Unit IVth

Spectroscopy

It is the branch of science that deals with the study of interaction of matter with light.

OR,

It is the branch of science that deals with the study of interaction of electromagnetic radiation with matter.

Principles of Spectroscopy

- The principle is based on the measurement of spectrum of a sample containing atoms / molecules.
- Spectrum is a graph of intensity of absorbed or emitted radiation by sample verses frequency (ν) or wavelength (λ).
- Spectrometer is an instrument design to measure the spectrum of a compound.

Types of Spectroscopy

1) Absorption Spectroscopy:

The study of absorbed radiation by molecule in the form of spectra.

Eg: UV-Visible, IR, NMR

2) Emission Spectroscopy:

The radiation emitted by molecules can also be studied to reveal the structure of molecule.

Eg: Mass spectroscopy

3) Scattering Spectroscopy:

It measure the amount of light that a substance scatters at certain wavelengths, incident angles, and polarization angles. The scattering process is much faster than the absorption / emission process.

Eg: Raman spectroscopy

UV-Visible Spectroscopy

Principle:

- UV-visible spectroscopy measure the response of a sample to ultra violet and visible range of electromagnetic radiation.
- Molecules have either n, π or σ electrons. These electrons absorb UV radiation and undergo transitions from ground state to excited state.
- Far UV spectroscopy is studied under vacuum condition.
- The common solvent used for preparing sample to be analyzed is either ethyl alcohol or hexane.
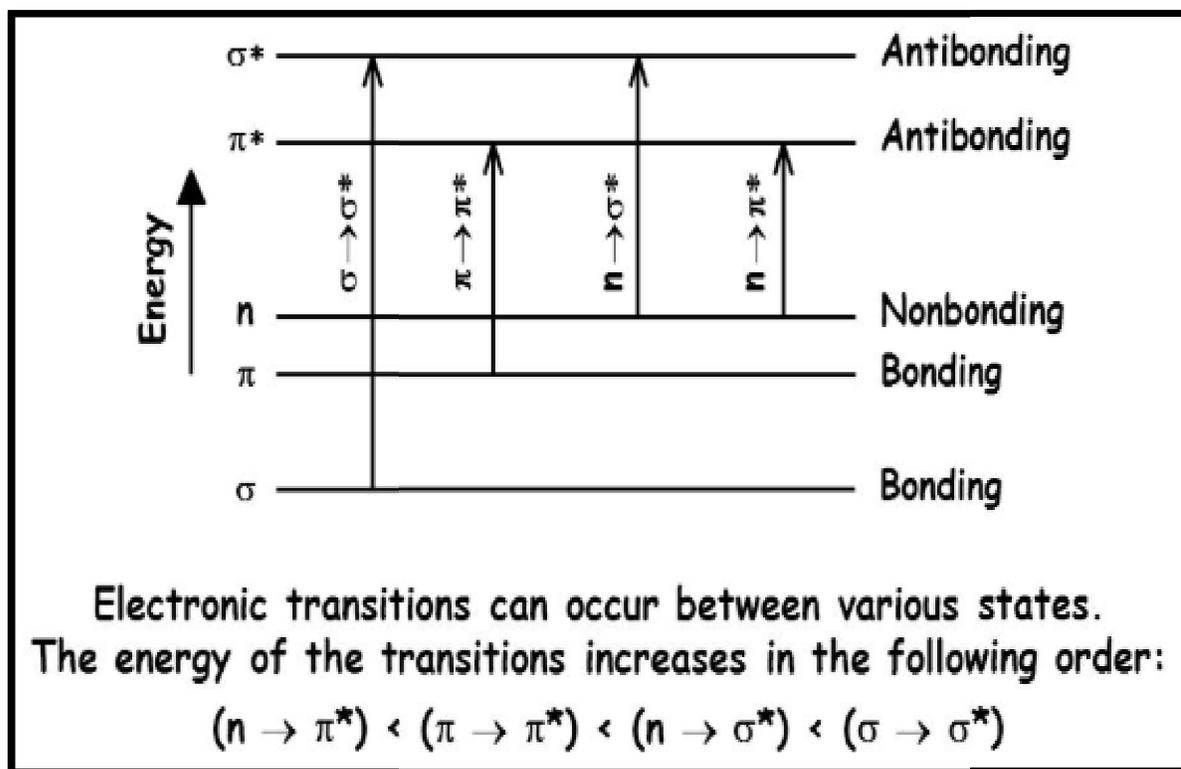
Electronic Transitions:

- A transition of an electron from occupied to an unoccupied energy level can be caused by UV radiation.
- In U.V spectroscopy molecule undergo electronic transition involving σ, π and n electrons.

TYPES OF TRANSITIONS:

Four types of electronic transition are possible.

i. σ → σ* transition

ii. n → σ* transition

iii. n → π* transition

iv. π → π* transition

Electronic transitions can occur between various states. The energy of the transitions increases in the following order:

$(n \rightarrow \pi^*) < (\pi \rightarrow \pi^*) < (n \rightarrow \sigma^*) < (\sigma \rightarrow \sigma^*)$

i. σ → σ* Transition :

An electron in a bonding σ orbital of a molecule is excited to the corresponding anti-bonding orbital by the absorption of radiation. To induce a σ → σ* transition it required large energy.

Ex: Methane

ii. n → σ* transition :

In this type saturated compounds containing atoms with unshared electron pairs are undergo n → σ* transition. It require less energy than the σ → σ* type. Most of the absorption peaks appearing below 200nm. In the presence of polar solvents the absorption maximum tends to shift shorter wavelength.

Ex: Water, ethanol.

iii. n → π* transition:

An electron from non-bonding (n) orbital is promoted to anti-bonding

Ex: Compounds containing double bond involving hetero atoms (C=O, N=O, CN) undergo such transitions. π* orbital.

iv. π → π* transition:

π electron in a bonding orbital is excited to corresponding anti-bonding orbital π*.

Ex: Compounds containing multiple bonds like alkenes, alkynes, carbonyl, nitriles, aromatic compounds, etc undergo $\pi \rightarrow \pi^*$ transitions.
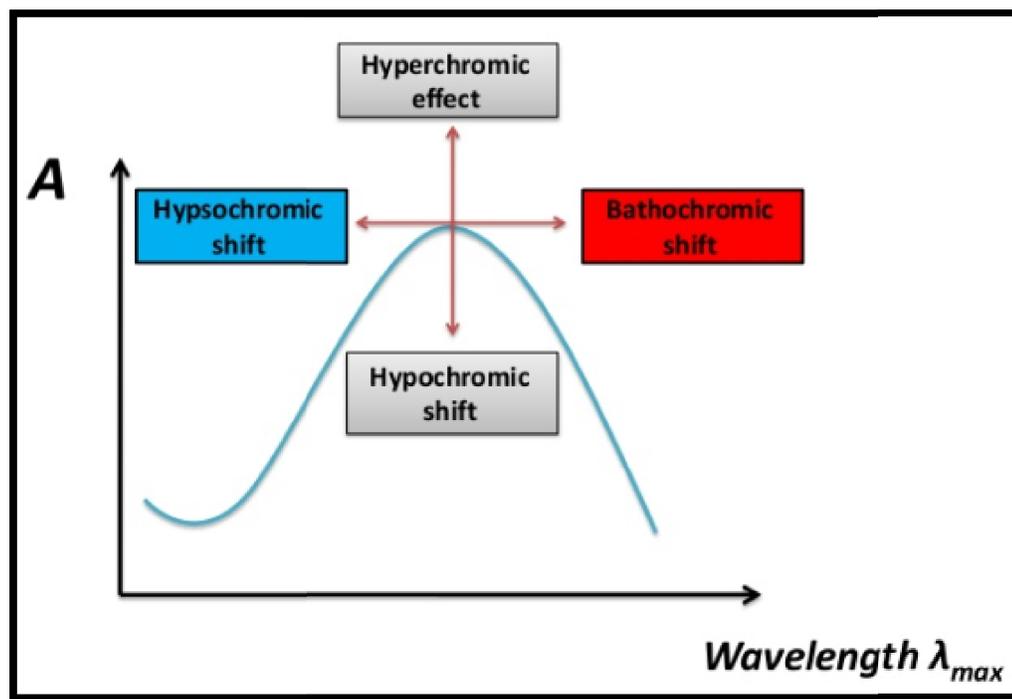
Chromophore

Bathochromic shift (red shift)- A shift to longer wavelength; lower energy

Hypsochromic shift (blue shift) – Shift to shorter wavelength; higher energy

Hyperchromic effect – An increase in intensity

Hypochromic effect – A decrease in intensity

Beer-Lambert Law

The Beer-Lambert law is a linear relationship between the absorbance and the concentration, molar absorption coefficient and optical coefficient of a solution.

$$A = \varepsilon c l$$

A	Absorbance	
ε	Molar absorption coefficient	$M^{-1}cm^{-1}$
c	Molar concentration	M
l	optical path length	cm

Q.1. A solution of Tryptophan has an absorbance at 280nm of 0.54 in a 0.5cm length cuvette. Given the absorbance coefficient of trp is 6.4 * 10^3 LMol^{-1}cm^{-1}.

What is the concentration of solution?

Solution:

A= $\varepsilon c l$

ε = 6.4 * 10^3 LMol^{-1}cm^{-1}

A = 0.54

l = 0.5cm

C = ?

So, c = A/εl

$$= 0.54/6.4 * 10^3 * 0.5$$

$$= 0.000168M$$

Q.2. The absorbance of a Cu sulphate solution containing 0.500mg Cu/ml was reported as 0.3500 at 440nm.

a) Calculate the specific absorptivity, including units, of Cu sulphate on the assumption that a 1.00cm cuvette was used.

b) What will be the absorbance if the solution is diluted to twice its original volume.

Solution:

a) $l = 1.00cm$

$c = 0.500$ mg/ml

$A = 0.3500$

$\varepsilon = ?$

So, $\varepsilon = A/lc$

$= 0.3500/1.0 * 0.500$

$= 0.7cm^{-1} (mg/Ml)^{-1}$

b) $c = 0.250mg/ml$

$\varepsilon = 0.7cm^{-1}(mg/ml)^{-1}$

$l = 1.00cm$

$A = ?$

So, $A = \varepsilon cl$

$= 0.7cm^{-1}(mg/ml)^{-1} * 1.00cm * 0.250mg/ml$

$= 0.175$

Questions

Q. The ultraviolet spectrum of benzonitrile shows a primary absorption band at 224 nm. If a solution of benzonitrile in water, with a concentration of 1x 10^{-4} molar, is examined at a wavelength of 224 nm, the absorbance is determined to be 1.30. The cell length is 1 cm. What is the molar absorptivity of this absorption band?
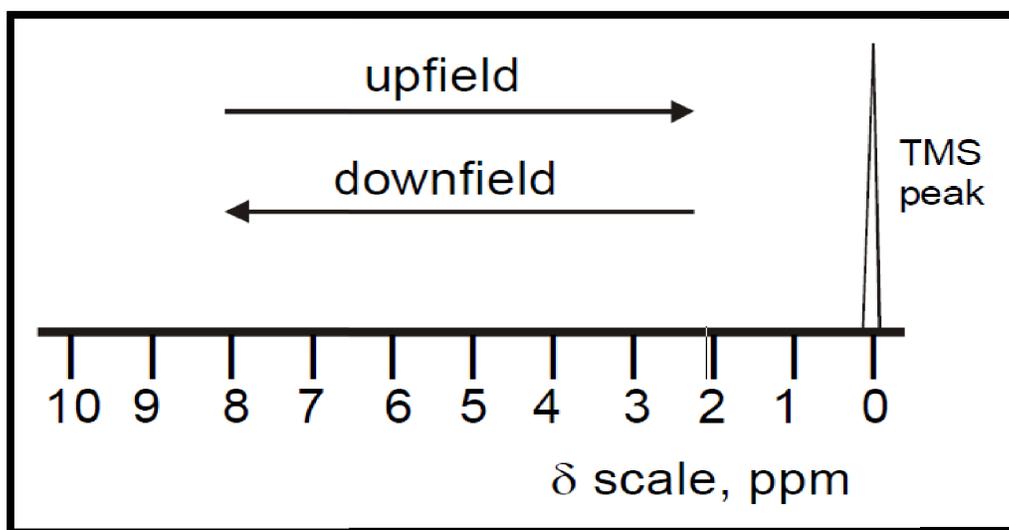
NMR Spectroscopy

Nuclear Magnetic Resonance (NMR) is a spectroscopy techniques which is based on the absorption of electromagnetic radiation in the ratio frequency region 4 to 900 MHz by nuclei of the atoms.

Proton Nuclear magnetic resonance spectroscopy is one of the most powerful tools for elucidating the number of hydrogen or proton in the compound.

It is used to study a wide variety of nuclei:

^1H, ^{13}C, ^{15}N, etc

NMR spectrum

The NMR spectrum is a plot of intensity of NMR signals vs magnetic field (frequency) in reference to TMS

Chemical shift

A Chemical shift is defined as the difference in parts per million (ppm) between the resonance frequency of the observed proton and tetramethylsilane (TMS) hydrogens.

TMS is the most common reference compound in NMR, it is set as δ = 0 ppm
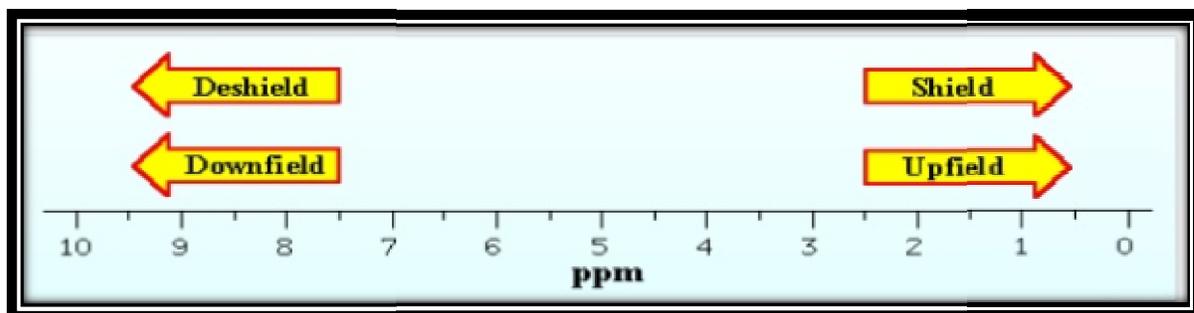
$$\text{Chemical shift, } \delta = \frac{\text{frequency of signal} - \text{frequency of reference}}{\text{spectrometer frequency}} \times 10^6$$

Shielding of protons

High electron density around a nucleus shields the nucleus from the external magnetic field and the signals are upfield in the NMR spectrum.

Deshielding of protons

Lower electron density around a nucleus deshields the nucleus from the external magnetic field and the signals are downfield in the NMR spectrum.

Interpretation of ^{1}HNMR spectra

No. of signals – Indicate how many different kinds of protons are present.

Position of signals – Indicates something about (chemical shift) magnetic (electronic) environment of protons

Relative intensity of signals – Proportional to number of protons present

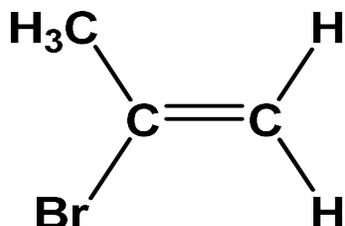Splitting of signals – Indicates the number of nearby nuclei usually protons

Number of NMR Signals

In a molecule, protons in the same magnetic environment absorb at the same applied magnetic field strength, H_o; different environment – different H_o .
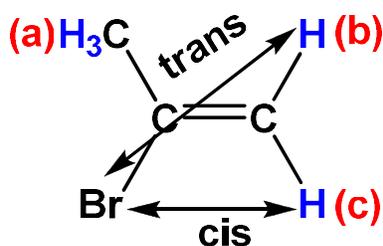
A set of protons with the same magnetic environment are called equivalent. Therefore, the number of signals may reveal how many "kinds" of protons are in the molecule. Often, magnetically equivalent protons are chemically equivalent.

      eg CH3CH2OH   3 NMR signals

             a   b   c

How many signals?

$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-O-CH_3$

Solve:

(a) (c)
(a) $H_3C-\overset{\displaystyle CH_3\ H}{\underset{\displaystyle H\ \ H}{C-C}}-O-CH_3$ (d)
(b) (c)

There would be four signals because there are four sets of equivalent protons (sets a, b, c, and d).

To be chemically equivalent, protons must be stereochemically equivalent —

How many NMR signals?

$\overset{\displaystyle H_3C}{\underset{\displaystyle H_3C}{}}C=C\overset{\displaystyle H}{\underset{\displaystyle H}{}}$

Solve:

(a)H_3C ⟍ ⟋ H (b)
          C=C
(a)H_3C ⟋ ⟍ H (b)

Two signals (a and b)

How many NMR signals?

Solve:

Three signals

The two vinylic protons, b and c are not equivalent. One is *cis* to the bromine, the other is *trans*.
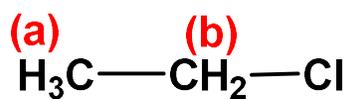
n+1 rule:-

- The multiplicity of signal is calculated by using n+1 rule.

- This is one of the rule to predict the splitting of proton signals. This is considered by the nearby hydrogen nuclei.

Therefore, n = Number of protons in nearby nuclei

➤ Zero H atom as neighbour n+1 = 0+1 = 1 (singlet)

➤ One H atom as neighbour n+1 = 1+1 = 2 (doublet)

➤ Two H atom as neighbour n+1 = 2+1 = 3 (triplet)
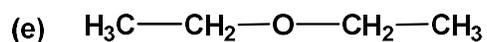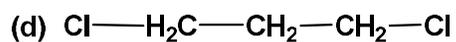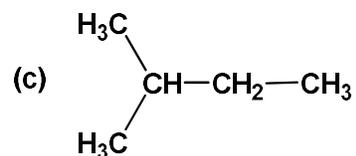
➤ Three H atom as neighbour n+1 = 3+1 = 4 (quartet)

Eg:

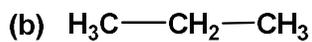$$\overset{\textbf{(a)}}{H_3C}\!\!-\!\!\overset{\textbf{(b)}}{CH_2}\!\!-\!\!Cl$$

Two signals

(a) = n+1 = 2+1 = 3 (Triplet)

(b) = n+1 = 3+1 = 4 (quartet)

Q. Allocate the signals and splitting of the given following compounds.

(a) $H_3C-CH_2-CH_2-Cl$ (b) $H_3C-CH_2-CH_3$ (c)

$$\begin{array}{c} H_3C \\ \diagdown \\ \quad CH-CH_2-CH_3 \\ \diagup \\ H_3C \end{array}$$

(d) $Cl-H_2C-CH_2-CH_2-Cl$ (e) $H_3C-CH_2-O-CH_2-CH_3$

IR Spectroscopy

Infrared spectroscopy (**IR spectroscopy** or **vibrational spectroscopy**) involves the interaction of infrared radiation with matter. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemical substances.

It refers to that part of the electromagnetic spectrum between the visible and microwave regions.

The major use of infrared spectroscopy is to determine the functional groups of molecules, relevant to both organic and inorganic chemistry.

Vibrational modes

A vibrational mode in a sample to be "IR active", it must be associated with changes in the dipole moment (μ).

> - Symmetrical molecules are IR- inactive since they do not have dipole movement (O_2, F_2, H_2, Cl_2).
> - Diatomic molecule with dipole moment are IR-active (HCl, HF, CO, HI).

A molecule can vibrate in many ways, and each way is called a vibrational mode.

For molecules:-

- linear molecules have 3N – 5 degrees of vibrational modes,
- non-linear molecules have 3N – 6 degrees of vibrational modes (also called vibrational degrees of freedom).

Example: H_2O a non-linear molecule, will have 3 × 3 – 6 = 3 degrees of vibrational freedom, or modes.

Molecular Vibrations

There are two types of vibrations

1. Stretching vibrations
2. Bending vibrations

1. Stretching vibrations:-

- Vibration or oscillation along the line of bond.
- Change in bond length resulting from change in interatomic distance (r)
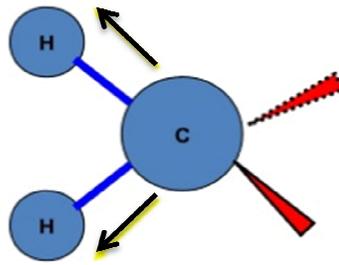- Occurs at higher energy: 4000-1250 cm^{-1}

It is two types:

1. Symmetric stretching
2. Asymmetric stretching

1. Symmetric stretching:-

Two bonds increase or decrease in length simultaneously.

It is IR-inactive (no change in µ).

2. Asymmetric stretching:-

In this, one bond length is increased and other is decreased.

2. Bending vibrations:-

- Vibration or oscillation not along the line of bond.
- These are also called as deformations
- In this, bond angle is altered
- Occurs at low energy: 1400-666 cm^{-1}

Two types:

a. In plane bending: scissoring, rocking

b. Out plane bending: wagging, twisting

a. In plane bending:-

Scissoring:

- This is an in plane blending
- 2 atoms approach each other
- Bond angles are decrease

lecrease

Rocking:

Movement of the atoms takes place in the same directions.

ms take plac

b. Out plane bending:

Wagging:

Two atoms move to one side of the plane. They move up and down the plane.

ıe side o

Twisting:

One atom moves above the plane and other atom move below the plane.

above the p
w the plane

Factor affecting carbonyl frequency:-

➢ **+ I effect decrease C=O stretching**

   HCHO – 1750

   CH_3CHO – 1745

   CH_3COCH_3 - 1718

➢ **- I effect increase C=O stretching**

   CH_3COCH_3 – 1718

   CH_3COCH_2Cl – 1725
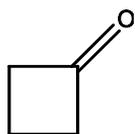
   $CH_3COCHCl_2$ - 1740
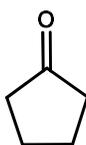
➢ **Ring strain increase C=O stretching**
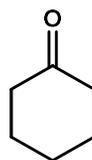

   1855   1788   1746   1720

➢ **Conjugation decrease C=O stretching**

   CH_3-CHO – 1745

   CH_2=CH-CHO – 1723

Application of UV-Visible spectroscopy

1. Detection of Impurities : It is one of the best way for detecting impurities in organic compounds. Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw material. By also measuring the absorbance at specific wavelength, the impurities can be detected.

2. Detection of geometrical isomers: UV spectroscopy can be used for detecting the geometrical isomers of a given compound. Trans isomers exhibit λ_{max} at slightly longer wavelengths and have larger extinction coefficients than the cis-isomers. For example, the two geometrical isomers of Stilbene show λ_{max} at 294 nm and 278 nm respectively. The former is therefore trans and the later cis.

3. Dissociation constants for weak acids and bases can be determined by UV spectroscopy.

4. Chemical kinetics: UV spectroscopy can be used to study the kinetics of Chemical reactions. The UV radiation is

passed through the reaction cell and the absorbance changes can be observed.

5. UV spectroscopy is used for characterizing aromatic compounds and conjugated olefins.

6. Quantitative analysis: UV absorption spectroscopy can be used for the quantitative determination of compounds that absorb UV radiation. This determination is based on Beer's law which is as follows:

$$A = \varepsilon c l$$

A	Absorbance	
ε	Molar absorption coefficient	M⁻¹cm⁻¹
c	Molar concentration	M
l	optical path length	cm

7. Structure of chloral can be confirmed by UV spectroscopy.

8. Nickel can be determined as its complex with β-mercaptopropionic acid by measuring its absorbance at 330 nm.

Application of IR Spectroscopy

1. **Detection of Functional Groups:** Since a particular functional group absorbs IR radiation of nearly same wavelength in all molecules, the presence of characteristic absorption band in that range confirms the presence of that functional group in a molecule. For example, compounds having C=O group such as aldehyde, ketones, acids, esters, etc., give absorption bands in the range 1650-1750 cm^{-1}.

It is obvious that if a spectrum does not contain an absorption band typical of a particular functional group, the molecule does not contain that group.

2. **Determination of Molecular Structure:** Infrared spectroscopy is very useful in determining the molecular structures of unknown compounds. The absorption bands in the functional group region (2.5-7 μm) tell about the nature of the functional group(s) present in the molecule while those in the finger print region (7-11 μm) give substantial information about the structure of the molecule, particularly about the patterns of substitution. Thus, a careful analysis of

the IR spectrum may lead to the molecular structure of the compound under study.

3. IR spectroscopy is often used to establish the identity of a given compound.

4. It is useful to study the progress of chromatographic separations.

5. IR spectroscopy has been used to determine molecular weight of polymers by measuring end group concentrations.

6. It is useful in the determination of the shape or symmetry of a molecule.

7. It can be used in studying tautomeric equilibria such as keto-enol.

Application of ^{1}H NMR

1. Proton nuclear magnetic resonance (^{1}H NMR) is a spectroscopic technique usually used for structural determination of molecules.

2. In recent years, this technique has been employed for easy and quick recognition of microorganisms, in

antimicrobial susceptibility tests and even for the diagnosis of different infectious conditions.

3. ^{1}H NMR has been used to directly analyse biofluids and to diagnose different diseases directly from body fluids.

4. ^{1}H NMR has been applied to the diagnosis of hepatitis C virus infection.

Application of Mass Spectroscopy

1. Mass spectrometry has both qualitative and quantitative uses. These include identifying unknown compounds, determining the isotopic composition of elements in a molecule, and determining the structure of a compound by observing its fragmentation.

2. Mass spectrometry is now commonly used in analytical laboratories that study physical, chemical, or biological properties of a great variety of compounds.

3. Mass spectrometry is an important method for the characterization and sequencing of proteins.

4. Mass spectrometers were used in hospitals for respiratory gas analysis.

5. The primary function of mass spectrometry is as a tool for chemical analyses based on detection and quantification of ions according to their mass-to-charge ratio.

Disadvantages of Hard Water:

✓ It is harmful for drinking. It results in deposition of calcium in the bone joints.

✓ It causes scale formation in boilers and pipes.

✓ The blockage of passage occurs when water is used for cooling, due to scale deposition.

✓ It does not form lather with soap or detergents.

Methods used for softening of water:

1) Lime-soda process

2) Zeolite or, permutit process

3) Ion exchange process

1) Lime-soda process:

❖ **Advantages of Lime-soda process:**

✓ Lime-soda process is economical.

✓ Treater water is alkaline and hence has less corrosion tendencies.

✓ Due to alkaline nature of treated water, amount of pathogenic bacteria in water is considerably reduced.

✓ It removes not only hardness causing salts but also minerals.

✓ Iron and manganese are also removed from the water to some extent.

✓ If the process is combined with sedimentation with coagulation, lesser amounts of coagulants shall be needed.
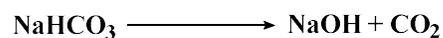
Disadvantages:

✓ The process requires careful operation and skilled supervision for economical and efficient softening.

✓ Sludge disposal is a problem.

✓ The process can remove hardness only upto 15ppm, which is not good for high pressure boilers.

2) **Zeolite or, permutit process:**

❖ **Limitations of zeolite process:**

- If the supplied water is turbid, the suspended matter must be removed before the water is fed to the zeolite bed. Otherwise the pores of the zeolite bed will get clogged by the turbidity, thereby making it inactive.

- If water contains large quantities of coloured ions like Mn^{2+} and Fe^{2+}, they must be removed because these ions produce manganese and iron zeolites that cannot be regenerated easily.

- If mineral acids are present in water, they destroy the zeolite bed and hence they must be neutralized with soda in advance, before feeding the water into the zeolite bed.

- The water to be softened should not be hot as the zeolite tends to dissolve in it.

- Anions are not removed by this process. The bicarbonates present in hard water get converted to $NaHCO_3$ that goes into soft water effluent. If it is used as boiler feed, under the boiler conditions $NaHCO_3$ dissociates to

$$NaHCO_3 \longrightarrow NaOH + CO_2$$

- Both the products are not desirable. Since NaOH may lead to caustic embrittlement and CO_2 makes the condensed water into acidic and corrosive. Thus, it is desirable to remove temporary hardness before subjecting the raw water to zeolite process.

- Compared to ion-exchange process, water treated by zeolite process contains 25% ore dissolved salts. The higher cost of the plant and materials are also limiting factors.

Advantages:

- The hardness is nearly completely removed and water of about 10ppm hardness is produced.

- The equipment used is compact and occupies less space.

- It is quite clean and rapid process that requires less time for softening.

- Less skill is needed for maintainance as well as operations.

- Impurities are not precipitated, so there is no danger of sludge formation.

✓ The process automatically adjusts itself to waters of different hardness.

Disadvantages:

✓ The outgoing water (treated water) contains more sodium salts.

✓ This method only replaces Ca^{2+} and Mg^{2+} ions.

✓ Zeolite process leaves all the acidic ions (like carbonate and bicarbonate) as such in the softened water.

✓ High turbidity water cannot be softened efficiently by zeolite process.

✓ When softened water (from zeolite process) is used in boilers for steam generation, CO_2 liberated by the decomposition of $NaHCO_3$, causes corrosion.

3) Ion-exchange process:

Advantages:

✓ The process can be used to soften highly acidic or, alkaline waters.

✓ The process produces water of very low hardness (2ppm), SO, the treated water is very good for use in high pressure boilers.

Disadvantages:

✓ Capital cost is high since chemical and equipment both are costly.

✓ If water contains turbidity then the efficiency of the process is reduced. The turbidity must be below 10 ppm. If it is more, it has to be removed first by coagulation and filtration.

Benefits of Treating Boiler Feed Water

✓ Ensure proper and efficient operation of steam generation system

✓ Improve operation & steam purity

✓ Improve condensate corrosion control

✓ Reduce fuel costs through lower heat loss and increased boiler cycles

✓ Reduce boiler system chemical treatment costs

- ✓ Reduce risk

- ✓ Reduce external treatment costs; particularly if previously using cold or hot lime softening, ion exchange and / or re-generable DI

- ✓ Remove / reduce hazardous acid and caustic chemicals

Water:

Water is a universal solvent. It is a chemical substance which is transparent, colorless, odorless and tasteless. Water is categorized in two types. They are hard water and soft water. These two types are not differentiated based on their touch and feel or appearance. This difference is based on the mineral content of each

Hard water:

"Hard water is water which does not readily form a lather with soap"

OR

The water with naturally present minerals like magnesium and calcium with detectable amount is called hard water

Hardness of water:

Hardness of water is a measure of its capacity to precipitate soap and is caused mainly by the presence of divalent cations of Ca^{2+}, Mg^{2+} and other multivalent cations also cause water hardness such as Fe^{3+}, Sr^{2+}, Zn^{2+}, Mn^{2+}. In

other word soap destroying property due to presence of bicarbonates, sulphates and chlorides of calcium and magnesium.

Type of hardness of water:

The hardness of water is two type

- (i)   Temporary hardness
- (ii)   Permanent hardness

Temporary hardness:

- It is due to the presence of bicarbonates of calcium and magnesium.
- It can be removed by simple boiling

Permanent hardness:

- It is due to the presence of sulphates, nitrates and chlorides of calcium and magnesium.
- It can be remove by treatment of water

Measurement of water hardness

Water hardness is measured in "grains" per gallon, in milligrams of calcium (Ca) per liter, or parts per million or mili-equavilant / liter

1 mili-equavilan /liter= 50mgs.of $CaCO_3$/litre

Removal of hardness:

Temporary hardness removal : It can be removed by following processes -

- Boiling
- Addition of lime

Permanent hardness removal: It can be removed by following processes -

- Addition of lime

- Addition of sodium carbonate

- Base Exchnage method/permutit (zeolite) process

Soft water:

- Soft water is surface water that contains low concentrations of calcium and magnesium ions and other certain metal cations in hard water.
- Soap lathers easily.

Difference between Hard water and Soft water

Hard water

- It is rich in minerals
- Soap is not so effective
- Contains minerals like magnesium and calcium
- Hair and skin become dry
- Example: Groundwater like deep wells

Soft water:

- Contains very few elements
- Soap is easily effective
- Bubbly lather from soaps
- Contains sodium ion
- Example : Rainwater
- Hair and skin become soft

Water softening:

Water softening is the removal of calcium and magnesium, and certain other metal cations in hard water.

Softening of water by zeolite process:

Zeolite:

- Zeolite is hydrated sodium alimino silicate.
- It is a microporus mineral which is used as adsorbents, catalysts.
- The term zeolite was given by Swedish mineralogist Axel Fredrik Cronstedt in 1756.
- It is also known as permutits and capable of exchanging reversibly its sodium ions for hardness-prodcing ions in water.

Chemical structure of zeolite: $Na_2O.Al_2O_3.xSi_2O.yH_2O$

Where X=2-10 and Y=2-6

Type of zeolite: zeolites are of two types

- **Natural zeolites** – eg: $Na_2O.Al_2O_3.xSi_2O.yH_2O$, Natrolite.
- **Synthetic zeolites** – porous has high exchange capacity it is prepared by heating together china clay, fledspar, and soda ash.

Zeolite process:

For softening of water by zeolite process, hard water is percolated at a specified rate through a bed of Zeolite, kept in a cylinder. The Hardness causing ions (Ca^{2+}, Mg^2, etc.) are retained by the zeolite as CaZe and

MgZe while the outgoing water contains sodium salts. The following reactions take place during softening process.

Ion-exchange process:

The Na^+ ions present in the zeolite get exchanged with the cation present in the raw water such as Ca^{2+}, Mg^2, etc. The water coming out of this column is free from hardness causing ions but contain sodium salt in it.

$$Na_2Ze + CaCl_2 \longrightarrow CaZe + 2NaCl$$

$$Na_2Ze + MgSO_4 \longrightarrow MgZe + Na_2SO_4$$

Ze = zeolite

Regeneration:

When all exchangeable Na^+ present in the zeolite get exchanged with hardness causing ions such as Ca^{2+} and Mg^2 present in the water, it gets exhausted and has to be regenerated by treating concentrated NaCl.

$$CaZe + 2NaCl \longrightarrow Na_2Ze + CaCl_2$$

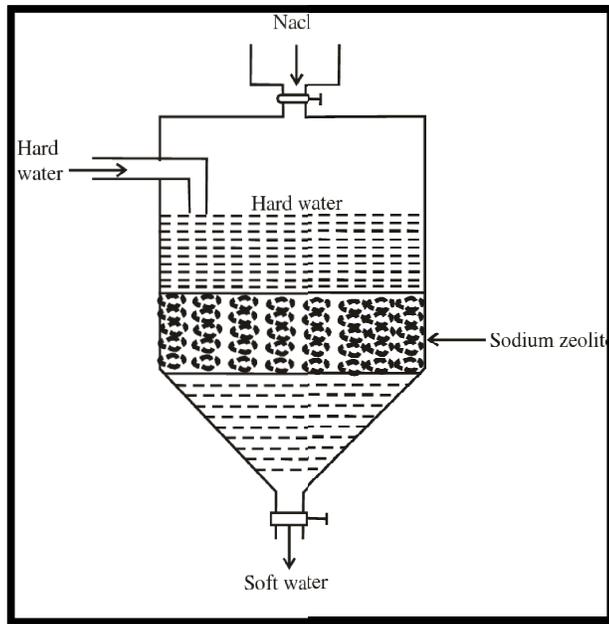$$MgZe + 2NaCl \longrightarrow Na_2Ze + MgCl_2$$

Fig . Zeolite process

To remove temporary hardness: It is due to the presence of bicarbonates of calcium and magnesium which can be removed by boiling of water and also with the help of zeolite. The following reactions take place-

$$Na_2Ze + Ca(HCO_3) \longrightarrow CaZe + 2NaHCO_3$$

$$Na_2Ze + Mg(HCO_3) \longrightarrow MgZe + 2NaHCO_3$$

Ionexchangeprocess:
(Demineralizationprocess/deionizationprocess)

It involves the complete removal of cation and anion present in water

Ionexchange resin:

It is made up polymer like polystyrene polymer etc. Ionexchange resin is two type

- Cation change resin (R-H where R is a polymeric gp and H is any acidic gp .
- Anion change resin (R-H where R is a polymeric gp and OH is any basic gp .

In ion exchange or demineralization process follwing reaction take place

$$R\text{-}H + Ca^{2+} \longrightarrow R_2Ca + H+$$

$$R\text{-}OH + Cl^- \longrightarrow R\text{-}Cl + OH^-$$

Regeneration process:

$$R_2Ca + HCl \longrightarrow R\text{-}H + CaCl_2$$

$$R\text{-}Cl + NaOH \longrightarrow R\text{-}OH + NaCl$$
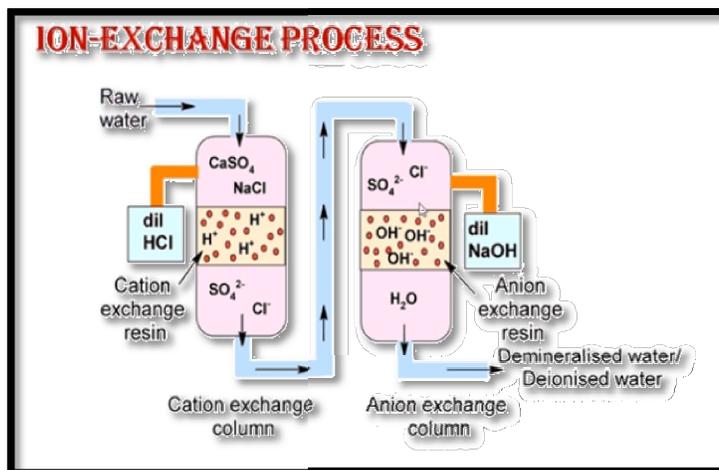

ION-EXCHANGE PROCESS

Fig: Ion-exchangeprocess

Lime soda process:

Lime soda process is method of softening hard water. In this process calcium and magnesium ions are precipitated by the addition of lime $Ca(OH)_2$ and soda ash (Na_2CO_3). Carbonate hardness is removed by lime and non carbonate hardness is removed by soda.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow Ca(HCO_3)_2 + 2Mg(OH)_2\downarrow$$

Questions:

Q.1 What is hard and soft water? define the types of hardness of water

Q.2 Define the different method of softening of water

Q.3 What are zeolites process for removing the hardness of water?

Q.4 What is hard and soft water and what cause of hardness?

Q.5 What is zeolite ? explain the ion-exchange, regeneration and soda-lime process in softening of water

Treatment of boiler feed water:

Boiler feed water:

Boiler feed water is an main part of boiler operations. The feed water is put into the steam drum from a feed pump. In the steam drum the feed water is then turned into steam from the heat. The feed water is never open to the atmosphere. This cycle is known as a closed system or Rankine cycle.

Necessity of feed water treatment:

Boiler water treatment is used to control alkalinity, prevent scaling, correct pH, and to control conductivity. The boiler water needs to be alkaline and not acidic, so that it does not ruin the tubes. Boiler water is treated to prevent scaling, corrosion, foaming, and priming. Chemicals are put into boiler water through the chemical feed tank to keep the water within chemical range. These chemicals are mostly oxygen scavengers and phosphates.

Chemicals used in boiler water treatment:

Chemicals which are used in boiler water treatment are Oxygen Scavengers, Amines, Phosphates, Polymers, and Alkalinity Builders.

- Oxygen Scavengers - Most common type is 38%, pH < 4. ...
- Boiler Alkalinity Builders - Potassium Hydroxide or Sodium Hydroxide are the most common boiler alkaline products.

Boiler feed water treatment system:

A boiler feed water treatment system is **a system made up of several individual technologies that address your specific boiler feed water treatment needs.**

Treating boiler feed water is essential for both high- and low-pressure boilers. Ensuring the correct treatment is implemented before problems such as fouling, scaling, and corrosion occur, will go a long way in avoiding costly replacements/upgrades down the line.

An efficient and well-designed boiler feed water treatment system should be able to:

- Efficiently treat boiler feed water and remove harmful impurities prior to entering the boiler
- Promote internal boiler chemistry control
- Maximize use of steam condensate

- Control return-line corrosion
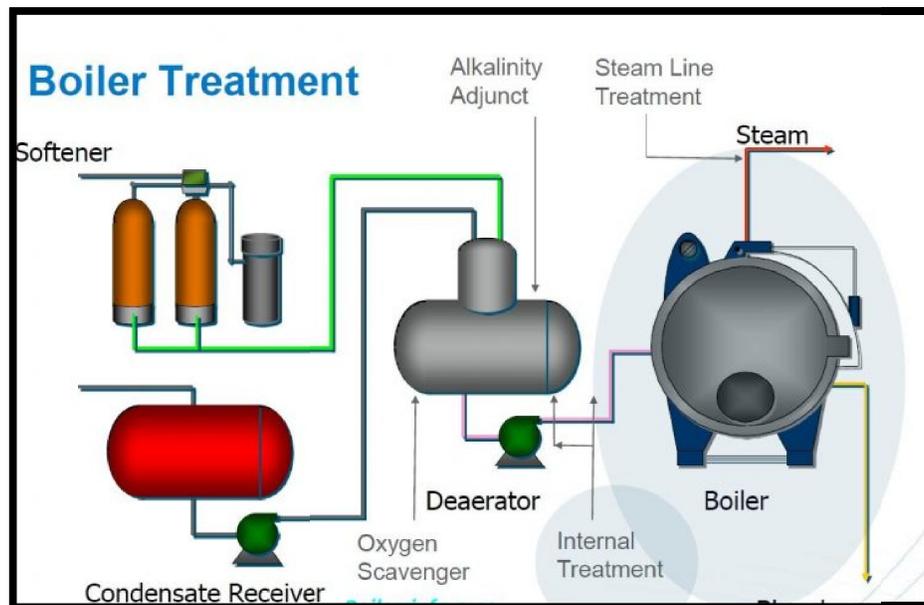- Avoid plant downtime and boiler failure
- Prolong equipment service life

Fig: Boiler water treatment

Methods use in the treatment of boiler water:

- Filtration and ultrafiltration.
- Ion exchange.
- Membrane processes such as reverse osmosis and nano filtration.
- Deaeration/degasification.
- Coagulation/chemical precipitation.

Calgon process:

It involves the addition of calogon or sodium hexametaphosphate to boiler water. This substance reacts with calcium ions and forms highly soluble complex and thus prevents the precipitation of scale forming salt.

Calogen is a trade name of a complex salt, sodium hexametaphosphate $(NaPO_3)_6$. It is used for softening of hard water. The addition of Calgon to hard water causes the calcium and magnesium ions of hard water to displace sodium ions from the anion of Calgon. Sodium hexametaphosphate $Na_2[Na_4(PO_3)_6]$ is commonly use calgon . When calgon is added to hard water, Ca^{2+} and Mg^2 ions present in it combine with sodium hexametaphosphate to form soluble complex of calcium and maganesium salts.

$$2CaCl_2 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Ca_2(PO_3)_6] + 4NaCl$$

$$2MgSo_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Mg_2(PO_3)_6] + 2Na_2SO_4$$

Q.1.Write calgon's method for removal of permanent hardness of water

Q.2 *What's included in a basic boiler feed water treatment system?*

Q.3 What are the chemicals used in boiler water treatment?

Q.4 What is Calgon process?