene:**

- Obtained by addition polymerisation of chloroprene in the presence of oxygen.
- They can be vulcanized in the presence of magnesium oxide.
- They are very resistant to oils and chemicals.
- They are resistant to heat and light and atmospheric oxidation.
- Used to make hoses, shoe- heels, containers for hydrocarbons and corrosive chemicals.
- Used for making conveyer belts, gaskets, pipes etc.

SYNTHETIC FIBRES

- Synthetic fibres are synthetic polymers which are drawn into long filament like materials whose lengths are at least 100 times their diameters.

1)POLYAMIDES:

- Polymers having amide linkages in the polymer chains are called polyamides. They are prepared by the polycondensation between dicarboxylic acids and diamines.

a)Nylon66

- Nylon 66 is prepared by the polycondensation of hexamethylene diamine and adipic acid at about 523 K.
- Nylon 66 is tough and strong. It is used for making socks and fabrics like hosiery. It is also used to make fishing nets, brush bristles, ropes, etc.

b)Nylon 6(perlon or capron)

- Nylon 6 is a polyamide which is derived from the 6-carbon compound caprolactam.
- When caprolactum is heated with traces of water, it hydrolysis to aminocaproic acid which on further heating polymerises to give nylon 6.
- Nylon-6 has good tensile strength and is used in the manufacture of fabrics, ropes, tyre cords, etc.

2)POLYESTERS

- Polymers having ester linkages in the polymer chains are called polyesters. They are obtained by the polycondensation between a dicarboxylic acid and a diol.

Terylene(Dacron)

- Prepared by polycondensation of terepthalic acid and ethylene glycol at 423-473K.
- Terylene has good mechanical strength up to 450 K. It is resistant to heat and moisture and is unattacked by many chemicals. It is extensively used to make fabrics. It is also used to make seat belts and sails.

PLASTICS

- Polymers which exhibit flow properties at elevated temperatures are called plastics. They can be moulded under these conditions and then cooled to give hard utility articles.
- Plastics can be divided into thermoplastics and thermosetting plastics.

(a) Thermoplastics

l. *Polythene or polyethylene:*

- There are two varieties of polythene: low-density polythene and high-density polythene.

Low-density polythene or low-density polyethylene (LDPE).

- It is prepared by the polymerisation of ethylene at about 473 K under high pressure in the presence of traces of oxygen as initiator.
- It is extremely flexible and is resistant to chemicals and moisture. It is used to packing and wrapping films, laboratory ware, wash bottles, irrigation pipes, etc. and for insulating electric wires and cables.

High-density or high-density polyethylene (HDPE).

- Prepared by polymerisation of ethylene at moderate temperature (323-393K) and moderate pressure(1-20atm) in solvent like hexane or cyclohexane in an inert atmosphere in the presence of Ziegler-Natta catalyst.
- They have high tensile strength, stiffness and hardness and are resistant to chemicals and moisture. It is used to make toys and other household articles.

2. Polystyrene:

- Prepared by the polymerisation of styrene at 353 K in the presence of benzoyl peroxide as initiator.
- Polystyrene is resistant to acids, alkalis, oxidants and reducing agents. It has brittleness, poor heat resistance and poor weathering properties. It is used to make jars, bottles, TV and radio cabinets, toys, foamed plastics etc.

3. Polyvinyl chloride (P.V.C)

- Prepared by the polymerisation of vinyl chloride at low temperature (293 K) in the presence of hydrogen peroxide.
- P. V.C is a tough and horn-like material which is resistant to acids, alkalis, oxidising agents, reducing agents. It is widely used in the manufacture of pipes, equipment parts and for covering wires and cables.

4. Polytetrafluoroethylene (PTFE) or Teflon:

- Prepared by the polymerisation of tetrafluoroethylene in the presence of oxygen or H_2O_2 as initiator.
- It is unattacked by almost all chemicals except alkali metals. It is tough and has excellent heat resistance. It is used for making pump valves and pipes, for Insulation of motors, coils, capacitors, generators, transformers, etc. and for coating cookware to produce non-stick cooking utensils.

(b) Thermosetting plastics

1. Phenol-formaldehyde resins or Bakelites:

- Formed by polycondensation between phenol and formaldehyde, catalysed by acids or bases. The first step in the reaction is the formation of addition compounds called methylol phenols.
- The methylol phenol further condense either with phenol or among themselves through methylene linkages.
- If excess of formaldehyde is taken and the reaction is continued a crosslinked three-dimensional polymer will be obtained.
- When combined with suitable fillers, these phenol-formaldehyde resins have chemical resistance, heat-resistance and stability.
- Soft bakelites with low degree of polymerisation are used in lacquers, etc. and as heat-setting adhesives for plywood.
- Hard bakelites with high degree of cross-linked polymerisation are used for making electrical items, telephone instruments, combs, fountain pen barrels, household utensils, etc.

2. Melamine-formaldehyde resin— “Melmac”

- Formed by the condensation polymerisation of melamine and formaldehyde under suitable conditions of temperature, pressure and catalyst.
- Melamine-formaldehyde resins are used in the manufacture of unbreakable crockery, including kitchen utensils, dinnerware and bowls.
- They are used in a series of laminated surfacing materials [Brand name: Formica] designed for interior use on countertops and cabinet facings.
- The resins are also used as insulating and soundproofing materials.

APPLICATIONS OF SOME OTHER COMMERCIALLY IMPORTANT SYNTHETIC POLYMERS

(a) Poly(para-phenyleneterephthalamide) — "Kevlar":

- It is an aromatic polyamide fibre made from the poly condensation of p-phenylenediamine and terephthaloyl chloride. It is a para aramid.
- The Kevlar fibre can be woven into fabrics or converted into the sheet form.

- On account of its high tensile strength, Kevlar is used to make bulletproof vests, military combat helmets and fireproof garments.
- It is used to manufacture gloves, sleeves, jackets, caps and other articles of protective clothing, designed to protect users from cuts, abrasions and heat.
- Kevlar is used as an inner lining for some bicycle tires.
- Its acoustic properties make Kevlar useful as a material on marching drums and the bows of stringed instruments.

(b) Poly(meta-phenyleneisophthalamide) — "Nomex":

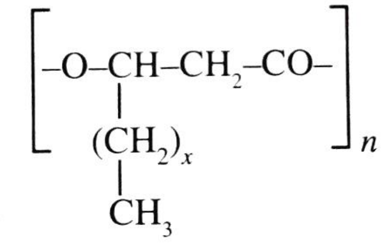
- It is an aromatic polyamide made from the polycondensation of m-phenylenediamine and isopthalolyl chloride. It is a meta aramid.
- It can be woven into fabrics or converted to sheet form.
- It has excellent heat and flame resistant properties. It is used in the fire fighters, apparels for military pilots, military tank drivers, race-car drivers. Also used in fire- fighters mask.
- It is used in thermal and electrical insulations.
- It is used in automobiles, high-temperature hoses and insulation for spark plugs. Nomex sheets are used as a substitute for asbestos.
- Nomex is both very strong and very light; It's often used inside helicopter blades and airplane tail fins, and in aerospace applications.
- For its acoustic qualities, Nomex is used in concert hall canopies and in the production of loudspeaker drivers.
- Nomex is also used blended with up to 60% Kevlar with increased tear-resistance and abrasion-resistance in several applications.
- A polycarbonate material is obtained by the polycondensation of bisphenol A (BPA) and phosgene ($COC1_2$).
- Lexan is a durable material with high impact-resistance. It has heat resistant and flame-retardant properties, Lexan is used in various products associated with electrical and telecommunications hardware, and as a dielectric in high-stability capacitors.
- Lexan is highly transparent to visible light. So, a hard coating of Lexan is applied to eyewear lenses can then protect the eye from UV light. It is used in sunglass lenses, safety swimming goggles and scuba masks. It is used in exterior automotive components like headlamp lenses.
- It is used for producing flat or curved glazing walls and domelights.
- Being light-weight and impact-resistant, Lexan is electronic display screens of mobile and portable devices. It is used in durable, lightweight luggage, digital audio player cases, computer cases shields and instrument panels,
- A major application of Lexan is in the production of CDs, DVDs, and Discs.

<u>BIODEGRADABLE POLYMERS</u>

- Biodegradable polymers are those that degrade as a result of the action of microorganisms and/or enzymes.

- Naturally occurring polymers with the ester groups are biodegradable. They hydrolysis in the presence of esterases produced by soil microorganisms. Products of degradation are quickly metabolized by microorganisms.

- Biodegradable polymers can be either natural or synthetic. The naturally occurring poly (β-hydroxyalkanoate) class of polyesters constitute one class of commercially important biodegradable polymers. These may be represented by the general fomula



$$\left[-O-\underset{\underset{CH_3}{|}}{\underset{(CH_2)_x}{\underset{|}{CH}}}-CH_2-CO- \right]_n$$

- The synthetic polymers in general offer greater advantages over the natural materials. They can be tailored to give a wider range of properties with predictable results upon application. Biodegradation can be accomplished by synthesizing polymers that have hydrolytically unstable linkages in the backbone. These most common chemical functional groups are esters, anhydrides and amides.

(1) Poly (glycolic acid) or Poly (glycolide), PGA:

- The thermoplastic polymer poly (glycolide) or PGA is the simplest biodegradable linear aliphatic polyester.

- The glycolide monomer is first synthesized from the catalytic dimerization of glycolic acid [$HO—CH_2—COOH$] by the action of heat. The ring opening polycondensation of glycolide in the presence of a catalyst (like Sb_20_3 or $SbC1_3$ or zinc lactate) at 195-230ºC then yields poly (glycolide), PGA.

- PGA was used to develop the first synthetic absorbable suture for surgery under the trade name of "Dexon" It is naturally degraded in the body by hydrolysis and is absorbed as monomers within six months. It has high initial tensile strength, it passes smoothly through tissue, it can be easily handled, and it can be easily tied into strong knots.

- PGA is commonly used for subcutaneous sutures in abdominal and thoracic surgeries. It is also used to produce implantable biomedical devices including pins, rods, plates and screws which, being biodegradable, do not require surgical removal at a later stage after implant.

- The high strength and modulus of PGA has disadvantages because its fibres are highly stiff, causing difficulty while being used as sutures. So, glycolide is copolymerized with other monomers to reduce the stiffness of the resulting fibres.

(2)Poly(lactic acid) or poly(lactide), PLA

- The lactide monomer is first prepared by inducing acid catalysed thermal dimerization of lactic acid. The ring opening polycondensation of lactide is then carried out in the presence of suitable metallic catalysts at suitable temperatures to get poly(lactide), PLA.

- PLA is used to make absorbable suture for surgery. PLA is used as medical implants in the form of clips, anchors, screws, plates, pins, rods, and as a mesh.
- PLA can also be used as a decomposable packaging material in the form of films that can also be used for food packaging. It can be moulded into bags, cups and disposable tableware. It has also been used in the production of biodegradable disposable garments, feminine hygiene products and diapers.

3. Poly(ß-hydroxybutyrate-co-hydroxyvalerate), PHBV:

- The thermoplastic polymer poly(ß-hydroxybutyrate-co-hydroxyvalerate) or PHBV is a biodegradable aliphatic polyester. It is a copolymer of 3-hydroxybutanoic acid.
- PHBV was commercialized under the trade name "Biopol". It is non-toxic and undergoes bacterial degradation into carbon dioxide and water. PHBV is brittle and has low impact resistance.
- PHBV is used in medical implants and orthopaedic devices. It also finds application in controlled release of drugs.
- PHBV is used in preparing speciality packaging films. It also finds application in the manufacture of various consumer goods like bottles.

MODULE -6-ENVIRONMENTAL POLLUTION

- The contamination of any part of our environment through human activities, by any undesirable substances or factors is called environmental pollution.
- The substances which cause environmental pollution is called pollutant.

Types of pollution

- On the basis of type of environment being polluted, they are classified into-

1. Air pollution- contamination of air in our atmosphere by undesirable substances.
2. Water pollution- contamination of water bodies and the ground water by undesirable substances or organisms or agents like heat.
3. Soil pollution- contamination of the soil by undesirable substances, organisms or agents that affect the quality of soil.

- On the basis of agents causing pollution, they are classified into

1. Noise pollution
2. Thermal pollution
3. Radiation pollution

AIR POLLUTION

- Contamination of air by undesirable substances which cause harmful effect on living organisms.
- Substance causing air pollution- air pollutants.
- Air pollutants are of 2 types-

1. Gaseous air pollutants- oxides of C,N,O and S, hydrocarbons, hydrogen sulphide etc.
2. Particulate air pollutants- Non-metallic, metallic, organic particulates, dust, mist, smokes, fumes etc.

Air pollution by oxides of carbon

- Pollutants- CO, CO_2
- Sources of CO-

1. By incomplete combustion of carbon.
2. Automobile exhausts.
3. Burning of domestic fuel, domestic waste and industrial fuel.
4. Reduction of CO_2 at high temperature.
5. Decomposition of CO_2 at higher temperature.

Harmful effects of CO-

- Combines with haemoglobin of blood to form a stable complex called carboxy haemoglobin. It prevents the bonding of O_2 with Hb and also displaces O_2 from Hb-O_2.

So, it blocks normal oxygen carrying ability of blood. This leads to a condition called asphyxia.

- Inhalation of CO at high level leads to head ache, dizziness, vomiting, mental aberrations, visual difficulty, breathing difficulty and unconscious.
- In plants, CO causes leaf drops, leaf curling, reduction in leaf size, decrease in chlorophyll content and premature ageing in plants.

Source of CO_2 –

- By combustion of fossil fuels
- Decomposition of limestone during manufacture of cement

Harmful effects of CO_2-

- Responsible for enhanced greenhouse effect
- Global warming

AIR POLLUTION BY OXIDES OF NITROGEN

- Pollutants –NO along with NO_2,N_2O,N_2O_3 and N_2O_5
- Source:

(a)NO formed by high temperature combination of N_2 and O_2 and is slowly oxidised to NO_2 and other oxides.

(b) Effluent gases from electric power industry, explosive industry etc.

- Harmful effects :-

(a) NO_2 has irritating effect, cause severe bronchitis and respiratory problems

(b) NO_2 disrupts some cellular enzyme system.

(c) NO_2 causes pulmonary edema leading to death.

(d) Cause Pneumonia, internal bleeding and lung cancer

(e) Cigarette smoke contains high level of NO_2 which cause lung disease

(f) Photochemical smog formation –

$2NO + O_2 \xrightarrow{\qquad} 2NO_2$

$NO_2 \xrightarrow{h\upsilon} NO + O$

$O + O_2 \longleftrightarrow O_3$

This ozone oxidises NO to NO_2

NO_2 and O_3 Reacts with unburnt hydrocarbons to produce formaldehyde, Acrolein, Peroxyacetyl nitrate (PAN)

(g) Leads to acid rain.

AIR POLLUTION BY OXIDES OF SULPHUR

- Pollutants- Oxides of Sulphur(SO_2 and SO_3)
- Source- (a) Burning of high sulphur content fuels in thermal power plants and industries.

$$S + O_2 \longrightarrow SO_2$$

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

(b) From automobile exhausts.

- Harmful effects-

a) SO_2 and SO_3 causes irritation of eyes

b) Damage respiratory tract.

c) Inhalation of SO_2 at higher level leads to bronchities, asthma and lung cancer.

d) Leads to formation of sulphurous smog (classical smog/London smog/ Reducing smog)

e) Leads to acid rain.

f) In plants, they are absorbed through stomata into the mesophyll of the leaves,it leads to tissue collapse, dwarfing, stiffness of flower buds.

EFFECTS OF AIR POLLUTION

1. DEPLETION OF OZONE

- Ozone is present in stratosphere
- Formation of ozone:

$$O_2 \xrightarrow{242\ nm} O+O$$

$$O_2 + O \longrightarrow O_3$$

- Decomposition of ozone:

$$O_3 \xrightarrow{220\ nm} O_2 + O$$

$$O + O_3 \longrightarrow O_2 + O_2$$

- An equilibrium concentration of ozone is maintained in stratosphere at an altitude of 25- 30 km from earth. Ozone forms an envelope in the lower layer of atmosphere. It act as a protective radiation shield for living organisms on Earth. They absorbs UV light in the region 220-330nm. It also maintains the thermal balance of Earth.

Ozone Hole formation

- The Chlorofluoro carbons and nitrogen oxides makes hole in the ozone layer. CFC's or freons are widely used as refrigerants and aerosol propellants. They generate chlorine free radicals in the stratosphere by the action of UV light.
- The chlorine radicals react with O_3 to produce O_2.
- The chlorine radicals are continuously generated and cause break down of ozone.

- Ozone layer depletion is also caused by NO_x gases. They are formed from supersonic aircrafts,nuclear explosions etc.

Impact of stratospheric depletion

- Exposure to ultraviolet-B rays cause skin cancer.
- Leads to leukemia and breast cancer.
- UV rays are absorbed by cornea and lenses leading to photokeratitis and cataract.
- Reduce the yield of agricultural crops.
- Decrease chlorophyll content of leaves.
- Destruct aquatic organisms.
- Leads to climatic change.

Remedy to prevent ozone depletion

- Low cost substitute compounds can be used.
- Stop completely the use of CFC's.

GREEN HOUSE EFFECT

- The progressive warming up of Earth's surface and atmosphere due to the blanketing effect of CO_2 and certain other gases in the atmosphere .
- Earth absorbs solar energy as radiations in the visible region and a balance is maintained by giving off this energy as IR. This outgoing radiation is absorbed by CO_2 and water vapour and is partly re- emitted to Earth's surface. This leads to heating up of Earth's surface.
- Large quantities of CO_2 are introduced into the atmosphere through combustion of fossil fuels and also by global deforestation. This large scale increase in atmospheric CO_2 leads to global warming through greenhouse effect.
- Other greenhouse gases are methane, N_2O and chlorofluoro carbons.

Consequences of Greenhouse effect

- Climatic changes- Due to Greenhouse effect, there arises temperature variation in different parts of the world. High evaporation of water causes changes in ocean currents and winds. There will be variation in amount of rainfall, increased desertification.
- Drop in agricultural production.
- Increase of temperature leads to melting of polar ice and hence sea level increses.
- Destruction of aquatic organism
- Refugee problems.

Control of greenhouse effect

- Control and reduce the input of CO_2 into atmosphere.

- Solar energy may be used as an alternative to fossil fuels.
- Control deforestation, industrialization.

ACID RAIN

- Air pollutants like nitrogen oxides and sulphur oxides are discharged into atmosphere through combustion of petroleum and fossil fuels. These pollutants are converted into HNO_3 and H_2SO_4 in the presence of light, water, oxygen etc. these acids come downto the earth during rain. This is called acid rain.

Adverse effects of acid rain

- Acid rain increases acidity of soil and cause damage to agricultural crops.
- Damages leaves of trees, reduce photosynthesis.
- Adversely affect aquatic species.
- They cause neurological, digestive and respiratory disease in humans.
- They cause extensive damage to buildings by formation of soluble sulphates and nitrates.

Control of acid rain

- Solar energy can be used instead of fossil fuels.
- Reduce the production of nitrogen oxides and sulphur oxides.

WATER POLLUTION

Water pollution by sewage

- Sewage consist of organic and inorganic waste matter carried by water.
- Sewage induces a foul smell and impart colour to water.
- Sewage contain human and animal excreta, so it is the carrier of several pathogenic microorganism. Leads to typhoid, cholera etc.
- Sewage causes depletion of dissolved oxygen.
- Sewage contains huge nutrients and this leads to eutrophication.

They can be controlled by sewage treatment before discharge.

Water pollution by industrial effluent

- Effluent from pulp and paper mills, sugar factories etc. causes the depletion of dissolved oxygen. Many of these effluents are highly poisonous to aquatic organisms.
- Effluents from fertilizer industries cause eutrophication.
- Metal plating industries release large quantities of heavy metals and cyanide. They are toxic.
- Chemical factories release acidic and alkaline compounds that are harmful to aquatic organisms.
- Paper mill release mercuric compounds. They are highly poisonous and carcinogenic.

- Radioactive wastes discharged into water cause radiation pollution.

  Industrial effluents must be treated before discharged.

Water pollution by soaps and detergents

- Soaps are hydrolysed to the corresponding fatty acids which increase the organic content of water. This leads to depletion of dissolved oxygen.
- Some detergents which are not fully biodegradable enter the water bodies. They settle to the bottom as sediments.
- Presence of detergents causes foaming and thereby reducing the aeration of water.
- Phosphate containing detergents causes eutrophication.
- Detergents are toxic to several species of animals and plants and suppress their growth.
- Many of the detergents causes alteration in the infrastructure of cell. They affect the external sensory organs.

Water pollution by fertilizers

- Pesticides like DDT, chlordane, lindane, malathion etc enter into water bodies by various ways. They remain in water and enter into the food chain through bacteria, phytoplankton etc. the concentration of pesticides increases on moving up in food chain by biomagnification. So, fish, aquatic birds, and man have concentration of pesticides.
- Higher concentration of pesticides cause hormonal imbalance, cancer, leukemia etc.
- Pesticides cause hypertension and damage to kidneys.
- They interfere with transmission of nerve impulse and leads to paralysis.
- They inhibit production and functioning of sex hormones.
- Pesticides is toxic to aquatic organisms and plants.

Water pollution by fertilizers

- Contamination of water by fertilizers (nitrogenous , potash etc) leads to

1. Eutrophication

   Fertilizers make fresh water bodies nutrient rich. This favours massive algal growth on the water surface. This leads to reduction of oxygen concentration in water and affect aquatic life.

- The process in which the nutrient- enriched water bodies support a dense plant population that kills animal life by depriving it of oxygen is called eutrophication.

b) Blue baby syndrome

- When water polluted with nitrates are consumed by humans, nitrates are reduced to nitrites by intestinal bacteria. This nitrites interfere with oxygen carrying capacity of blood causing damage to respiratory system. This is called blue baby Syndrome (Methemoglobinaemia).

- Control measures: use of biofertilizers which involves microorganisms like Rhizobium, Azetobacter etc.

Water pollution by heavy metals

1. Lead

- Source- Industries such as petroleum, paint, battery etc.
- Harmful effects-

a) Highly toxic.
b) Accumulates in bones of humans and animals.
c) Causes denaturation of proteins and enzymes.
d) Damage to nervous system, kidney, brain.

2. Mercury

- Source- Industries like electrochemical industries, batteries etc.
- Harmful effects-

a) Highly toxic.
b) Bioaccumulate in the form of methyl mercury.
c) Leads to biomagnification.
d) Minamata disease was caused due to mercury poisoning.

3. Cadmium-

- Source- from electroplating, paint, plastic industries and from gold jewellery works.
- Harmful effects-

a) Undergo biomagnification through food chain.
b) Cause damage to lungs, kidneys.
c) In Japan, by the consumption of cadmium- ingested rice leads to a disease called itai-itai or ouch-ouch.

4. Chromium-

- Source- effluent from metal plating industries
- Harmful effect-
    a) Toxic to aquatic and terrestrial organisms.
    b) Cause respiratory disease.

5. Arsenic-

- Source- from pesticides

- Harmful effects-
  a) Inhibit the action of enzymes.
  b) Cause cancer.

BIOACCUMULATION AND BIOMAGNIFICATION

- The process of accumulation of pollutants in organism is called bioaccumulation.

Eg: Heavy metals or pesticides can accumulate in aquatic organisms

- The process in which a stable and non- biodegradable pollutant increases in concentration at each higher level as it passes from one organism to another through food chain is called biomagnification.

WATER QUALITY PARAMETERS

1. **Dissolved oxygen(DO)-**

- It is expressed as weight of oxygen in milligrams present per litre of water or as parts per million(ppm)
- The value of DO for good quality water is 4-6 mg/l
- DO is determined iodimetrically.

2. **Biochemical oxygen demand(BOD)-**

- The amount of dissolved oxygen used by aquatic microorganisms for the oxidation of organic matter incubated for a period of 5 days at 20ºC.
- For pure water BOD is 1-3mg/l

3. **Chemical oxygen demand(COD)-**

- The oxygen equivalent required for the oxidation of organic matter with the help of strong chemical oxidant, usually potassium dichromate in acid medium.
- For pure water value of COD is less than 250 ppm.

SOIL POLLUTION

Sources of soil pollution:

- Excess application of fertilizers, pesticides etc
- Dumping plastic wastes.
- Dumping radioactive wastes.
- Discharge of industrial waste into soil.
- Repture of underground storage tanks.

Adverse effect of soil pollution

- Loss of nutrients, reduction in soil fertility and reduction in crop yield.
- Increased salinity of soil.

- Absorption of toxic materials of crops will pass on to humans and animals.
- Damage soil structure.
- Pollution of drinking water sources.

Pollution due to plastics.

- Plastic pollution is the accumulation of man- made plastic products in the environment and cause problems for living organisms and their habitats.

Adverse effects of plastic solution

- Plastics are quite resistant to environmental degradation process. They prevent the passage of rain water into the soil and thus affect the underground water level.
- The chemicals involved in the making of plastics are highly toxic. They can cause several diseases like cancer, damage the nervous system and immune system, affect kidneys and blood.
- The disposal of plastic is challenging. Recycling of plastic is uneconomical. Burning of plastics releases poisonous dioxins to air. Landfilling plastics results in contamination of soil.
- Plastics causes clogging of drainage system.

Remedies

- Cut down the use of plastics.
- Use biodegradable plastics.
- Reuse the plastic things.

THERMAL POLLUTION

- Thermal pollution refers to the undesirable effects arising due to the addition of heat to water bodies through human activities.

Source of thermal pollution

- Discharge of warm water from industrial source.
- Discharge of condenser cooling water from electric power generating plants

Effects of thermal pollution

- Most fishes and other aquatic organisms survive only within certain temperature ranges. Tropical marine animals cannot withstand a small increase of temperature.
- Higher temperature of water decreases the solubility of oxygen in water. It also increases the metabolic rates of aquatic species which leads to faster depletion of dissolved oxygen.
- Some aquatic species flourish in warm water. This changes the diversity of fauna in that region.
- Thermal pollution leads to climatic changes. The heat added to environment causes global warming.

Control of thermal pollution

- Water is cooled and then be discharged to the water body. This cooled water can also be recycled back to the plant. Some of the methods for cooling are-
- Cooling pond method- warm water is allowed to flow to a large artificial pond. Evaporation takes the heat to atmosphere and water gets cooled.
- Cooling tower method- warm water is sprayed downwards over vertical sheets kept in a cooling tower. This warm water is allowed to meet cool air. Heat exchange occurs between the water and air. The excess heat is passed into the atmosphere.

RADIOACTIVE POLLUTION

- The pollution of the environment caused by extremely dangerous radiations produced by human activities is called radiation pollution.

Source of radioactive pollution

- Radiotherapy- radionuclides used in radiotherapy constitute a source of pollution.
- Nuclear tests and radioactive fall outs- Nuclear radiation test carried out by different countries introduce a large quantities of radionuclides. The radioactive dust that falls to the earth after a nuclear explosion is called radioactive fallout.
- Nuclear reactors and nuclear power plants.
- Radioactive wastes from nuclear reactors and nuclear power plants
- Radioactive ore processing- radionuclides from mining and processing units pollute soil, water and air.
- Industrial and medical research.

Harmful effects of radioactive pollution

- Exposure to small doses can cause nausea, vomiting, diarrhoea while exposure to high doses may lead to death.
- Exposure to radiations would cause cancer in different parts of body or leukemia.
- Radiations break down enzymes, proteins, nucleic acids and thus cause metabolic disorders.
- Radiation can cause internal bleeding.
- They can damage eye cells and cause cataract.
- They cause gene mutations.

Control of radioactive pollution

- High chimneys and high ventilators should be used at places where contamination is high.

- Masks, gloves, hoods etc must be used while working with radionuclides.
- Care should be taken during disposal of radioactive wastes.
- Nuclear explosion tests and production of nuclear weapons should be stopped completely.

MODULE-7- CHEMISTRY IN DAILY LIFE

1. FUELS FROM PETROLEUM INDUSTRY

1. Petroleum

- Complex mixture of hydrocarbons including alkanes (C_1-C_{40}) and cycloalkanes + unsaturated hydrocarbons + aromatic hydrocarbons + Small quantities of N, S and O compounds.

2. Natural gas

- Consists of low boiling alkanes (C_1-C_5), 60-90%) methane.[also, ethane, propane, butane, CO_2, H_2S and N_2]

Refining of petroleum – petroleum distillation

- Since petroleum contains thousands of hydrocarbons, separation of pure compound is necessary

- The fractions obtained from distillation of petroleum are still mixtures of hundreds of hydrocarbons and are called ***petroleum fractions***

Rating of fuels in internal combustion engine

Knocking:

Beyond a compression limit mixture burns rapidly and it cause uncontrolled explosion of fuel causing a violent jerk against the piston by a 'knocking' or 'pinging' sound in the engine.

Octane number

- Antiknocking property of gasoline is measured in terms of octane number or octane rating.

- ***Octane number is an arbitrary scale for rating the relative antiknocking property of gasolines when they are used in a standard test engine.***

- Straight chain **heptane (O.N = 0)**
- Branched chain **2,2,4-trimethylpentane (isooctane) (O.N =100)** are taken as standards.
- ***The percentage of isooctane present in a mixture of n-heptane and isooctane which has the same knocking characteristics as the fuel sample under consideration when examined in the test engine.***
- Higher the octane number higher will be antiknocking properties

Determination of octane number

- First using gasoline in standard engine and record the knocking properties.
- The results are compared with behaviour of mixtures of n heptane and isooctane
- Percentage of isooctane in the mixture with identical knocking properties is called octane number.

Cetane number

- ***Cetane number – arbitrary scale of rating the relative ignition properties of Diesel oil when using in a standard test engine.***
- Straight chain **hexadecane (C.N=100)**
- Branched chain **1-methylnaphthalene (C. N=0)** are taken as standards.
- ***The percentage of cetane present in a mixture of cetane and 1-methylnaphthalene which has same ignition characteristics as the fuel sample under consideration when examined in the test engine under consideration.***
- Higher the cetane number of a diesel fuel better will be the ignition characteristics.

Flash point

- ***Flash point of a particular liquid fuel is the minimum temperature at which it gives off enough flammable vapour to ignite in air giving a flash, when an ignition source is brought near its surface***

Examples

- Kerosene – 37-72°C
- Unleaded gasoline – 43°C
- Diesel oil – 50-100°C
- Higher the flash point, safer it is for transportation and storage

LPG (Liquefied petroleum gas)

- Liquefied at 15°C T
- Pressure 1.7-7.5 bar
- Stored in pressurized steel cylinders.
- Produced as a by product of natural gas professing, petroleum refining and petroleum cracking.
- Main components are Hydrocarbons –
  - propane and butane (main)
  - Propene, butene (Small amount)
- A sulphur based odourant (mercaptan) is normally added for leak detection.

Uses

- Domestic fuel for cooking and heating purposes
- In scientific laboratories
- As an automobile fuel
- As a fuel for heating purposes in industry
- As a refrigerant

CNG (Compressed natural gas)

- Stored at high pressure tanks at 200-250atm

- Produced using natural gas
- Components
    - Methane (60-90%)
    - Ethane, propane, butane
    - Gases like CO_2, H_2S, N_2 etc.
- Mercaptan is added for leak detection.

Uses

- Used as a fuel in automobiles such as buses and trucks
- Fuel in locomotives

2. PHARMACEUTICALS

Compounds manufactured for the use as medicinal drug

Drugs

- Low molecular mass (100-500u)
- When absorbed to body of living organism interact with macromolecular targets and produce a biological response.
- When this response is healing and beneficial, it is called medicine – used in diagnosis, prevention and treatment of disease.

Pharmaceutical drug or medicine

- A chemical substance used in the treatment, cure, prevention or diagnosis of disease or used to otherwise enhance physical or mental well-being is called a medicine.

Chemical name generic name and trade name of drugs

Chemical name	Generic name	Trade name
Systematic name for it from which a chemist should be able to write its complete structure	The name that is generally accepted substitute for its Actual name	Manufacture’s name for it in the medicinal market

Examples

1. N-(4-hydroxyphenyl)ethanamide

- ❖ Chemical name : N-(4-hydroxyphenyl)ethanamide or 4- acetamidophenol
- ❖ Generic name : Paracetamol or acetomorphin
- ❖ Trade name: crocin, Calpol, Metacin, Dolo etc.

CLASSIFICATION OF DRUGS

1. Antipyretics

- ➢ Drugs that reduce fever or drugs that reduce body temperature.

Examples:

- ❖ *Paracetamol or acetaminophen*
- ❖ *Aspirin or acetylsalicylic acid*
- ❖ *Phenacetin*
- ❖ *Ibuprofen*
- ❖ *Naproxen*

- *salicylates like choline salicylate, magnesium salicylate and sodium salicylate*.

2. Analgesics

- Drugs that relieve pain
- Classified into two

a) Non-narcotic (non – addictive) analgesics

- Analgesics that neither produces sleep/unconsciousness nor addiction in any person using them.

Examples

- Paracetamol or Acetaminophen.
- Aspirin
- NSAIDs including Ibuprofen, Etoricoxib, diclofenac, aceclofenac and naproxen.

b) Narcotic analgesics

- Drugs that are potentially addictive (habit – forming) which, when administered in medicinal doses, relieve pain and produce sleep.
- Mainly used for the relief of post-operative pain, cardiac pain, obstetric pain and terminal cancer pain

Examples

- Morphine
- Codeine
- Heroine
- Meperidine
- Methadone

3. Antibiotics

- It is a drug derived from certain microorganisms (bacteria, fungi and moulds) or produced wholly or partly by chemical synthesis which in low concentration inhibits the growth of or destroys disease - causing microorganisms by intervening in their metabolic processes.

Examples:

*Chloramphenicol, azithromycin, erythromycin, roxithromycin, tetracyclin, ciprofloxacin, ofloxacin, vancomycin, streptomycin, cephalexin, bacitracin, aminoglycosides (like gentamycin, neomycin, trobramycin and kanamycin)*etc.

Classification:

Antibiotics

Bactericidal

Kill microorganisms in the body directly

Examples:

Penicillin, ampicillin, amoxicillin, ofloxacin, aminoglycosides

Bacteriostatic

Inhibit the growth of microorganisms in the body

Examples:

Erythromycin, tetracycline, chloramphenicol

- The capability of various antibiotics in fighting against invading microorganisms is expressed in terms of their *spectrum* of action based on the range of microorganisms that are affected by them.

Antibiotics

Narrow spectrum antibiotics

- Antibiotics effective mainly against either Gram positive or

Broad spectrum antibiotics

- Antibiotics that kill or inhibit a wide range of Gram positive and negative bacteria.

Examples

- Ampicillin, amoxicillin, ciprofloxacin, chloramphenicol,

4. Antacids

- The walls of human stomach contain thousands of cells that secrete HCl, the main purpose of which are to kill microorganisms and to aid digestion.
- Hyperacidity is a condition in which the level of acid in the gastric juices is excessive, causing discomfort. If not controlled, it leads to ulcer.
- *The drugs that provide relief from the ailment symptoms of hyperacidity are known as* **antacids.**
- Most common ingredients in antacids are $NaHCO_3$, $CaCO_3$, $Al(OH)_3$, $Mg(OH)_2$, etc. in combination with other drugs like *simethicone* (anti-foaming agent) to help break down gas bubbles in stomach.

Examples :

Acigon, Riflux, Gelusil, Diovol, Ulgel, Digene

- These drugs neutralize the excess acid in the stomach and raise the pH to appropriate level. They do not control the cause for the condition.
- Several antacids that are acidity regulators capable of preventing the root cause of hyperacidity are

  a. Cimetidine (Trade names: Tagamed, Ulciban, C-Met, Cimetin etc.)

  b. Ranitidine (Trade names: Zinetac, Rantac, Ranitin etc.)

  c. Omeperazole (Trade names: Ocid, Omez, Lomac etc.)

d. Esomeperazole (Trade names: Izra, Esoz, Nexpro etc.)

e. Rabeprazole (Trade names : parit, Rabicip, Rabiloc, Rabium etc.)

5 Antiseptics

- Chemicals which are used either to prevent the growth of or kill microorganisms are called **antiseptics;** these are not harmful to living tissues and hence can be safely applied on cuts, wounds, ulcers, and diseased skin surfaces.

Examples:

1. Dettol (chloroxylenol and terpineol)
2. Bithionol in soaps
3. Iodine (2-3% of solution in alcohol-water mixture is **tincture of iodine**.)
4. Iodoform (CH_3I) – antiseptic for wounds.
5. Boric acid (H_3BO_3) – weak antiseptic for eyes.

3. CHEMICALS IN FOOD

Food:

Any substance which when consumed, digested and assimilated provides nutritional and energetic support to the body.

Food Additives:

Substances added to food products for

1. Preservation
2. Improving appeal
3. Maintaining and enhancing nutritional quality

a) Food preservatives

- Chemicals added to food in small quantities to prevent its microbial and/or catalytic decomposition and deterioration.

- Function by inhibiting the growth and activity of microorganisms or preventing undesirable enzymatic and catalytic chemical reactions.

Examples

1.Sugar (fruit in a concentrated sugar solution)

2.Table salt (salted meat)

3.Vinegar

4.Vegetable oils

Commonly used food preservatives are

1. Sodium benzoate (C_6H_5COONa)

- Used in jams, jellies fruit juices, pickles etc.
- Act as **antimicrobial agent**
- In acidic conditions sodium benzoate yield benzoic acid (C_6H_5COOH) which is active against bacteria, yeast etc.

2. Citric acid

- Used in jams, jellies, drinks, syrups etc
- Act as **sequestrants** for trace metals (*i.e.*, it reacts with trace metals in foods, tying them up in complexes so that these metals will not catalyse the decomposition of food)

3. Potassium metabisulphate ($K_2S_2O_5$)

- Used to preserve mango chutney, lemon squashes, juices of colourless fruits like apple.

- It reacts with acid in fruits or juice to produce SO_2, which kills the microorganism.

b) Artificial sweeteners

Sweeteners of food other than natural sweeteners like sucrose

1. Saccharin

- Ortho-sulphobenzimide
- Sweetness is about 550 times that of cane sugar
- Contribute no calories to the diet because it is not metabolized by the human body.
- It is excreted from the body in urine in the same form it is ingested.
- It is thus entirely inert and completely harmless when ingested
- It is heat stable hence a good choice for use in cooking, baking and canning
- it has been extremely useful for diabetic patients and also for people who need a low calorie diet
- Used in baked items, jams, soft drinks, tinned fruits, chewing gum, candy etc
- Also used in tooth pastes and pharmaceutical products

2. Aspartame

- 180-200 times sweeter than sucrose
- It is a dipeptide derivative made from aspartic acid and methyl ester of phenylalanine
- It can be digested but its caloric value is insignificant as compared to sugar because only a small amount is consumed through food.
- People suffering from the genetic disease *phenylketouria* are advised to avoid aspartame because they are not able to metabolize phenylalanine.
- Disadvantage : It is not stable at cooking temperatures
- It changes chemically at higher temperatures and loses its sweetness, so it is limited to cold foods and soft drinks
- The stability in aqueous solution depends on pH as it is hydrolysable into its constituent amino acids.

- It is most stable at pH 4.3, with half-life about 300 days,
- At Ph 7 its half-life is only a few days
- Most of the soft drinks have pH between 3-5

3. Sucralose

- Non-nutritive sweetener
- Trichloro derivative of sucrose obtained by the replacement of three OH groups of sucrose by three Cl
- It is 600 times sweeter than sucrose but can be consumed by diabetics.
- White crystalline solid and is highly soluble in water.
- It is calorie free, does not interact with components of food and does not have any bitter aftertaste.
- When consumed, most of the sucralose is not absorbed by the body and is eliminated through excretion
- It is stable over a broad range of pH
- It is stable at cooking temperatures and hence can be used in baked goods.
- Also used in candy, breakfast cereals, salad dressings and soft drinks.
- It does not promote dental cavities and is commonly found in oral health products, such as chewing gum.

4. Alitame

- Non-nutritive high potency artificial sweetener.
- 2000 times sweeter than sucrose.
- It is a dipeptide of L-aspartic acid and D-alanine
- Major portion of alitame is absorbed and hydrolysed to aspartic acid and alanine amide.

- The aspartic acid is hydrolysed normally and alanine amide is excreted in the urine as a solfoxide.
- It is about 10times more sweeter and more heat-stable than aspartame.

4. DYES

- Dyes are coloured organic compounds having the property of imparting colour to other substances such as textile fibers, wool, silk, leather, paper, inks, toys, hair, foodstuffs etc.

Examples:

Malachite green, Orange - I, Orange - II, Alizarin, Indigo, Congo red, para red, mauveine, etc.

Requirements of a dye

1) It must have suitable color.
2) It must be capable of ‘fixing’ itself (*i.e.*, attaching itself permanently) to the material being dyed.
3) When fixes to the material, it must retain its colour (a) even on prolonged exposure to sunlight, heat and other atmospheric conditions, and (b) when treated with water and soap during washing. This property is called *fastness* of dye.
4) It must be ‘fast’ to other ordinary chemicals that are used during dry cleaning of dyed clothes.
5) Soluble in water

Theories of colour and constitution

- Colours of compounds arise from electronic transitions between energy levels with spacings that correspond to the wavelengths in the visible region of the EM spectrum.
- When a compound absorbs a photon of visible light of one colour, we observe its complementary colour.

e.g., When white light is passed through a substance that absorbs violet light, we see yellow-green colour; this is because, after absorption of violet, the complementary colour yellow-green predominates visually.

a) Witt's theory

- Proposed by Otto Witt (1876)

1. The structure of dye consists of two parts - chromophores and auxochromes.
2. Chromophore (Greek: chroma = colour; phoros = to bear) - group that produces colour. The presence of at least one such group is essential to produce a colour in an organic compound. A compound containing at least one chromophore is called a **chromogen.**
3. Most of the chromophoric groups have an unsaturation in them.
4. Greater the number of chromophores, greater is the intensity. The intensity also increases with increase in the extent of conjugation.
    - Ethene ($CH_2=CH_2$) is colourless, but the compound $CH_3-(CH=CH)_6-CH_3$ is yellow in colour.
    - Nitrobenzene ($C_6H_5-NO_2$) is pale yellow and azobenzene ($C_6H_5-N=N-C_6H_5$) is orange-red.
    - Certain chromophores like the carbonyl ($>C=0$) produce colour only when two or more of them are present in a molecule and they are conjugated. Thus, while acetone ($CH_3-CO-CH_3$) is colourless, biacetyl ($CH_3-CO-CO-CH_3$) is yellow.
5. An auxochrome (Greek: auxein = to increase; chroma = colour) is a group which not producing any colour by itself, can intensify the colour of a compound when present together with a chromophore.
    - Auxochromes in the increasing order of their colour-deepening effect

$$-OR < -X \text{ (halogen)} < -OH < -NH_2 < -NHR < -NR_2$$

6. The presence of auxochromes is essential for a chromogen to function as a dye.

Conclusion:

- According to Witt's theory, it is the combined presence of chromophoric groups and auxochromic groups that enables a compound to act as dye.

b) Valence Bond Theory

- Explains the role of resonance in the formation of colour

1. Chromophores, (groups that produce colour) - π electrons get excited from lower levels to higher levels by absorption of radiation quanta in the visible region. This produces colour in those chromogens.
2. Auxochromes (groups which intensify the colours of chromogens) produce resonance in the chromogens by allowing interaction of their lone pairs (present on the N or O atoms) with the π electrons of the chromogens,

   e.g., aromatic rings. This enhancement of resonance results in a ***bathochromic shift*** or red shift, i.e., a shift of absorption from lower to higher wavelength.

Examples for dyes

(a) Martius yellow
(b) Indigo (or Indigotin)
(c) Alizarin (Alizarin red)

5. CEMENT

- Form of cement commonly used is called *Portland cement.*
- Fine grey powder
- Consist of mixture of calcium silicate and aluminates.

Manufacture of cement

- Raw materials used - limestone and clay (silica and Alumina and some Fe_2O_3)
- Finely powdered limestone is mixed with finely powdered clay and made into slurry in water.

- It is heated at 1400 – 1500°C in a large Steel Rotary kiln lined with fire bricks and heated by burning coal gas.

- Dehydration occurs. At the higher temperature of the kiln, CaO formed from the decomposition of limestone $CaCO_3$ combines with silica and Alumina of the clay to give a mixture of silicates aluminates and aluminoferrites.

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$2CaO + SiO2 \longrightarrow (2CaO).SiO2$$

$$3CaO + SiO2 \longrightarrow (3CaO).SiO2$$

$$3CaO + Al_2O_3 \longrightarrow (3CaO).Al_2O_3$$

$$(3CaO).Al_2O_3 + CaO + Fe_2O_3 \longrightarrow (4CaO).Al_2O_3.Fe_2O_3$$

- The resulting product is known as *cement clinker* - in the form of marble sized lumps having greenish - black colour.

- The clinker is first cooled to about 150°C by circulating cold air. Then it is mixed with sufficient amount to (2-3%) of gypsum ($CaSO_4.2H_2O$) and ground to a fine powder.

- Gypsum acts as retardant of quick initial setting of cement

- By controlling the amount of gypsum added we can control the setting time of the final product, which is *Portland cement*

Composition of Portland cement

- 10-20 % dicalcium silicate ($2(CaO).SiO_2$), 50-70% tricalcium silicate ($3(CaO).SiO_2$), 5-10 % tricalcium aluminate ($3(CaO).Al_2O_3$), and 3-8% tetracalciumaluminoferrite ($4(CaO).Al_2O_3.Fe_2O_3$), as small amounts of MgO present in the original raw materials corresponding silicates and aluminosilicates of Mg will also be present.

Setting of cement

- Cement mixed with half its quantity of water is quite plastic and can be easily applied to the masonry or concrete.

- But as the mixture dries it sets into a hard mass this is called *setting of cement* and involves hydrolysis and hydration reactions.
- Setting of cement is due to the precipitation of colloidal gels formed by the hydration of the constituent and their rearrangement.
- The hydrated gels formed include $2CaO.SiO_2.xH_2O$ (hydrated gel of dicalcium silicate), $3CaO.Al_2O_3.6H_2O$ (hydrated gel of tricalcium aluminate), etc.
- These lose water slowly and eventually set to a hardened mass.
- The $Ca(OH)_2$ and Aluminium Hydroxide formed by the partial hydrolysis of silicates and auminates bind the particles together, fill all the interstices and the seal all the pores in to make a Mass leak proof.
- The gypsum is added combines with the fast setting tricalcium aluminate to give calcium sulphoaluminate which does not have the property of quick hydration.
- This reaction increases the setting time and thereby improve the strength of the mass obtained after setting.

$$(3CaO).\ Al_2O_3 + 3(CaSO_4.2H_2O) \longrightarrow (3CaO.\ CaSO_4).Al_2O_3.6H_2O$$

Uses of cement

- Used in construction of bridges dams and buildings
- Plastering of walls
- Used to make concrete and reinforced concrete

Concrete and reinforced concrete

- Concrete is a mixture of cement with sand and ballast.
- Water is added at the time of application to build the required structure; when set, a hard soldered mass is formed.
- It is used for foundations, floors, roof of buildings and also in the construction of roads, dams, Canal bridges etc.

- Reinforced concrete is concrete allowed to set on structures having an iron/steel rod/bar framework.
- This gives extra strength to the structures.
- Used for the construction of buildings, bridges, roads and dams is in the form of reinforced concrete.

6. GLASS

- Glass is a transparent material
- obtained when a complex mixture of highly viscous molten silicates upon moderately rapidly cooling, solidifies to amorphous rigid body without crystallization
- Super cooled liquid

Types of glasses and their uses

1. Soda glass

- Soft glass or ordinary glass or Window glass.
- Obtained by fusing together quartz/sand, sodium carbonate and Calcium Carbonate.
- Approximate composition is SiO_2 = 75%, Na_2O = 15%, CaO = 8%, Al_2O_3 = 2%
- softens at relatively low temperatures and can be easily moulded into desired objects
- Used to make window panes, cheap table wares, reagent bottles etc. which do not have to withstand very high temperature

2. Potash glass

- Hard glass
- Obtained by fusing together quartz/sand, potassium carbonate and Calcium Carbonate
- It has a higher melting point and hence is able to withstand higher temperatures than the soda glass

- Used for combustion tubes and chemical glassware.

3. Flint glass

- Obtained by fusing together mainly quartz/sand, lead carbonate along with some sodium carbonate, potassium carbonate and Calcium Carbonate.
- Approximate composition is SiO_2=45%, PbO=44% , Na_2O=4%, K_2O=4%, CaO=3%
- Heavy and durable glass characterized by brilliance, clarity, high refractive index, and high transparency.
- Used for making optical instruments like lenses and prism, artificial diamonds and other imitation gems.
- It absorbs most UV light but comparatively little visible light hence
- used for telescope lenses

4. Pyrex glass

- Borosilicate glass - contains B_2O_3 as one of the ingredients
- Obtained by fusing together mainly Quartz/sand, sodium carbonate, Aluminium oxide and boric oxide.
- Approximate composition is SiO_2=80%, B_2O_3=12%, Na_2O=4%, Al_2O_3=3%, K_2O=0.5%, CaO=0.5%
- Very low coefficient of thermal expansion, able to withstand large temperature changes.
- Used for making laboratory glassware and cookware that can be heated to high temperature.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