Chandigarh Engineering College, CGC-Landran, Mohali

Department of Applied Sciences

Reference Material for Weak Students

Chapter-1 (Periodicity)

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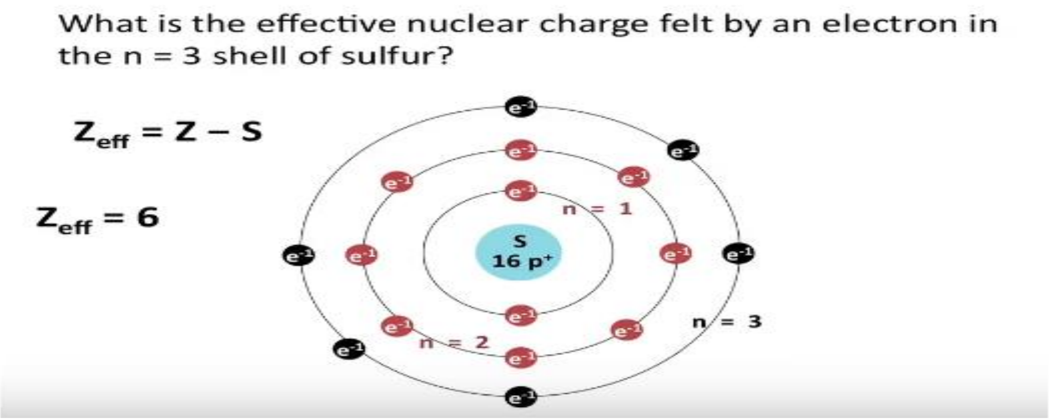
1. **Define Effective Nuclear Charge and penetration of orbital's?**

Ans. The effective nuclear charge is the net positive charge experienced by valence electrons. It can be approximated by the equation: $Z_{eff} = Z - S$,

Where Z is the atomic number and S is the number of shielding electrons.



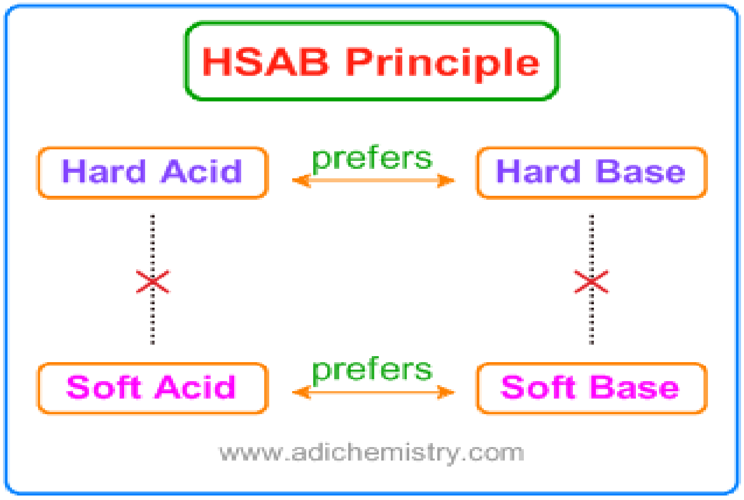
2. **What is electron affinity? Which element has highest electron affinity?**

Ans. Electron affinity is defined as the amount of energy is released when an electron is added to the neutral isolated gaseous metal atom. Chlorine is having the highest Electron affinity. Fluorine is the most electronegative element but still its electron affinity is less than that of chlorine. It is because of the small size of fluorine. All the electrons in the atom repels the incoming electron significantly, this nullify the effect

of higher electronegativity of fluorine over chlorine.

3. **Explain HSAB Principle?**

The Hard/Soft Acid/Base (HSAB) Principle. The basic premise of Hard/Soft Acid/Base Theory is very simple: Hard acids prefer hard bases; soft acids prefer soft bases.

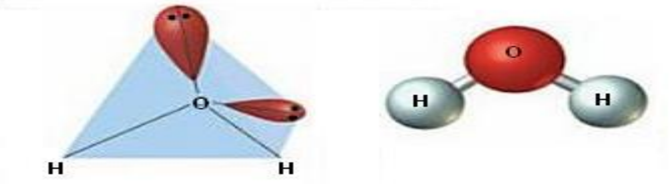


4. **Which has smallest size, Cl or Cl and why?**

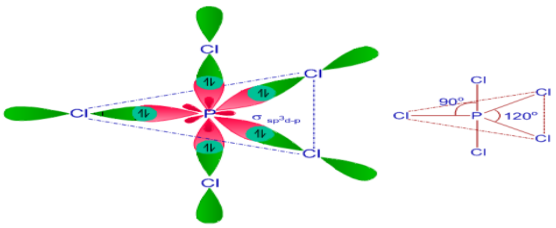
Answer: The size of an ion compared to its corresponding atom is influenced by the addition or removal of electrons. When a Cl atom gains an electron to form a Cl- ion, the extra electron increases the electron-electron repulsion, causing the electron cloud to expand and the ion to become larger than the atom. Therefore, the size of Cl is greater than Cl.

5. On the basis of VSEPR theory explain the structure of H_2O, PCl5, BF3 molecule.

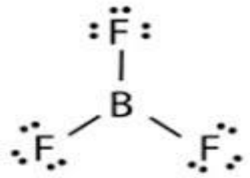
Lewis structure of H_2O

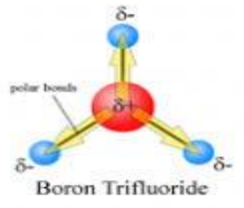


Molecular geometry of H_2O

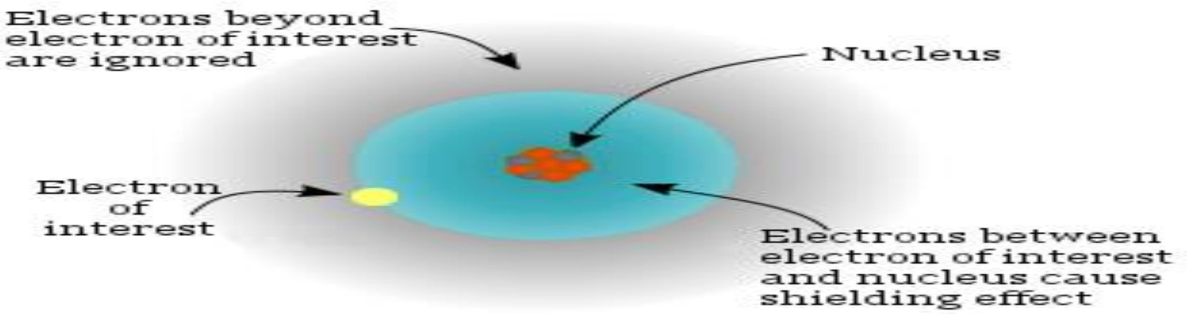


Trigonal bipyramidal structure of PCl_5





6. The Penetration effect of s orbital is the maximum because of the closeness to the nucleus than are the p, d and f orbital's.Thus an s orbital, due it's more penetration effect, releases greater amount of energy than p orbital when it accepts an electron.Similarly the energy released by a d orbital is more than that of a f orbital but less than that of a p orbital . Inner shell (core) electrons screen the outer (valence) electrons from the nuclear charge.



Chapter-2

(Stereochemistry)

7. **What are the necessary and sufficient conditions for a molecule to become optical active?**

Ans: 1.The compound must contain an asymmetric carbon atom.

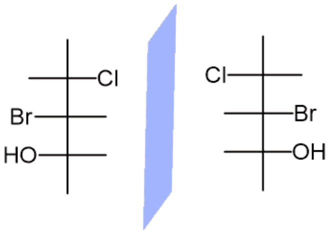
2. Its three-dimensional structure should not have a plane of symmetry.
3. The two possible formulas should be non-superimposable mirror-images.

8. **Explain enantiomerism and diasteromerism in detail.**

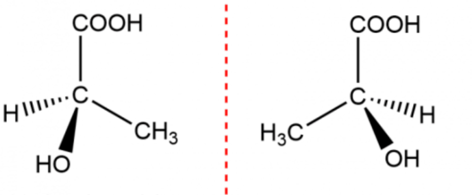
Ans.. Enantiomers are a type of stereoisomers, which are molecules with the same molecular formula and connectivity but differ in the spatial arrangement of their atoms. Specifically, enantiomers are non-superimposable mirror images of each other.

Characteristic features of enantiomers:

- Enantiomers have identical physical properties (bp, mp, density, solubility and refractive index) but there is a difference in direction of rotation of plane polarized light.
- They have identical chemical properties except in chemical reactions with other optically active compounds.
- They have different biological properties E.g. (+)-Dextrose plays an important role in animal metabolism, where as (-)-Dextrose is not metabolized.
- When equal quantities of enantiomers are mixed an optically inactive compound racemic mixture is formed



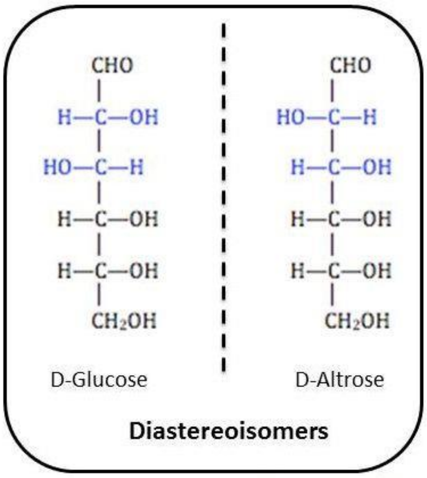
Enantiomers



(-)-lactic acid (+)-lactic acid

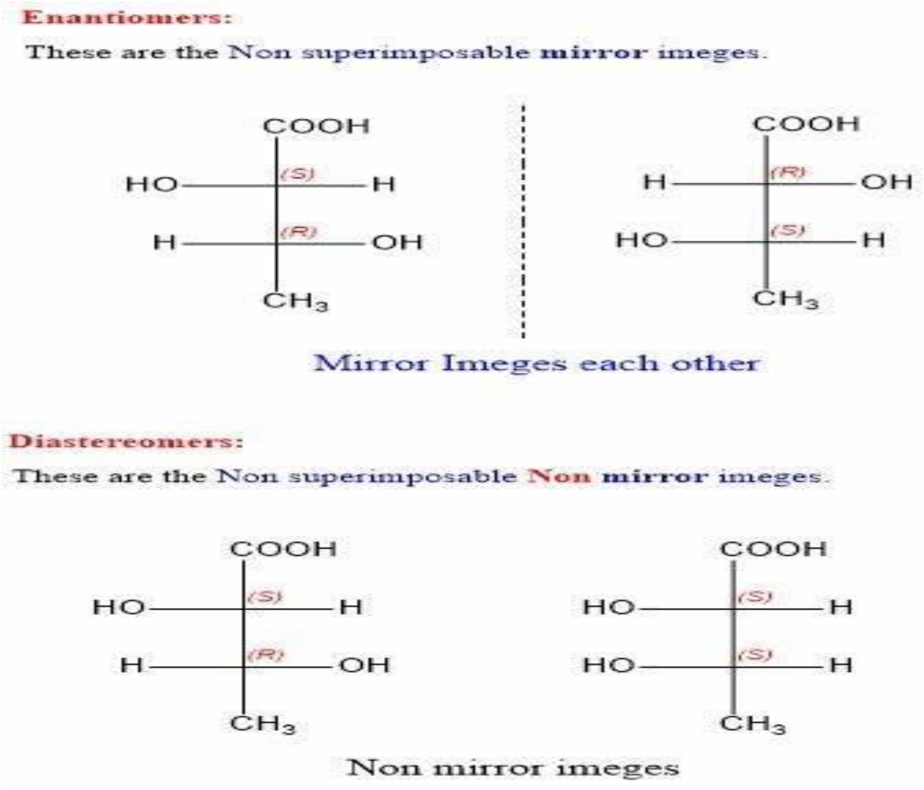
Enantiomers

Diasteroiomers: Stereomers of a substance that are not mirror images of each other are termed as Diastereomers. Two chiral carbon must be present in the molecule.



Characteristics:

- They have different physical properties like m.p, b.p, solubility, density and refractive index, etc.
- Diastereomers have different specific rotation but they may have same or opposite sign of rotation



Enantiomers:

These are the Non superimposable mirror imeges.

Mirror Imeges each other

Diastereomers:

These are the Non superimposable Non mirror imeges.

Non mirror imeges

9. What are meso compounds.

Ans: Meso compound is a molecule is a molecule with multiple stereocenters that is superimposable on its mirror image. Meso compounds are achiral compounds that has multiple chiral centers. Meso compounds are optically inactive. It has an internal symmetry plane that divides the compound in half. A Meso compound should contain two or more identical substituted stereocenters.

For example Tartaric acid. Where one part is exactly same as that of second part.

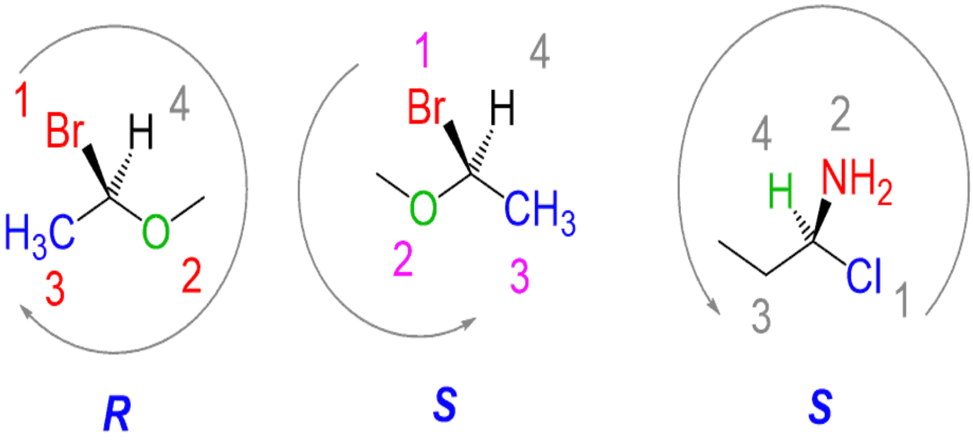
10. Assign R and S configuration to the following molecules:

Ans: Rules for Assigning R and S Configuration:

- Assigning Priority: Assign priority to the substituents based on the atomic numbers of the atoms directly attached to the stereo center.

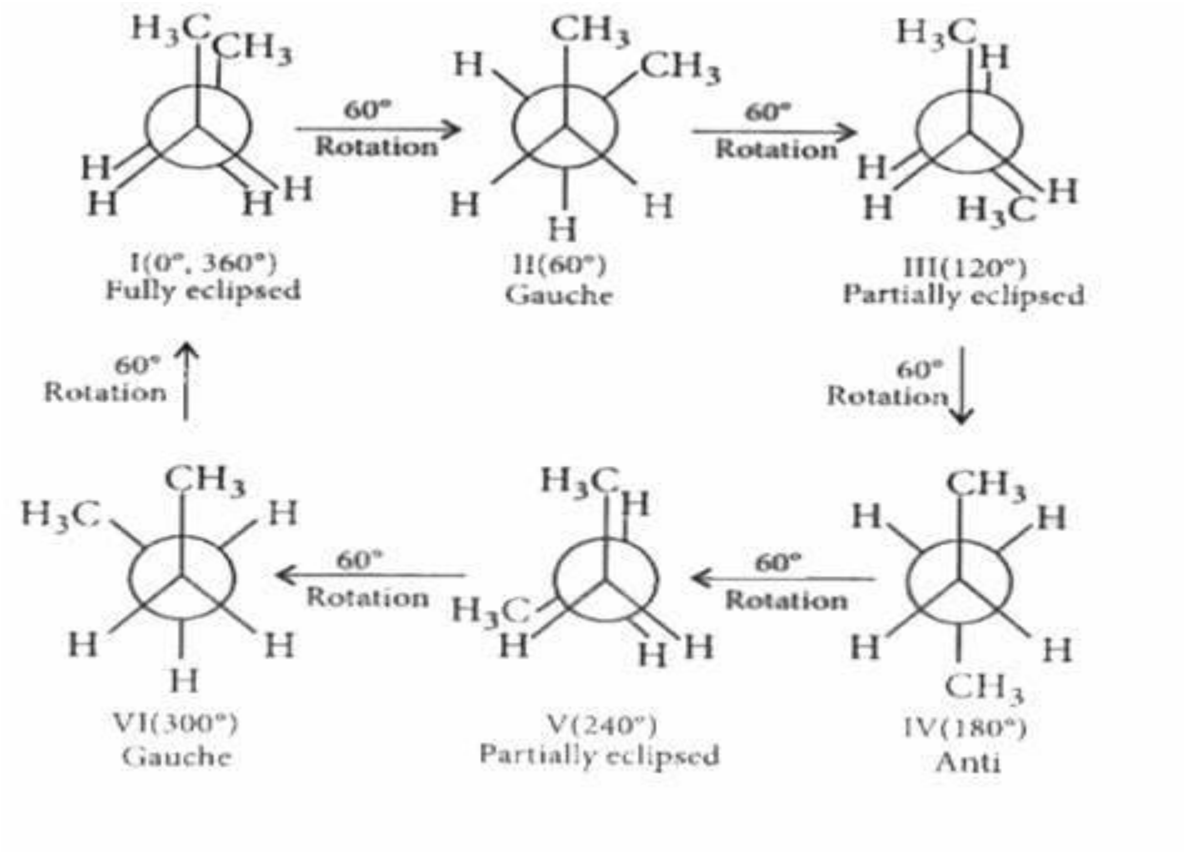
- The atom with the highest atomic number gets the highest priority. Orienting the Molecule: Orient the molecule so that the substituent with the lowest priority (usually hydrogen) is pointing away from you.
- Determining Configuration: Observe the sequence of the remaining three substituents. If the sequence is clockwise, it is R; if it is counterclockwise, it is S. Example: Consider a stereocenter with substituents A, B, C, and D. If their priorities are assigned as follows: A > B > C > D
- If the sequence ABC is clockwise, the configuration is R. If the sequence ABC is counterclockwise, the configuration is S.

The lowest priority (in this case the H) must be pointing back:

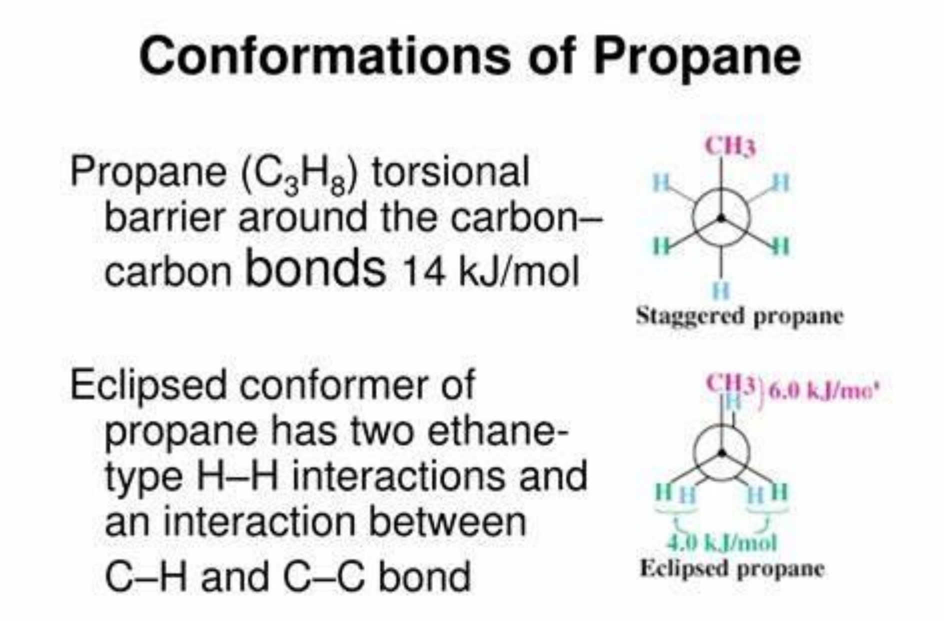


There are, however, different ways to determine the configuration if the lowest priority is not pointing back.

11. CONFORMATIONAL ISOMERISM IN BUTANE AND Propane: Butane is an organic compound which consists of an alkane with 4 carbon atoms.



CONFORMATIONAL ISOMERISM IN PROPANE



Conformations of Propane

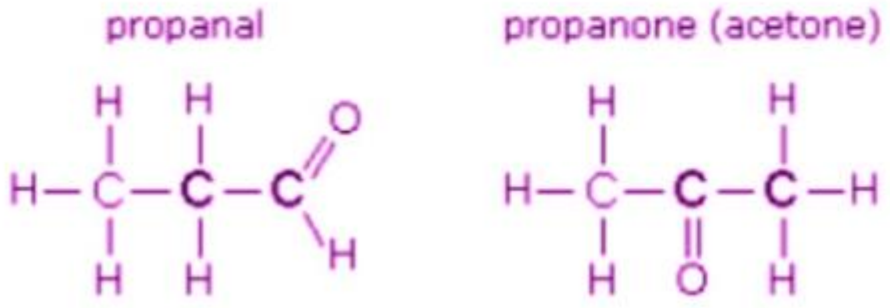
Propane (C_3H_8) torsional barrier around the carbon–carbon bonds 14 kJ/mol

Eclipsed conformer of propane has two ethane-type H–H interactions and an interaction between C–H and C–C bond

12. Write a short note on functional isomerism and metamerism.

Ans. It is also known as functional group isomerism.

As the name suggests, it refers to the compounds that have the same chemical formula but different functional groups attached to them. example



Metamerism: This type of isomerism arises due to the presence of different alkyl chains on each side of the functional group. It is a rare type of isomerism and is generally limited to molecules that contain a divalent atom (such as sulphur or oxygen), surrounded by alkyl groups. Example: $C_4H_{10}O$ can be represented as ethoxyethane ($C_2H_5OC_2H_5$) and methoxy-propane ($CH_3OC_3H_7$).

$$C_4H_{10}O$$

$CH_3—O—CH_2CH_2CH_3$

1-Methoxypropane

$CH_3CH_2—O—CH_2CH_3$

Ethoxyethane

$$C_5H_{10}O$$

$CH_3—CO—CH_2CH_2CH_3$

Pentan-2-one

$CH_3CH_2—CO—CH_2CH_3$

Pentan-3-one

Chapter-3 (Atomic Structure)

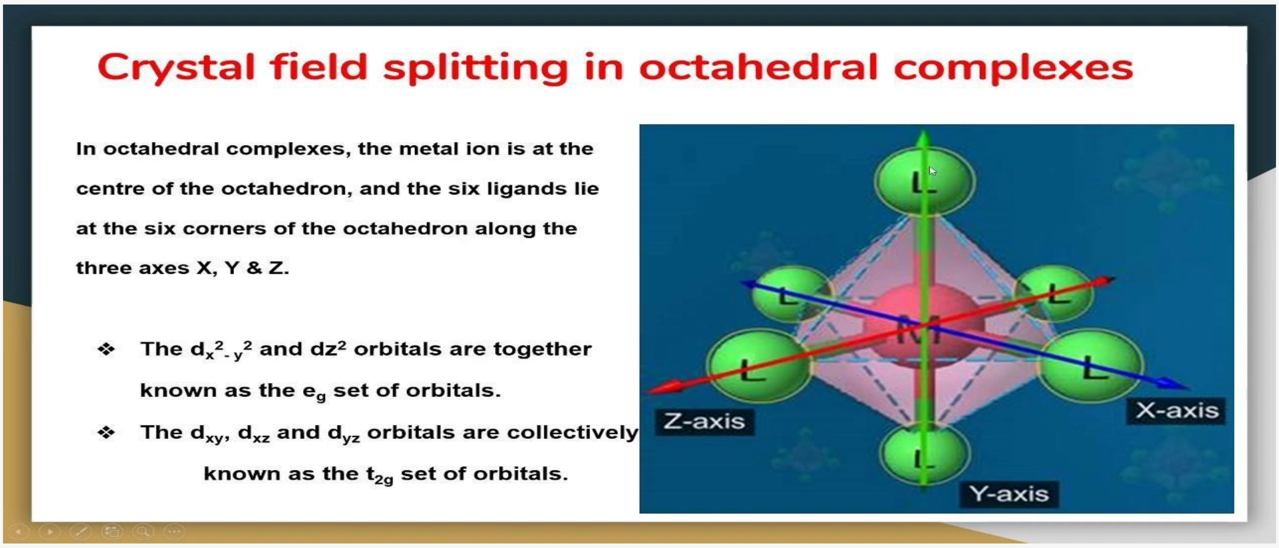
13. Explain CFT in octaedral complexes.

- Ans. In the case of an octahedral coordination compound having six ligands surrounding the metal atom/ion, we observe repulsion between the electrons in d orbitals and ligand electrons.
- This repulsion is experienced more in the case of $d_{x^2-y^2}$ and d_{z^2} orbitals as they point towards the axes along the direction of the ligand.
- Hence, they have higher energy than average energy in the spherical crystal field.
- On the other hand, d_{xy}, d_{yz}, and d_{xz} orbitals experience lower repulsions as they are directed between the axes.
- Hence, these three orbitals have less energy than the average energy in the spherical crystal field.

Thus, the repulsions in octahedral coordination compound yield two energy levels:

- t_{2g}– set of three orbitals (d_{xy}, d_{yz} and d_{xz}) with lower energy
- e_g – set of two orbitals ($d_{x^2-y^2}$ and d_{z^2}) with higher energy

The energy gap is referred to as D (10 D_q) , the **crystal field splitting energy**.

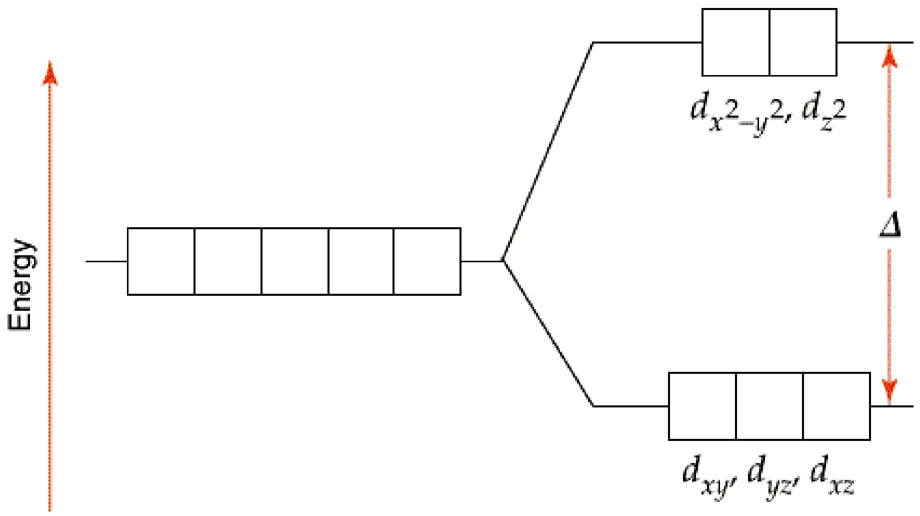


Crystal field splitting in octahedral complexes

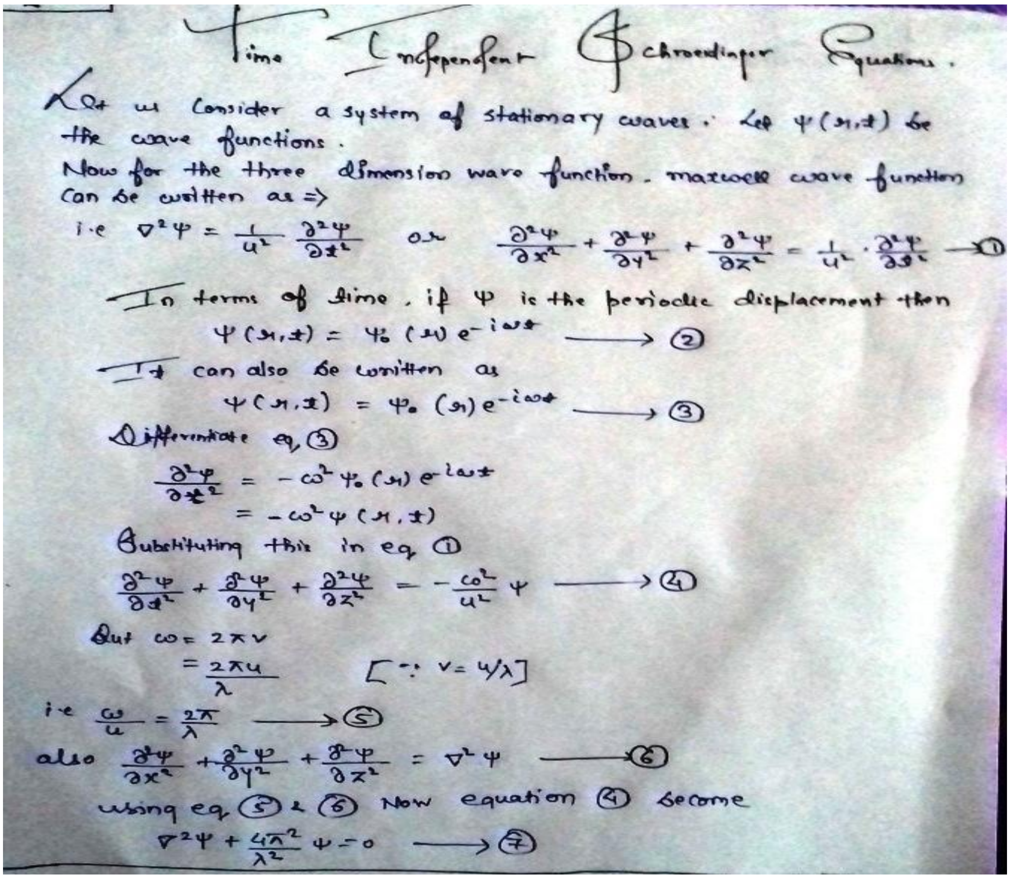
In octahedral complexes, the metal ion is at the centre of the octahedron, and the six ligands lie at the six corners of the octahedron along the three axes X, Y & Z.

❖ The $d_{x^2-y^2}$ and dz^2 orbitals are together known as the e_g set of orbitals.

❖ The d_{xy}, d_{xz} and d_{yz} orbitals are collectively known as the t_{2g} set of orbitals.



14. Obtain the time-dependent Schrödinger wave equation for a particle.



Time Independent Schroedinger Equations.

Let us Consider a system of stationary waves. Let $\psi(r,t)$ be the wave functions.

Now for the three dimension wave function. maxwell wave function Can be written as =>

i.e $\nabla^2\psi = \frac{1}{u^2}\frac{\partial^2\psi}{\partial t^2}$ or $\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = \frac{1}{u^2}\cdot\frac{\partial^2\psi}{\partial t^2} \longrightarrow ①$

In terms of time, if ψ is the periodic displacement then

$\psi(r,t) = \psi_0(r)\, e^{-i\omega t} \longrightarrow ②$

It can also be written as

$\psi(r,t) = \psi_0(r)\, e^{-i\omega t} \longrightarrow ③$

Differentiate eq ③

$\frac{\partial^2\psi}{\partial t^2} = -\omega^2\psi_0(r)\, e^{i\omega t}$

$= -\omega^2\psi(r,t)$

Substituting this in eq ①

$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{\omega^2}{u^2}\psi \longrightarrow ④$

But $\omega = 2\pi v$

$= \frac{2\pi u}{\lambda}$ $[\because v = u/\lambda]$

i.e $\frac{\omega}{u} = \frac{2\pi}{\lambda} \longrightarrow ⑤$

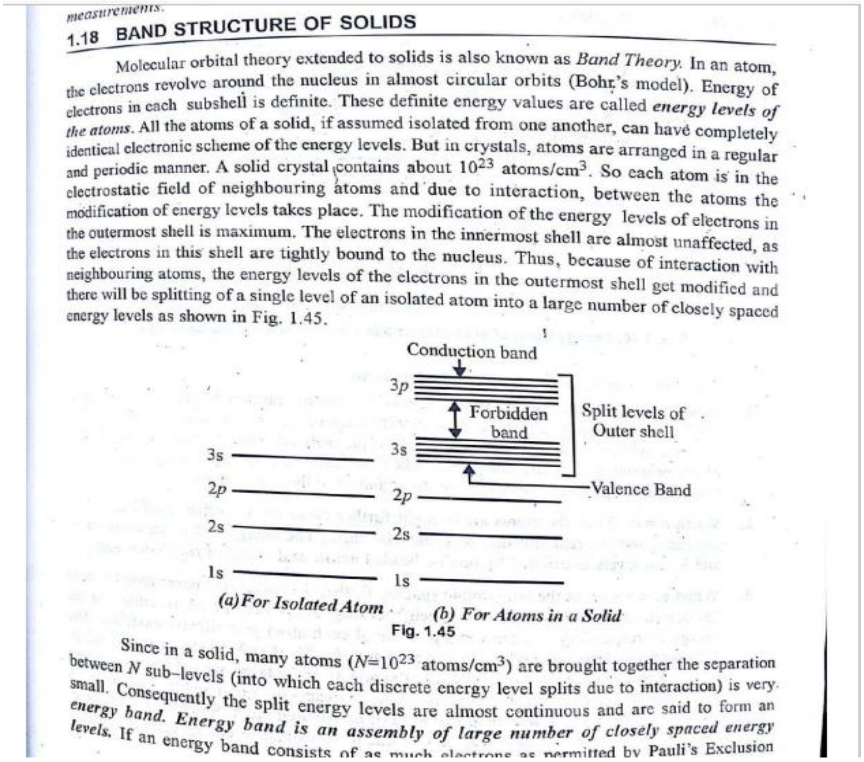
also $\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = \nabla^2\psi \longrightarrow ⑥$

using eq ⑤ & ⑥ Now equation ④ become

$\nabla^2\psi + \frac{4\pi^2}{\lambda^2}\psi = 0 \longrightarrow ⑦$

15. **Discuss the role of doping on the band structure of solids.** (2)

Ans. In semiconductor production, doping is the intentional introduction of impurities into an intrinsic semiconductor for the purpose of modulating its electrical, optical and structural properties. The doped material is referred to as an extrinsic semiconductor. A semiconductor doped to such high levels that it acts more like a conductor than a semiconductor is referred to as a degenerate semiconductor. In the context of phosphors and scintillators, doping is better known as activation. Doping is also used to control the color in some pigments.



measurements.

1.18 BAND STRUCTURE OF SOLIDS

Molecular orbital theory extended to solids is also known as *Band Theory.* In an atom, the electrons revolve around the nucleus in almost circular orbits (Bohr's model). Energy of electrons in each subshell is definite. These definite energy values are called ***energy levels of the atoms.*** All the atoms of a solid, if assumed isolated from one another, can have completely identical electronic scheme of the energy levels. But in crystals, atoms are arranged in a regular and periodic manner. A solid crystal contains about 10^{23} atoms/cm^3. So each atom is in the electrostatic field of neighbouring atoms and due to interaction, between the atoms the modification of energy levels takes place. The modification of the energy levels of electrons in the outermost shell is maximum. The electrons in the innermost shell are almost unaffected, as the electrons in this shell are tightly bound to the nucleus. Thus, because of interaction with neighbouring atoms, the energy levels of the electrons in the outermost shell get modified and there will be splitting of a single level of an isolated atom into a large number of closely spaced energy levels as shown in Fig. 1.45.

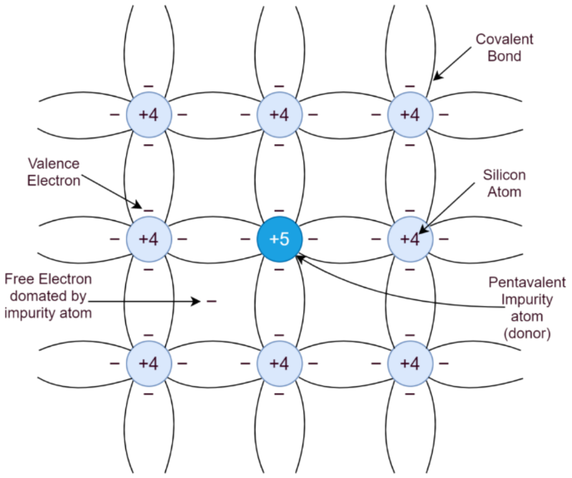
(a) For Isolated Atom *(b) For Atoms in a Solid*

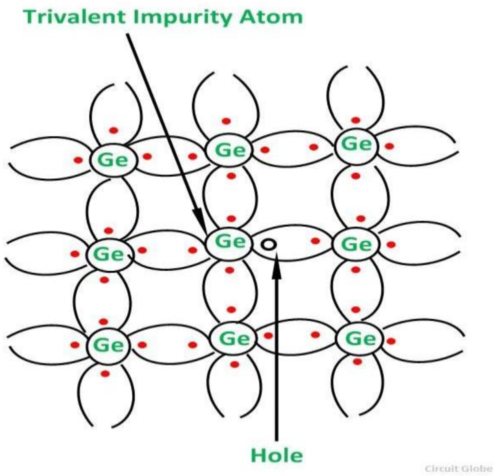
Fig. 1.45

Since in a solid, many atoms (N=10^{23} atoms/cm^3) are brought together the separation between N sub-levels (into which each discrete energy level splits due to interaction) is very small. Consequently the split energy levels are almost continuous and are said to form an ***energy band. Energy band is an assembly of large number of closely spaced energy levels.*** If an energy band consists of as much electrons as permitted by Pauli's Exclusion

16. Write Briefly: a) What are N type and P type semiconductors ?

Answer: The P-type semiconductor can be defined as, once the trivalent impurity atoms such as indium, gallium are added to an intrinsic semiconductor, and then it is known as a p-type semiconductor. In this semiconductor, the majority charge carriers are holes whereas minority charge carriers are electrons. The hole's density is higher than the electrons density. The accepts level mainly lies nearer to the valence band. The N-type semiconductor can be defined as, once the pentavalent impurity atoms such as Sb, As is added to an intrinsic semiconductor, and then it is known as an n-type semiconductor. In this semiconductor, the majority charge carriers are electrons whereas minority charge carriers are holes. The electrons density is higher than the density of the holes. The donor level mainly lies nearer to the conduction band





17. Explain the stability of O_2, O_2^-,O_2^+ and O_2^{2-}

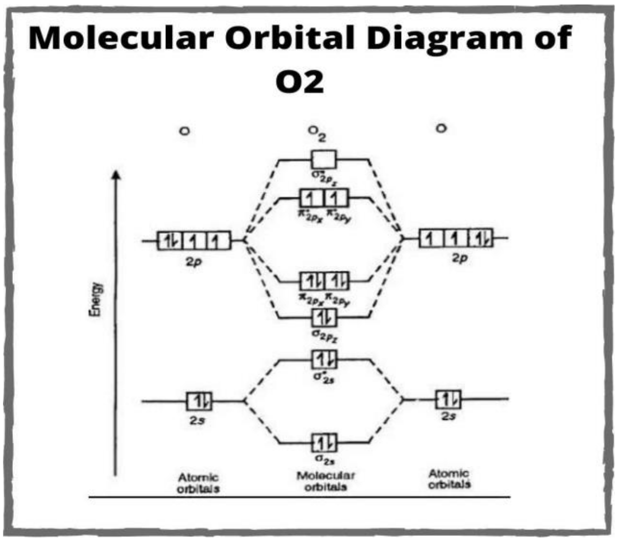
ANS: Higher the bond order , higher is stability

O_2 : B.O. $= (8 - 4)/2 = 2$

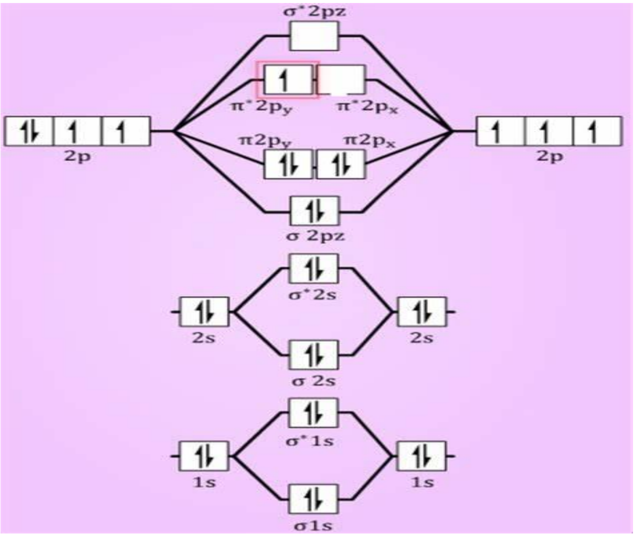
O_2^+ : B.O. $= (8 - 3)/2 = 2.5$

O_2^- : B.O. $= (8 - 5)/2 = 1.5$

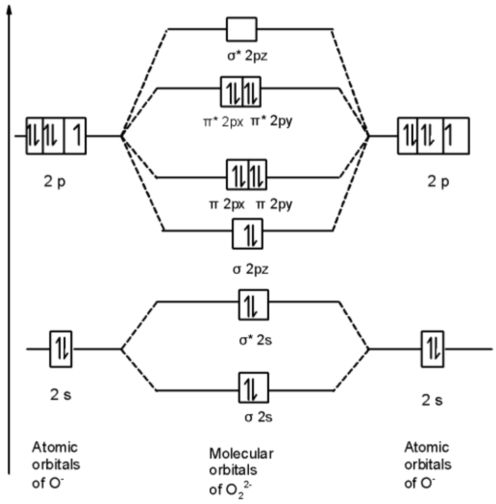
O_2^{2-} : B.O. $= (8 - 6)/2 = 1$



Diagrams of O_2



Diagrams of $O_2{}^{+}$



Diagrams of $O_2{}^{2-}$

Chapter-4 (Spectroscopy)

18. Define the following terms.

Bathochromic Shift

Auxochromes

Fluorescence

Hyperchromic Shift

Answer:

a) Bathochromic Shift: Bathochromic shift is a change of spectral band position in the absorption, reflectance, transmittance, or emission spectrum of a molecule to a longer wavelength (lower frequency). This can occur because of a change in environmental conditions: for example, a change in solvent polarity will result in solvatochromism. A series of structurally related molecules in a substitution series can also show a bathochromic shift.

b) Auxochromes: An auxochrome is a functional group of atoms with one or more lone pairs of electrons when attached to a chromophore, alters both the wavelength and intensity of absorption. If these groups are in direct conjugation with the pi- system of the chromophore, they may increase the wavelength at which the light is absorbed and as a result intensify the absorption. A feature of these auxochromes isthe presence of at least one lone pair of electrons which can be viewed as extendingthe conjugated system by resonance. Examples include the hydroxyl (−OH), amino
($-NH_2$), aldehyde (−CHO).

c) Fluorescence: Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation. It is a form of luminescence. In most cases, the emitted light has a longer wavelength, and therefore a lower photonenergy, than the absorbed radiation. A perceptible example of fluorescence occurs when the absorbed radiation is in the ultraviolet region of the electromagnetic spectrum (invisible to the human eye), while the emitted light is in the visible region;this gives the fluorescent substance a distinct color that can only be seen when the substance has been exposed to UV light.

d) Hyperchromic Shift: It is the shift where intensity of absorption maximum decrease. When the geometry of a molecule is distorted due to the introduction ofgroup, this type of shift may take place. For example, biphenyl absorbs at lower value, as compared to 2-methyl biphenyl.

1. Write short notes on :

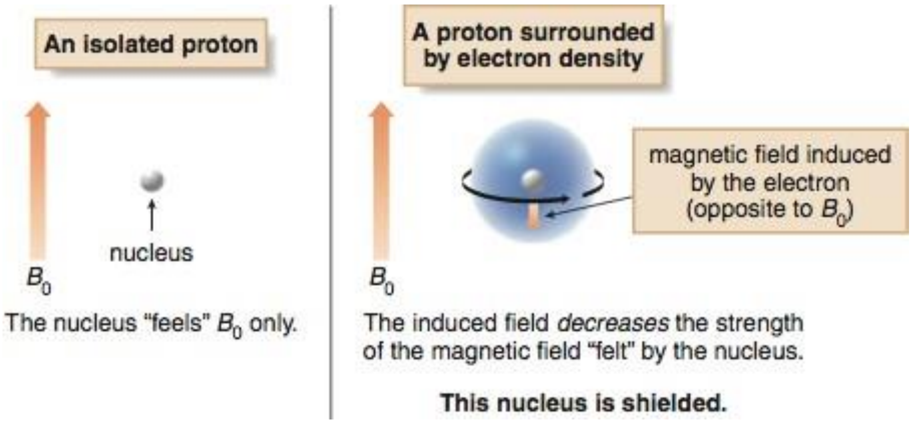
a) Shielding and deshielding of protons (4)

Ans. The basic principle of NMR is to apply an external magnetic field called B0 and measure the frequency at which the nucleus achieves resonance.

Electrons orbiting around the nucleus generate a small magnetic field that opposes B0. In this case we say that electrons are shielding the nucleus from B0.

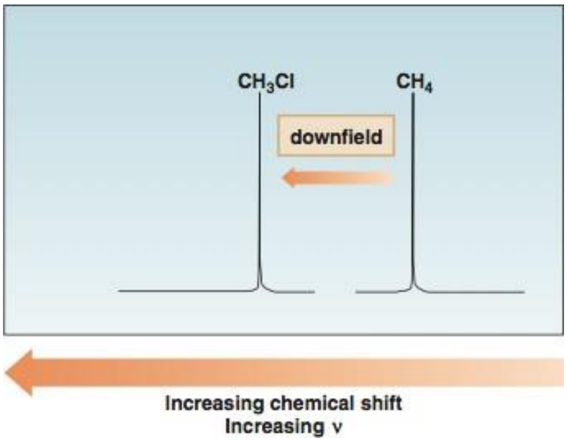
Shielding:

The higher the electron density around the nucleus, the higher the opposing magnetic field to B0 from the electrons, the greater the shielding. Because the proton experiences lower external magnetic field, it needs a lower frequency to achieve resonance, and therefore, the chemical shift shifts upfield (lower ppms) .



Deshielding:

If the electron density around a nucleus decreases, the opposing magnetic field becomes small and therefore, the nucleus feels more the external magnetic field B0, and therefore it is said to be deshielded. Because the proton experiences higher external magnetic field, it needs a higher frequency to achieve resonance, and therefore, the chemical shift shifts downfield (higher ppms).



b) Factors affecting vibrational frequency (4)

Ans. The value of vibrational frequency of a bond calculated by Hooke's Law is not always equal to their observed value. The force constant is changed with the electronic and steric effects. Factors affecting vibrational frequencies and IR Spectroscopy of Hydrocarbons causedby other groups present in the surroundings. Following are some important factors affecting.

the vibrational frequency of a bond.

1. Effect of Bond Order

Bond order affects the position of absorption bands. Higher the bond order larger is the band frequency. A C-C triple bond is stronger than a C=C bond, so a C-C triple bond has higher stretching frequency than does a C=C bond.

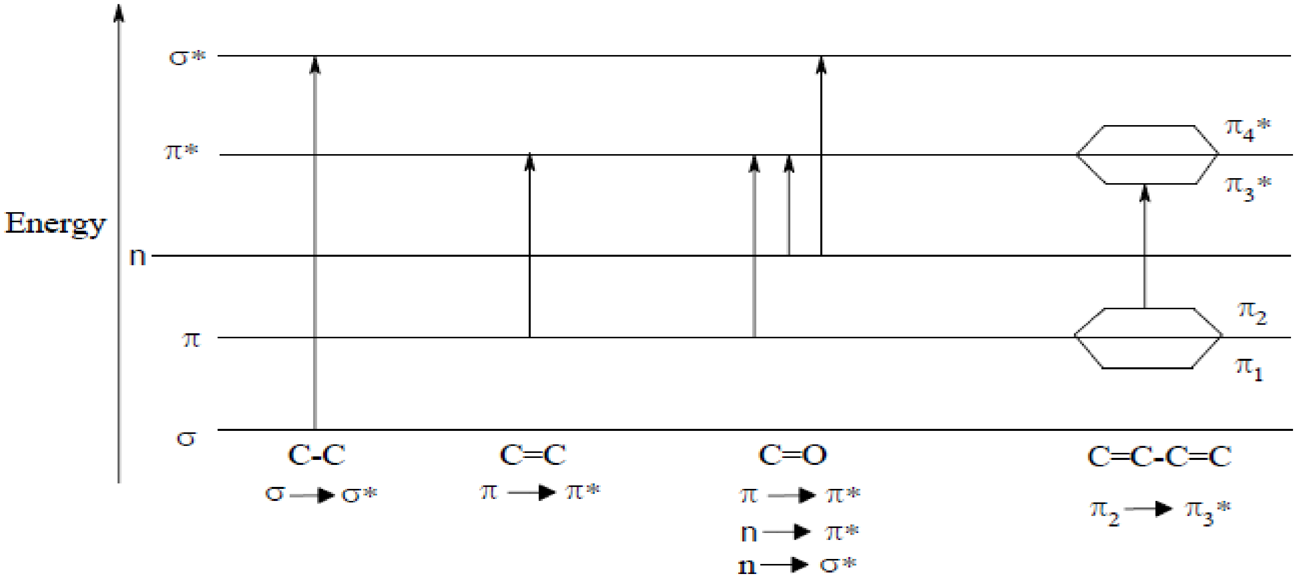
2. Resonance and Inductive Electronic Effects

A range of frequency for each stretch is usually assigned as the exact position of the absorption band depends on other structural features of the molecule, such as electron delocalization, the electronic effect of neighboring substituents, and hydrogen bonding.

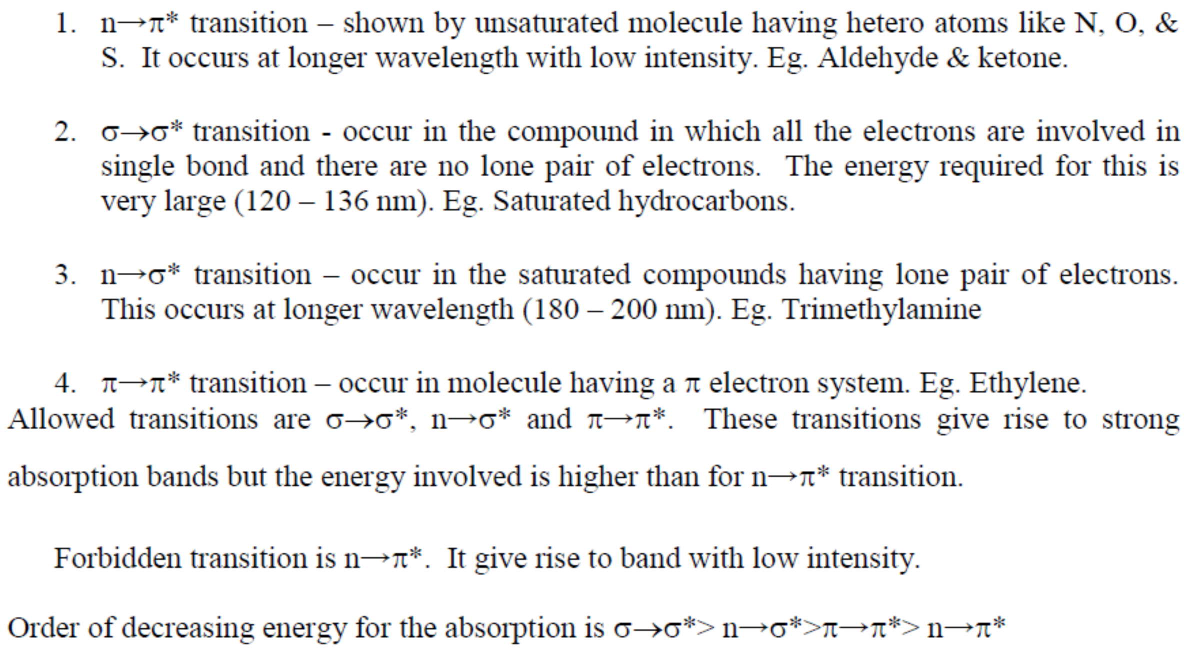
3. Hydrogen Bonding

The presence of hydrogen bonding changes the position and shape of an infrared absorption band. Frequencies of both stretching as well as bending vibrations are changed because of hydrogen bonding. The X-H stretching bands move to lower frequency usually with increased intensity and band widening.

19. Give the principle of electronic spectroscopy.



Relative energies of transitions



1. $n \rightarrow \pi^*$ transition – shown by unsaturated molecule having hetero atoms like N, O, & S. It occurs at longer wavelength with low intensity. Eg. Aldehyde & ketone.

2. $\sigma \rightarrow \sigma^*$ transition - occur in the compound in which all the electrons are involved in single bond and there are no lone pair of electrons. The energy required for this is very large (120 – 136 nm). Eg. Saturated hydrocarbons.

3. $n \rightarrow \sigma^*$ transition – occur in the saturated compounds having lone pair of electrons. This occurs at longer wavelength (180 – 200 nm). Eg. Trimethylamine

4. $\pi \rightarrow \pi^*$ transition – occur in molecule having a π electron system. Eg. Ethylene.

Allowed transitions are $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$. These transitions give rise to strong absorption bands but the energy involved is higher than for $n \rightarrow \pi^*$ transition.

Forbidden transition is $n \rightarrow \pi^*$. It give rise to band with low intensity.

Order of decreasing energy for the absorption is $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$

20. **Which of the following molecules will show IR spectra and why ?**

H_2, HCI, CH_4, CO_2, H_2O

Ans. HCI, CH_4, CO_2, H_2O these molecules will show IR spectra because these possess change in dipole moment when undergo asymmetric stretching. HCl is a polar molecule and CO_2, CH_4, H_2O possess dipole moment on absorption of IR radiation.

21. Tetra methyl silane used as standard compound in recording NMR.

Ans. TMS is used as standard reference compound in 1H NMR. Chemical shift of protons in different compounds are measured relative to standard reference compound TMS. TMS i.e. tetra methyl silane used as reference compound in recording 1H NMR.

TMS contains 12 H atoms which are equivalent , so show intense sharp signal at low concentrations.

2. TMS is chemically inert and miscible with almost all organic solvents.

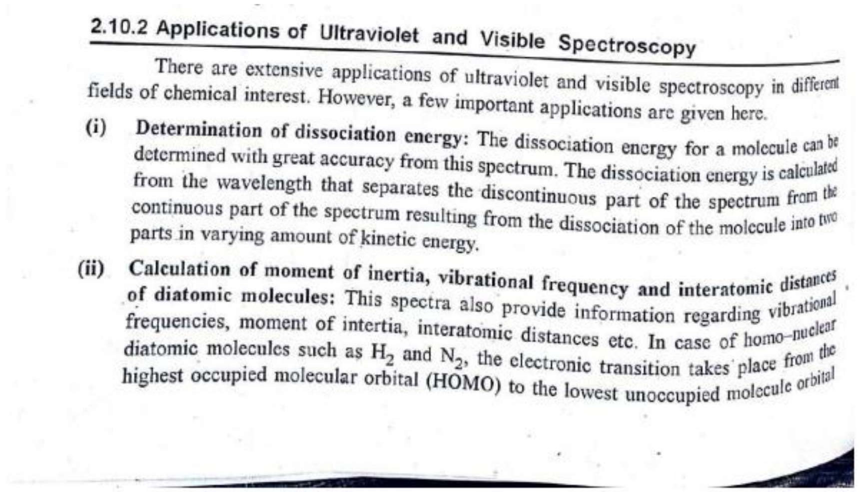
3. TMS has low boiling point(27° C), so it can be removed from compound easily after taking the NMR spectrum.

22. **What are Auxochrome and Chromophore ?**

Ans. An **auxochrome** (Greek auxo "to increase" and *chrōma*: "colour") is a group of atoms attached to a chromophore which modifies the ability of that chromophore to absorb light. Examples include the hydroxyl group (-OH), the amino group ($-NH_2$), the aldehyde group (-CHO), and the methyl mercaptan group (-SMe).

Chromophore : A chromophore is defined as functional group which shows a characterstick absorption in UV-visible region and which may or may not imparts colour to compound.

23. Applications of UV-visible spectroscopy.

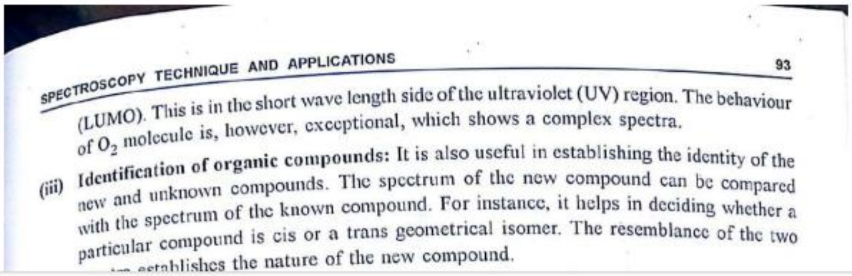


2.10.2 Applications of Ultraviolet and Visible Spectroscopy

There are extensive applications of ultraviolet and visible spectroscopy in different fields of chemical interest. However, a few important applications are given here.

(i) Determination of dissociation energy: The dissociation energy for a molecule can be determined with great accuracy from this spectrum. The dissociation energy is calculated from the wavelength that separates the discontinuous part of the spectrum from the continuous part of the spectrum resulting from the dissociation of the molecule into two parts in varying amount of kinetic energy.

(ii) Calculation of moment of inertia, vibrational frequency and interatomic distances of diatomic molecules: This spectra also provide information regarding vibrational frequencies, moment of intertia, interatomic distances etc. In case of homo-nuclear diatomic molecules such as H_2 and N_2, the electronic transition takes place from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecule orbital



(LUMO). This is in the short wave length side of the ultraviolet (UV) region. The behaviour of O_2 molecule is, however, exceptional, which shows a complex spectra.

(iii) Identification of organic compounds: It is also useful in establishing the identity of the new and unknown compounds. The spectrum of the new compound can be compared with the spectrum of the known compound. For instance, it helps in deciding whether a particular compound is cis or a trans geometrical isomer. The resemblance of the two establishes the nature of the new compound.

of O_2 molecule is, however, exceptional,

(iii) Identification of organic compounds: It is also useful in establishing the identity of the new and unknown compounds. The spectrum of the new compound can be compared with the spectrum of the known compound. For instance, it helps in deciding whether a particular compound is cis or a trans geometrical isomer. The resemblance of the two spectra establishes the nature of the new compound.

The absorption spectrum of an unknown compound is compared with those of a number of known *compounds*. If the absorption spectrum of the unknown compound tallies with a particular known compound, then the structure of the two will also be similar. The absorption spectra of synthetic (unknown) and natural vitamin A_2 are shown in Fig. 2.9. The similarity between the two spectra proved helpful in the identification and assignment of structure of synthetic vitamin A_2. The technique in which the spectrum of an unknown compound is tallied with those of known compounds, is known as *finger printing. The points marked as A and C in the Fig. 2.9, where the value of* λ_{max} *is the same for two compounds are called* ***isobestic points.***

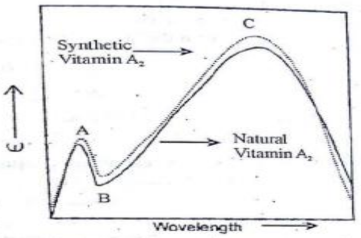
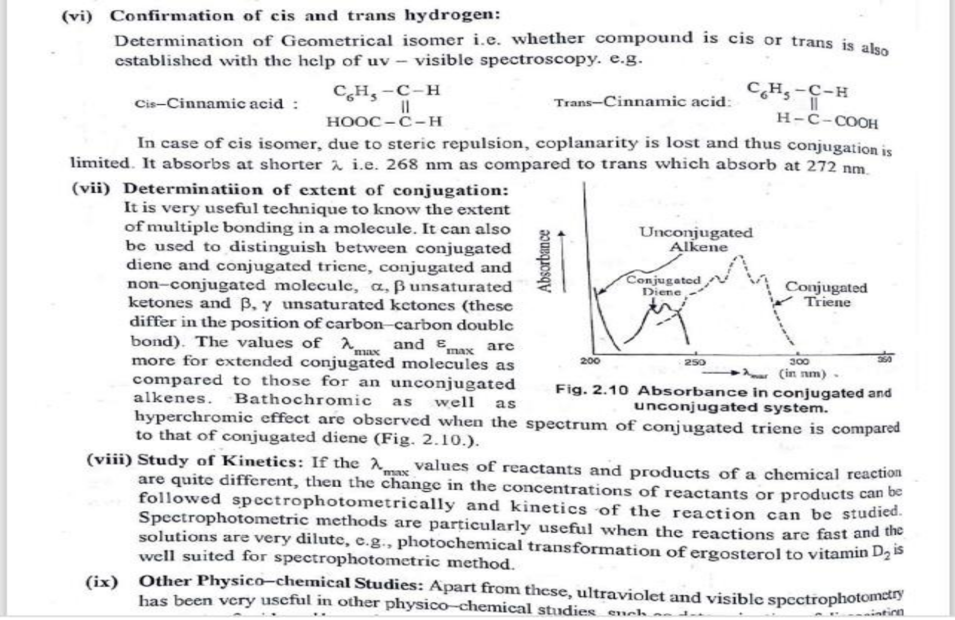


Fig. 2.9 Absorption spectrum of vitamin A_2 in ultraviolet Region.

(iv) Presence of impurities: It can be used to detect the presence of impurities in a substance. The spectrum of the compound is compared with the spectrum of pure compound. The impurities will certainly cause extra absorption bands, characteristic to their structures. Ultraviolet and visible spectrophotometry is used for the control of purification of a compound.

(v) Determination of structure of organic compounds: The fact that compounds having similar structures show similar absorption spectra can be utilized in deciding the constitutions of compounds where more than one possibility arise. For example, two



(vi) Confirmation of cis and trans hydrogen:

Determination of Geometrical isomer i.e. whether compound is cis or trans is also established with the help of uv – visible spectroscopy. e.g.

Cis–Cinnamic acid : $\begin{matrix} C_6H_5-C-H \\ \| \\ HOOC-C-H \end{matrix}$ Trans–Cinnamic acid: $\begin{matrix} C_6H_5-C-H \\ \| \\ H-C-COOH \end{matrix}$

In case of cis isomer, due to steric repulsion, coplanarity is lost and thus conjugation is limited. It absorbs at shorter λ i.e. 268 nm as compared to trans which absorb at 272 nm.

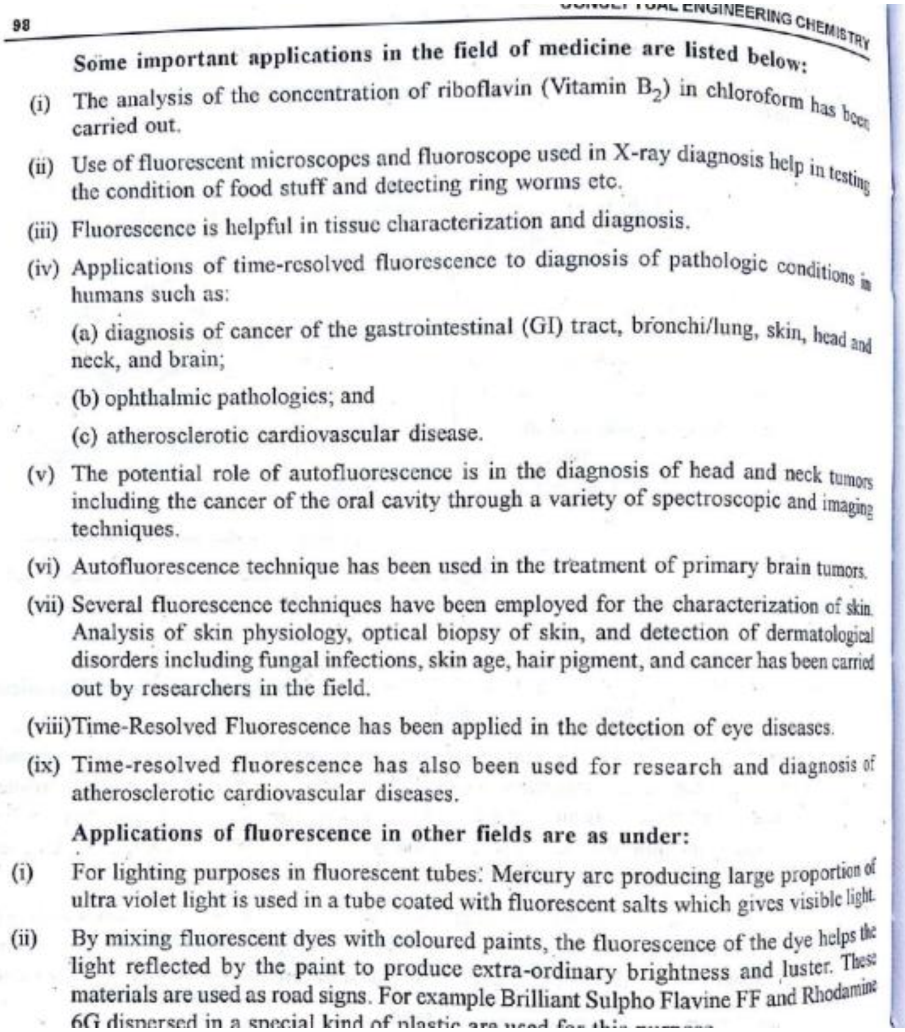
(vii) Determinatiion of extent of conjugation: It is very useful technique to know the extent of multiple bonding in a molecule. It can also be used to distinguish between conjugated diene and conjugated triene, conjugated and non–conjugated molecule, α, β unsaturated ketones and β, γ unsaturated ketones (these differ in the position of carbon–carbon double bond). The values of λ_{max} and ε_{max} are more for extended conjugated molecules as compared to those for an unconjugated alkenes. Bathochromic as well as hyperchromic effect are observed when the spectrum of conjugated triene is compared to that of conjugated diene (Fig. 2.10.).

Fig. 2.10 Absorbance in conjugated and unconjugated system.

(viii) Study of Kinetics: If the λ_{max} values of reactants and products of a chemical reaction are quite different, then the change in the concentrations of reactants or products can be followed spectrophotometrically and kinetics of the reaction can be studied. Spectrophotometric methods are particularly useful when the reactions are fast and the solutions are very dilute, e.g., photochemical transformation of ergosterol to vitamin D_2 is well suited for spectrophotometric method.

(ix) Other Physico–chemical Studies: Apart from these, ultraviolet and visible spectrophotometry has been very useful in other physico–chemical studies

24. Give applications of flouresecnece in medicine.



Some important applications in the field of medicine are listed below:

(i) The analysis of the concentration of riboflavin (Vitamin B_2) in chloroform has been carried out.

(ii) Use of fluorescent microscopes and fluoroscope used in X-ray diagnosis help in testing the condition of food stuff and detecting ring worms etc.

(iii) Fluorescence is helpful in tissue characterization and diagnosis.

(iv) Applications of time-resolved fluorescence to diagnosis of pathologic conditions in humans such as:

(a) diagnosis of cancer of the gastrointestinal (GI) tract, bronchi/lung, skin, head and neck, and brain;

(b) ophthalmic pathologies; and

(c) atherosclerotic cardiovascular disease.

(v) The potential role of autofluorescence is in the diagnosis of head and neck tumors including the cancer of the oral cavity through a variety of spectroscopic and imaging techniques.

(vi) Autofluorescence technique has been used in the treatment of primary brain tumors.

(vii) Several fluorescence techniques have been employed for the characterization of skin. Analysis of skin physiology, optical biopsy of skin, and detection of dermatological disorders including fungal infections, skin age, hair pigment, and cancer has been carried out by researchers in the field.

(viii)Time-Resolved Fluorescence has been applied in the detection of eye diseases.

(ix) Time-resolved fluorescence has also been used for research and diagnosis of atherosclerotic cardiovascular diseases.

Applications of fluorescence in other fields are as under:

(i) For lighting purposes in fluorescent tubes: Mercury arc producing large proportion of ultra violet light is used in a tube coated with fluorescent salts which gives visible light.

(ii) By mixing fluorescent dyes with coloured paints, the fluorescence of the dye helps the light reflected by the paint to produce extra-ordinary brightness and luster. These materials are used as road signs. For example Brilliant Sulpho Flavine FF and Rhodamine 6G dispersed in a special kind of plastic are used for this

Chapter-5 (Organic Chemistry)

1. Explain SN1 and SN2 reactions

Types of nucleophilic Substitution Reactions

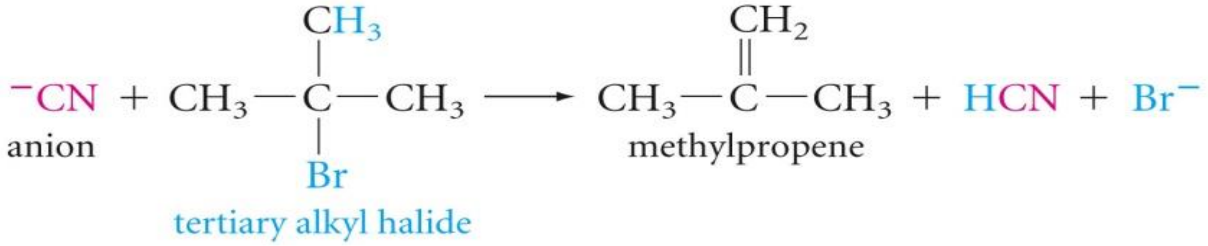
1. **Unimolecularnucleophilic Substitution (SN1) Reactions:**

Such reactions proceed in **two steps via formation of a carbocation** intermediate and the product obtained is a racemic mixture

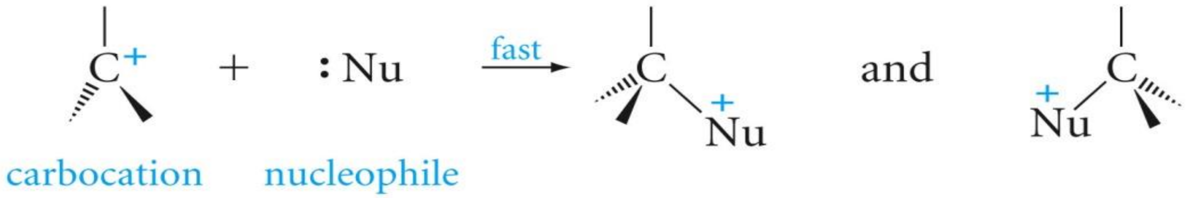
For example, the **hydrolysis of tertiary halides** follow SN1 pathway.

The initiation step is ionization of substrate which is slow and rate determining step.

The second step is a rapid reaction between the intermediate carbocation and the nucleophile.



$$^{-}CN + CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3 \longrightarrow CH_3-\overset{\overset{CH_2}{\|}}{C}-CH_3 + HCN + Br^{-}$$



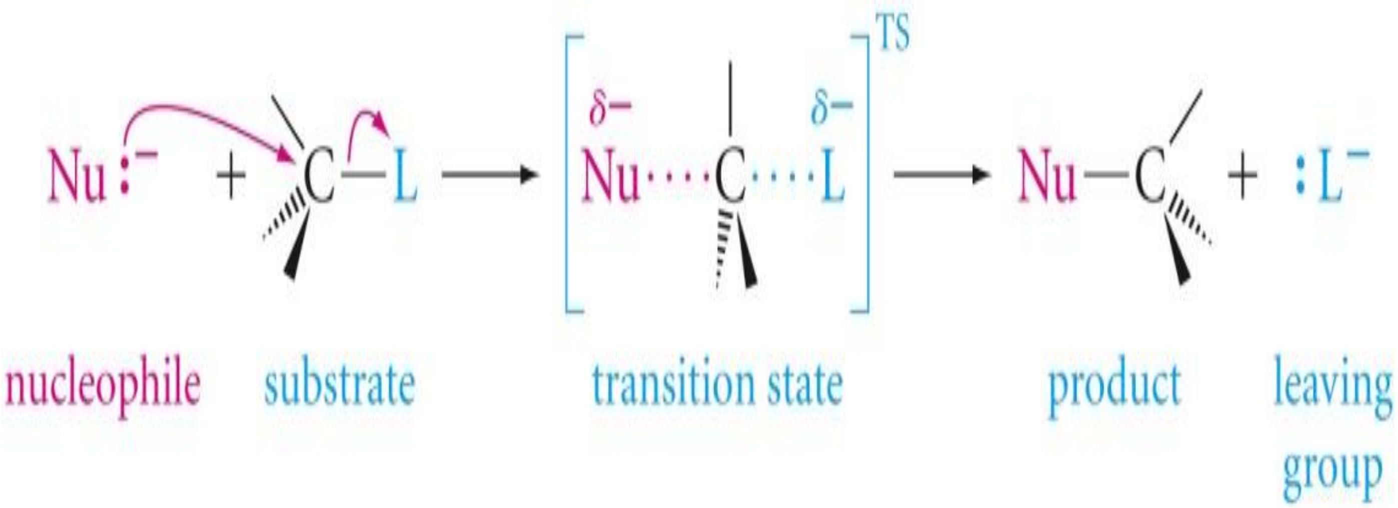
Factors influence the SN1 reaction

- ❖ Effect of solvent: In SN1 reactions (or E1), the rate determining step is forming the carbocation. It doesn't matter if the nucleophile is stabilized by a protic solvent as the carbocation attracts the nucleophile enough to still make it attack (the carbocation has a formal charge while the starting substance is a bit polar at most, in general). Thus, it doesn't matter if the solvent is protic or aprotic (but always polar).

- Effect of leaving group: S_N1 reaction speeds up with a good leaving group. This is because the leaving group is involved in the rate-determining step. A good leaving group wants to leave so it breaks the C-Leaving Group bond faster. Once the bond breaks, the carbocation is formed and the faster the carbocation is formed, the faster the nucleophile can come in and the faster the reaction will be completed.
- **Effect of nucleophile:**The strength of the nucleophile does not affect the reaction rate of SN1 because, as stated above, the nucleophile is not involved in the rate-determining step.
- **Substrate Effect:** In SN1 type of reaction proceed formation of carbocation in transition state. Hence carbocation stability is more important and increases as we go from primary to secondary to tertiary, the rate of reaction for the SN1 goes from primary (slowest) << secondary < tertiary (fastest)

Bimolecular Nucleophilic Substitution Reactions (S_N2 Reaction)

The S_N2 reaction is a nucleophilic substitution reaction where a bond is broken and another is formed simultaneously. Two reacting species are involved in the rate determining step of the reaction. The term 'S_N2' stands for – Substitution Nucleophilic Bimolecular. This reaction proceeds through a backside attack by the nucleophile on the substrate. The nucleophile approaches the given substrate at an angle of 180^o to the carbon-leaving group bond. The carbon-nucleophile bond forms and carbon-leaving group bond breaks simultaneously through a transition state.Now, the leaving group is pushed out of the transition state on the opposite side of the carbon-nucleophile bond, forming the required product. It is important to note that the product is formed with an inversion of the tetrahedral geometry at the atom in the centre. The S_N2 reaction mechanism for the nucleophilic substitution of chloroethane with bromine acting as the nucleophile is illustrated below.



Properties of SN2 reactions

- SN2 reactions are
- Bimolecular with simultaneous bond-making and bond-breaking steps.
- SN2 reactions do not proceed via an intermediate.
- SN2 reactions give inversion of stereochemistry at the reaction centre. Steric effects are particularly important in SN2 reactions.

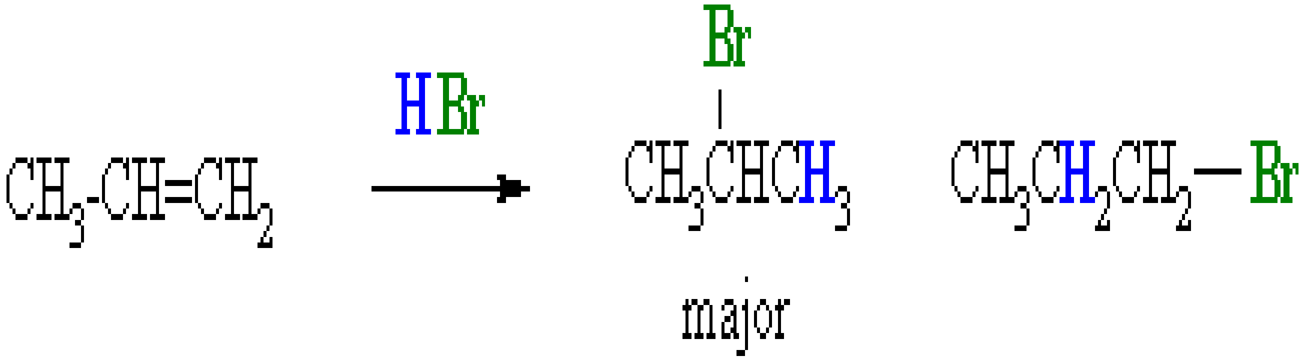
Factors influence the SN2 reaction

- **Effect of solvent :**In SN2 reactions (or E2), the nucleophile needs to react with the starting substance and this is the rate determining step. If the **solvent is polar** then it will **stabilize the nucleophile** so much that it basically won't attack. Thus **non polar solvent** will favor SN2 reaction.
- **Effect of Leaving group:** The better the leaving group the faster the reaction and therefore greater reaction rate.
- **Effect of nucleophile :** The SN2 tends to proceed with **strong** nucleophiles; by this, generally means negatively charged nucleophiles such as $CH_3O^{(-)}$, CN(-), RS(-), $N_3^{(-)}$, HO(-), and others.
- **Substrate Effect:** SN2 reactions are mainly sensitive to steric factors, since the rate of reaction is retarded by steric hindrance (crowding) at the site of reaction. In general, the order of reactivity of alkyl halides in SN2 reactions is: methyl > 1° > 2°. The 3° alkyl halides are so crowded that they do not generally react by SN2 mechanism.

2. What is Markonikov’s Rule?

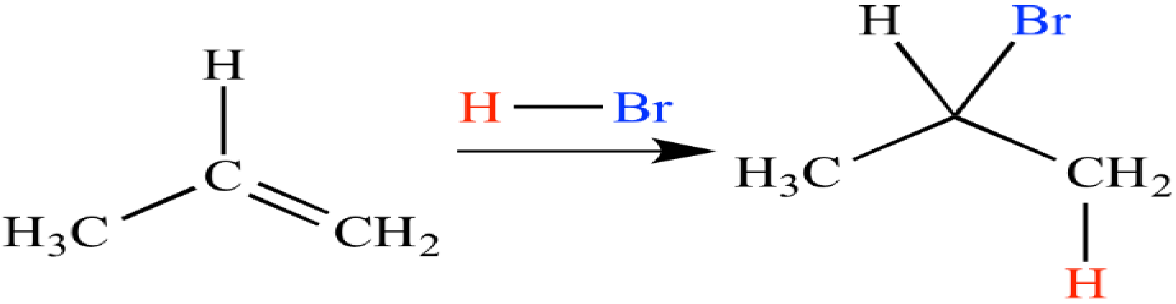
Ans. **Markovnikovs rule:**

When an unsymmetrical alkene reacts with a hydrogen halide to give an alkyl halide, the hydrogen adds to the carbon of the alkene that has the greater number of hydrogen substituents, and the halogen to the carbon of the alkene with the fewer number of hydrogen substituents".



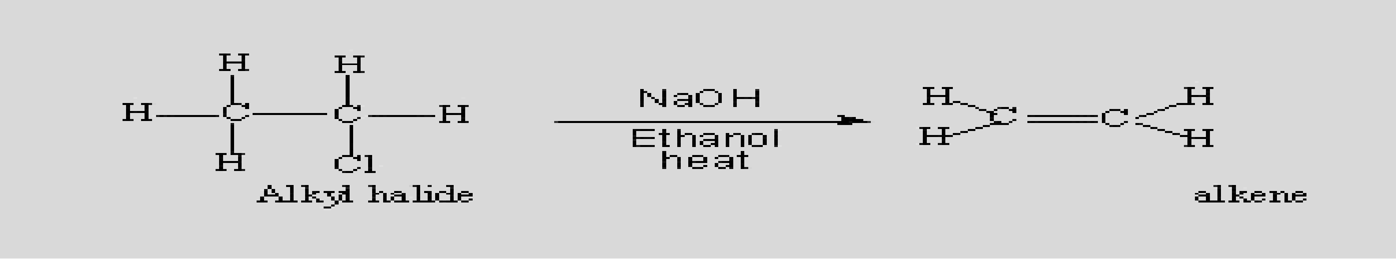
3. **What is Anti-Markovnikov rule(Peroxide effect)?**

Anti-Markovnikov addition-It is an addition reaction between an electrophile compound HX and either an alkene or alkyne in the presence of peroxide where the hydrogen atom of HX bonds to the carbon atom with the least number of hydrogen atoms in the initial alkene double bond or alkyne triple bond and the X bonds to the other carbon atom.



4. **Discuss Eliminations reactions**:

An elimination reaction is a type of organic reaction in which two substituents are removed from a molecule in either a one or two-step mechanism. The one-step mechanism is known as the E2 reaction, and the two-step mechanism is known as the E1 reaction. Elimination reaction is a type of reaction is mainly ***used to transform saturated compounds*** (organic compounds which contain single carbon-carbon bonds) ***to unsaturated compounds*** (compounds which feature double or triple carbon-carbon bonds).For exp. Preparation of alkenes.

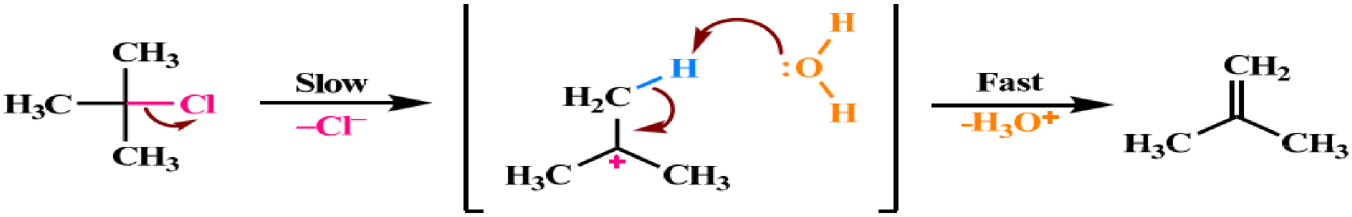


Types of Elimination Reactions

E1 Reactions (Unimolecuar eliminations)

It is a **two-step process** of elimination: ionization and deprotonation. Ionization: the carbon-halogen bond breaks to give a **carbocation intermediate**. Deprotonation of the carbocation.E1 typically takes place with **tertiary alkyl halides**, but is possible with some secondary alkyl halides.The reaction rate is influenced only by the concentration of the alkyl halide because carbocation formation is the slowest step, aka the rate-determining step. Therefore, **first-order kinetics apply (unimolecular).**

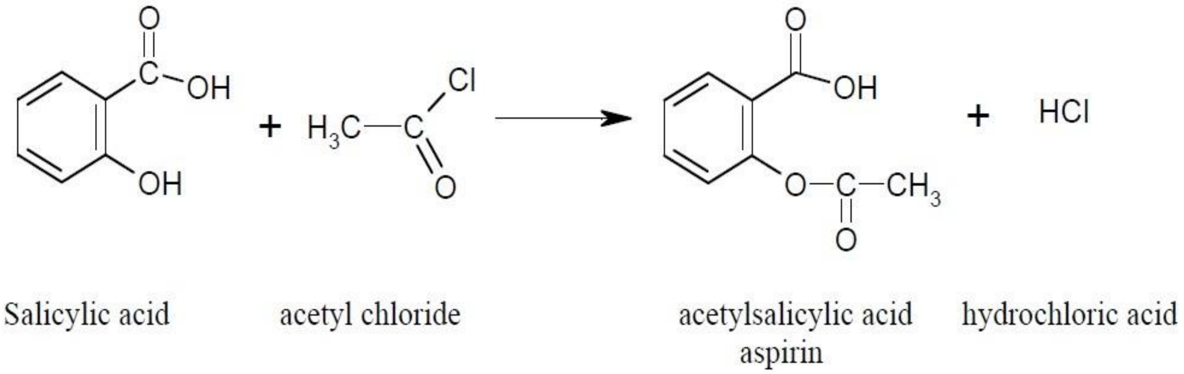
The reaction usually occurs in the **complete absence of a base** or the presence of only a weak base (acidic conditions and high temperature).



5. Explain Synthesis of common drug molecule.

SYNTHESIS OF ASPIRIN (acetylsalicylic acid):

- **It is synthesized from salicylic acid and acetyl chloride in the presence of pyridine**
- **The reaction involved is electrophilic substitution(Friedal craft acylation)**



- Allow the flask to cool to room temperature. If acetylsalicylic acid does not begin to crystallize out, scratch the walls of the flask with a glass rod. Cool the mixture slightly in an ice bath until crystallization is completed. The product will appear as a solid mass when crystallization is completed.
- Add 50 mL of water and cool the mixture in an ice bath. Do not add the water until crystal formation is complete.
- Vacuum filter the product using a Buchner funnel. You can use some of the filtrate to rinse the Erlenmeyer flask if necessary.
- Rinse the crystals several times with small portions (5 mL) of cold water and air dry the crystals on a Buchner funnel by suction until the crystals appear to be free of solvent. Test this crude product for the presence of unreacted salicylic acid using the ferric chloride test. Record the weight of the crude solid which probably contains water.
- Filter the solution through a Buchner funnel to remove any insoluble impurities or polymers that may have been formed. Wash the beaker and the funnel with 5 to 10 mL of water.
- Carefully pour the filtrate with stirring, a small amount at a time, into an ice cold HCl solution (*ca* 3.5 mL of conc. HCl in 10 mL of water) in a 150-mL beaker and cool the mixture in an ice bath. Make sure that the resulting solution is acidic (blue litmus paper) and that the aspirin has completely precipitated out.
- Cool the solution to room temperature and then in a ice-bath. Collect the product by vacuum filtration and rinse out of the flask with a few milliliters of cold petroleum ether.

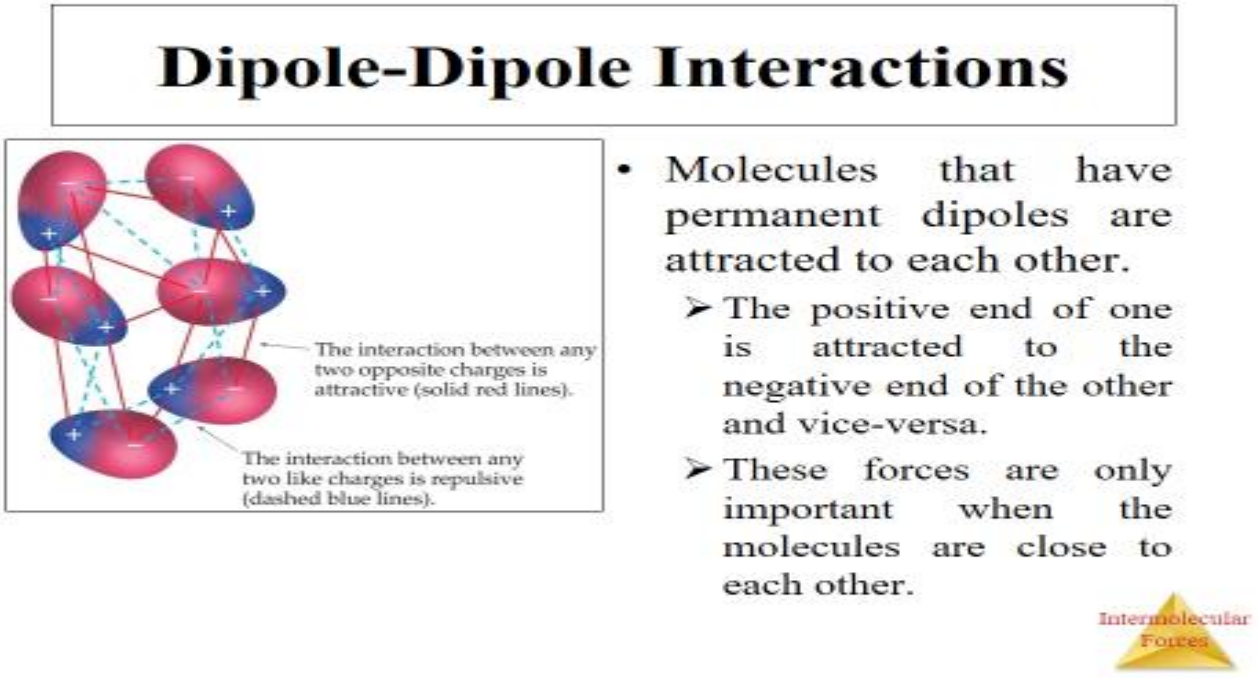
When the product is completely dry, weigh its weight, determine its melting point (lit mp 135 °C) and calculate the percentage yield of this recrystallized product. Calculate the % recovery of recrystallized material from crude material.

Chapter-6 (Intermolecular Forces)

6. Explain different Types of Intermolecular Forces.

Ans. Intermolecular forces as a group are referred to as van der Waals forces:

- **Dipole-dipole interactions**
- **Hydrogen bonding**
- **London dispersion forces**
- **Ion-Dipole Interactions**



Dipole-Dipole Interactions

The interaction between any two opposite charges is attractive (solid red lines).

The interaction between any two like charges is repulsive (dashed blue lines).

- Molecules that have permanent dipoles are attracted to each other.
  - The positive end of one is attracted to the negative end of the other and vice-versa.
  - These forces are only important when the molecules are close to each other.

London Dispersion Forces

London dispersion forces, or dispersion forces, are attractions between an instantaneous dipole and an induced dipole

Helium atom 2

The electrons in the 1*s* orbital of helium would repel each other (and, therefore, tend to stay far away from each other), it does happen that they occasionally wind up on the same side of the atom.

Though the Van der Waals constants *a* and *b* take into consideration the effect of attractive interactions in gaseous molecules, the exact nature of these interactions has to be understand. Since molecules are composed of positively charged nuclei and negatively charged electrons, whenever any two molecules come closer, interactions occur between the charge clouds of the nuclei and the electrons of the two molecules. At relatively large intermolecular distances, the attractive forces originating from attraction between electrons and atomic nuclei operate between the two molecules. At very small distances, however, the molecules strongly repel each other, the repulsion arising from the interaction between the similarly charged electron clouds. Thus, we expect the intermolecular potential energy to be composed of the long range *attractive term* and the short range *repulsive term.*

3. Ion-dipole forces: These are the strongest inter-nuclear forces. These occur between the ions formed by dissolving the ionic compound in polar solvents. The polar solvent is generally water but it can also include organic salts dissolved in polar organic compound, e.g. [Et_4N]Br in acetone. The negative end of the dipole will be attracted to positive ions and vice versa.

The magnitude of the interaction between these dipoles and ions depends upon the ionic charges and size of dipoles. These forces sharply decrease with increasing distance. Thus, they act over very short distance only.

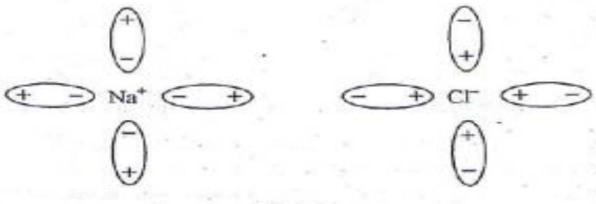
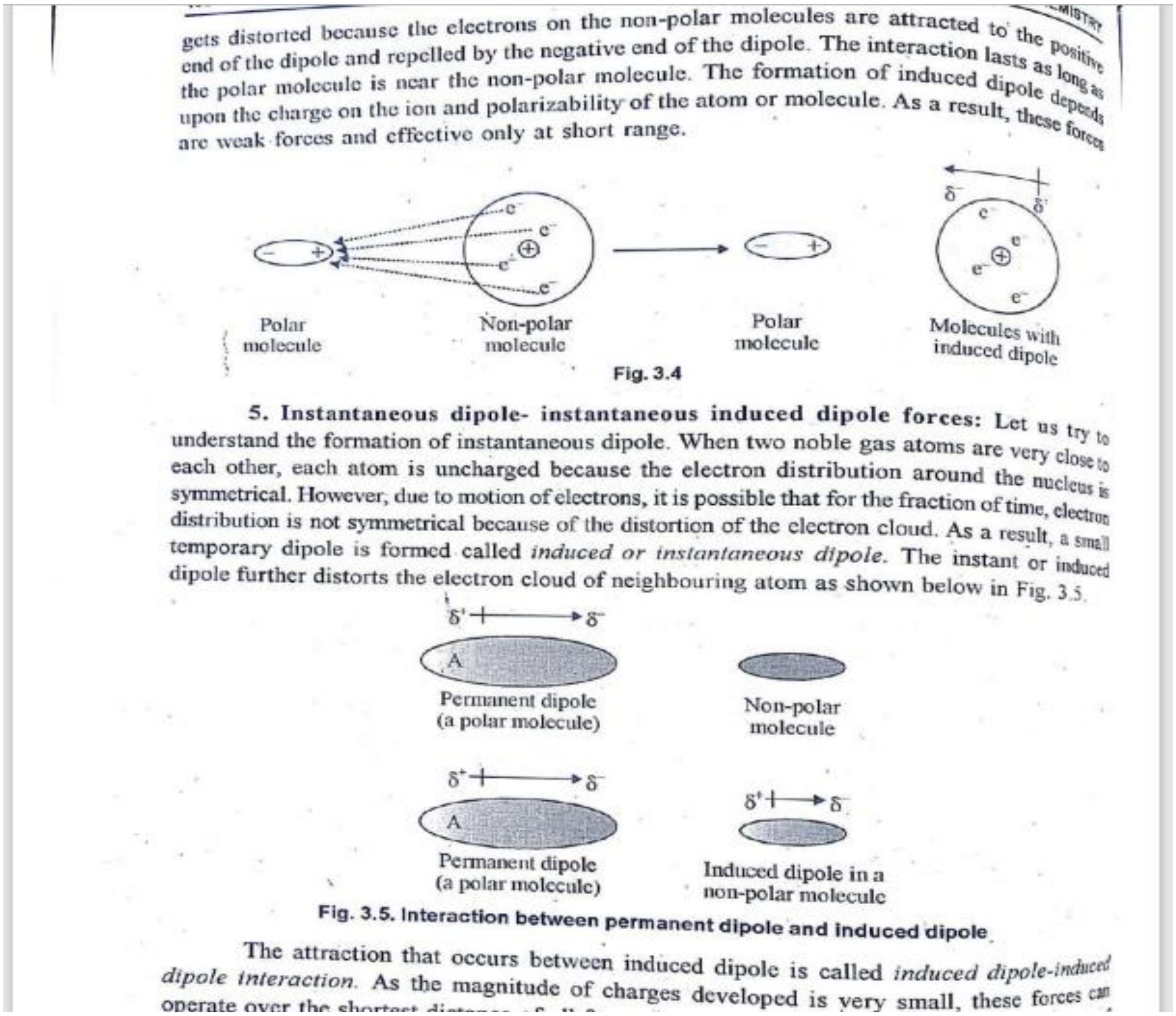


Fig. 3.3

4. Ion-induced dipole interactions: These interactions occur between an ion and the induced dipole, for example dissolving benzene in acetone. This occurs when the ion approaches towards non-polar molecule, the symmetrical distribution of non-polar molecule



gets distorted because the electrons on the non-polar molecules are attracted to the positive end of the dipole and repelled by the negative end of the dipole. The interaction lasts as long as the polar molecule is near the non-polar molecule. The formation of induced dipole depends upon the charge on the ion and polarizability of the atom or molecule. As a result, these forces are weak forces and effective only at short range.

Polar molecule

Non-polar molecule

Polar molecule

Molecules with induced dipole

Fig. 3.4

5. Instantaneous dipole- instantaneous induced dipole forces: Let us try to understand the formation of instantaneous dipole. When two noble gas atoms are very close to each other, each atom is uncharged because the electron distribution around the nucleus is symmetrical. However, due to motion of electrons, it is possible that for the fraction of time, electron distribution is not symmetrical because of the distortion of the electron cloud. As a result, a small temporary dipole is formed called *induced or instantaneous dipole*. The instant or induced dipole further distorts the electron cloud of neighbouring atom as shown below in Fig. 3.5.

Permanent dipole (a polar molecule)

Non-polar molecule

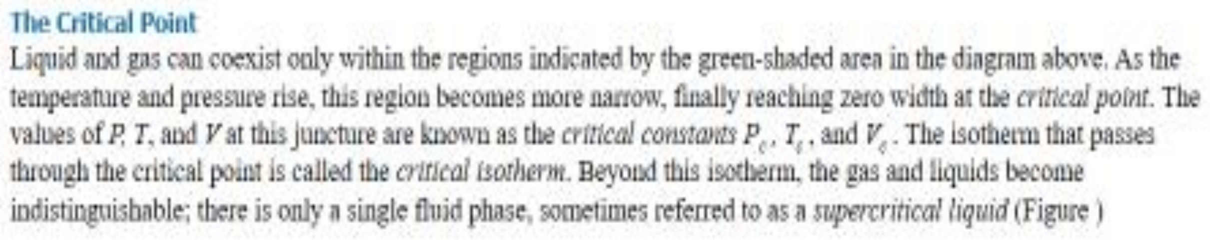
Permanent dipole (a polar molecule)

Induced dipole in a non-polar molecule

Fig. 3.5. Interaction between permanent dipole and induced dipole

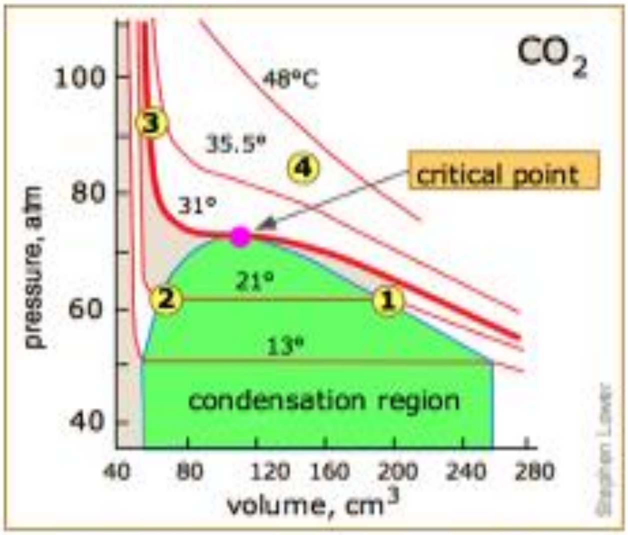
The attraction that occurs between induced dipole is called *induced dipole-induced dipole interaction*. As the magnitude of charges developed is very small, these forces can operate over the shortest

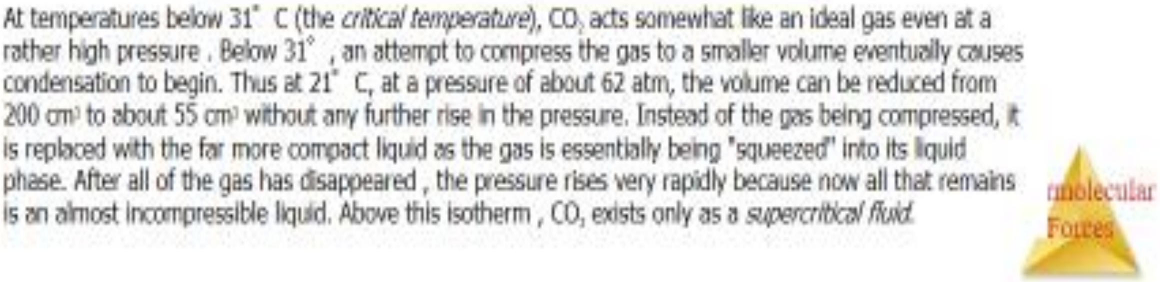
7. Discuss the critical phenomenon of CO_2.



The Critical Point

Liquid and gas can coexist only within the regions indicated by the green-shaded area in the diagram above. As the temperature and pressure rise, this region becomes more narrow, finally reaching zero width at the *critical point*. The values of *P*, *T*, and *V* at this juncture are known as the *critical constants* P_c, T_c, and V_c. The isotherm that passes through the critical point is called the *critical isotherm*. Beyond this isotherm, the gas and liquids become indistinguishable; there is only a single fluid phase, sometimes referred to as a *supercritical liquid* (Figure)





At temperatures below 31° C (the *critical temperature*), CO_2 acts somewhat like an ideal gas even at a rather high pressure . Below 31° , an attempt to compress the gas to a smaller volume eventually causes condensation to begin. Thus at 21° C, at a pressure of about 62 atm, the volume can be reduced from 200 cm^3 to about 55 cm^3 without any further rise in the pressure. Instead of the gas being compressed, it is replaced with the far more compact liquid as the gas is essentially being "squeezed" into its liquid phase. After all of the gas has disappeared , the pressure rises very rapidly because now all that remains is an almost incompressible liquid. Above this isotherm , CO_2 exists only as a *supercritical fluid*.

8. Derive van der waal equation of state.

Ans.

1. Volume correction

The assumption that actual volume of the molecules is negligible, does not introduce any appreciable error at low pressures. At high pressure when the molecules are quite close together, the volume occupied by the molecules themselves becomes considerable fraction of the total volume occupied by the gas.

According to Van der Waal the actual free space available inside the vessel for the movement of the molecules is not V, the volume of the container, but (V–b), where 'b' is the effective volume of the molecules. It can easily be shown that effective volume of molecules in motion is equal to about 4 times the actual volume of molecules at rest. The effective volume (b) is also called *co-volume or excluded volume*.

Let us consider two molecules approaching each other. Let δ and r represent the diameter and the radius of each molecule. The molecules cannot approach more closely than the distance δ as shown in Fig. 3.9. It is because the molecules are impenetrable. It is clear from the figure that within a sphere of radius δ (=$2r$), no volume will be occupied by this pair of molecules. Thus:

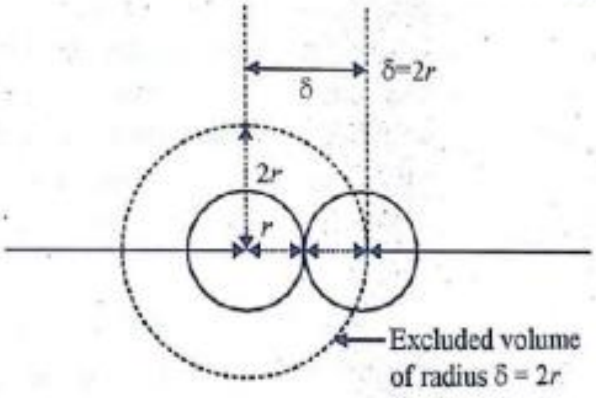


Fig. 3.9 Excluded volume of a pair of molecule

$$\text{The excluded volume per pair of molecules} = \frac{4}{3}\pi(2r)^3 = 8\left(\frac{4}{3}\pi r^3\right)$$

$$\text{So excluded volume for a single molecule} = \frac{8}{2}\left(\frac{4}{3}\pi r^3\right) = 4\ V_m$$

where V_m is the volume occupied by a single molecule.

Thus the excluded volume (b) for a mole of a gas is given as :

$$b = 4\left(\frac{4}{3}\pi r^3\right)\times N \quad = 4\ V_m\ N$$

where N being the Avogadro's number.

Hence, the corrected volume = (V–b)

where b is the volume to be excluded which is four times the actual volume of the molecules and it is a characteristic constant for each gas.

2. Attraction correction – Pressure correction

The assumption that molecules exert no appreciable intermolecular attraction is not justified especially at high pressure when *the molecules are quite close together.*

Consider particles A and B in the gas Fig. 3.10. The net force of intermolecular attraction on particle 'A' situated in the interior of the gas is nil, because it is surrounded by molecules which are equally distributed in opposite directions, thereby the attractions on all sides are mutually cancelled.

However, molecule 'B' just near the boundary which is about to strike the wall, is subjected to a net *inward force of attraction or pull* due to the interior molecules, So, when a molecule is about to strike the wall, this inward pull act, so as to reduce the force exerted by the impact and consequently *the measured pressure P is less than the ideal pressure*, i.e. when no attraction were there. The observed pressure is thus less than that would be expected from the Kinetic theory. This will tend to make PV less than RT and so will tend to cause a negative or under perfect deviation. Hence, a correction term p_a should be added to P to to get ideal pressure.

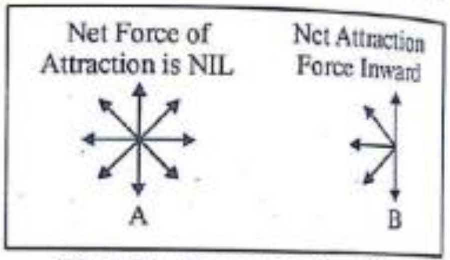


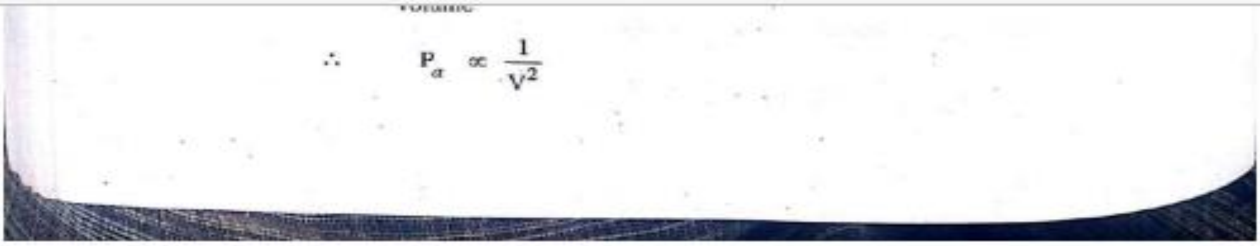
Fig. 3.10. Molecular attraction

$$\text{Ideal pressure} = P + p_a$$

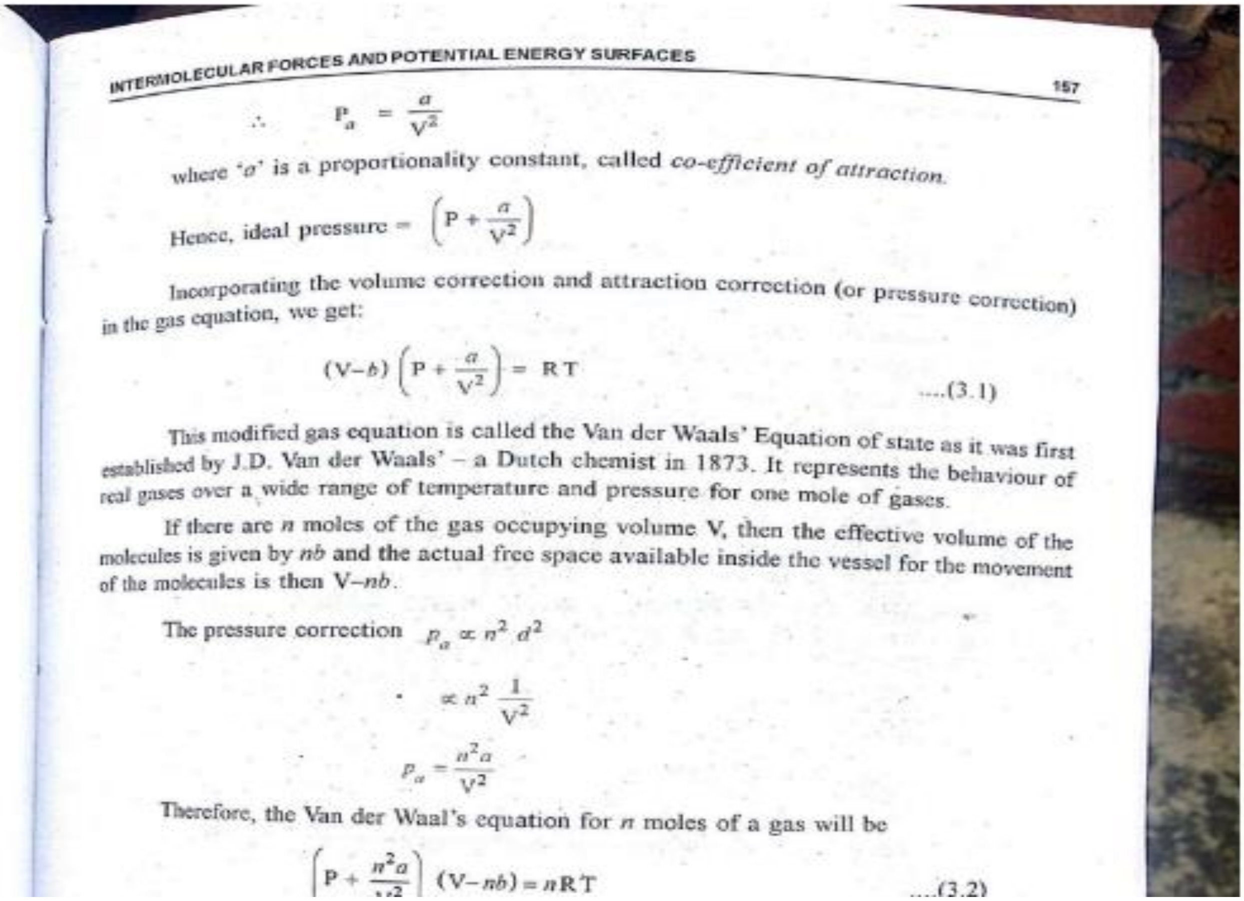
The inward force, p_a exerted on molecules about to strike the walls of the vessel is proportional to:

(i) *The number of molecules striking the wall at any given instant, which is proportional to the density of the gas.*

(ii) *The number of molecules in the interior which are attracting the striking molecules. which is also proportion to the density of the gas.*



$$\therefore \quad P_a \propto \frac{1}{V^2}$$



$$\therefore \quad P_a = \frac{a}{V^2}$$

where 'a' is a proportionality constant, called *co-efficient of attraction.*

Hence, ideal pressure = $\left(P + \frac{a}{V^2}\right)$

Incorporating the volume correction and attraction correction (or pressure correction) in the gas equation, we get:

$$(V-b)\left(P + \frac{a}{V^2}\right) = RT \qquad \text{....(3.1)}$$

This modified gas equation is called the Van der Waals' Equation of state as it was first established by J.D. Van der Waals' – a Dutch chemist in 1873. It represents the behaviour of real gases over a wide range of temperature and pressure for one mole of gases.

If there are n moles of the gas occupying volume V, then the effective volume of the molecules is given by nb and the actual free space available inside the vessel for the movement of the molecules is then $V-nb$.

The pressure correction $p_a \propto n^2 d^2$

$$\propto n^2 \frac{1}{V^2}$$

$$p_a = \frac{n^2 a}{V^2}$$

Therefore, the Van der Waal's equation for n moles of a gas will be

$$\left(P + \frac{n^2 a}{V^2}\right)(V-nb) = nRT \qquad \text{....(3.2)}$$

Chapter-7 (Free Energy Surfaces)

9. Write a short note on entropy.

Ans. Entropy

Entropy is a measure of the disorder of a system. Take your room as an example. Left to itself, your room will increase in entropy (i.e., get messier) if no work (cleaning up) is done to contain the disorder. Work must be done to keep the entropy of the system low. Entropy comes from the second law of thermodynamics, which states that all systems tend to reach a state of equilibrium. The significance of entropy is that when a spontaneous change occurs in a system, it will always be found that if the total entropy change for everything involved is calculated, a positive value will be obtained. Simply, all spontaneous changes in an isolated chemical system occur with an increase in entropy. Entropy, like temperature, pressure, and enthalpy, is also a state property and is represented in the literature by the symbol "**S**". Like enthalpy, you can calculate the change of **S** (ΔS).

$\Delta \mathbf{S} = \mathbf{S}_{\text{final}} - \mathbf{S}_{\text{initial}}$ or $\Delta \mathbf{S} = \mathbf{S}$ (products) - **S** (reactants)

10. Derive Nernst equation.

Ans. Nernst Equation & Equilibrium Constant

Nernst equation is a general equation that relates the Gibbs free energy and cell potential in electrochemistry. It is very helpful in determining cell potential, equilibrium constant etc. It takes into account the values of standard electrode potentials, temperature, activity and the reaction quotient for the calculation of cell potential. For any cell reaction, Gibbs free energy can be related to standard electrode potential as:

$\Delta G = -nFE$

Where,

ΔG= Gibbs free energy,

n = number of electrons transferred in the reaction,

F = Faradays constant (96,500 C/mol)

E= cell potential

Under standard conditions, the above equation can be given as,

$\Delta G^o = -nFE^o$

According to thermodynamics, Gibbs free energy under general conditions can be related to Gibbs free energy under the standard condition and the reaction quotient as:

$\Delta G = \Delta G^o + RT \ln Q$

Where,

Q= reaction quotient

R= universal gas constant

T= temperature in Kelvin

Incorporating the value of ΔG and ΔG^o, from the first two equations, we get:

$$-nFE = -nFE^o + RT \ln Q$$

$$\Rightarrow E = E^o - \frac{RT}{nF} \ln Q$$

Converting natural log to $\log_{10}$,

The above equation is known as the Nernst equation. Here, it relates the reaction quotient and the cell potential.

Special cases of Nernst equation: $\mathbf{E = E^o - (2.303RT/nF)\ \log_{10}Q}$

At standard temperature, T= 298K:

$\mathbf{E = E^o - (0.0592V/n)\ \log_{10}Q}$

At standard temperature T = 298 K, the 2.303RTF

term equals 0.0592 V and Equation

can be rewritten: E=E^o −0.0592 Vnlog10Q

- Under equilibrium condition: As the redox reaction in the cell proceeds, the concentration of reactants decreases while the concentration of products increases. This goes on until equilibrium is achieved. At equilibrium, $\Delta G = 0$. Hence, cell potential, $E = 0$. Thus, the Nernst equation can be modified to:

$$0 = E^\circ - \frac{2.303RT}{nF}\log_{10} K_{eq}$$

$$E^\circ = \frac{2.303RT}{nF}\log_{10} K_{eq}$$

Where,

K_{eq} = equilibrium constant,

F= faradays constant

Thus, the above equation gives us a relation between standard electrode potential of the cell in which the reaction is taking place and the equilibrium constant. For vibrant video lessons, download Byju's -The Learning App. Also, learn and practice questions related to the Nernst equation and equilibrium constant.

11. Discuss Dry corrosion.

Ans. **DRY or CHEMICAL CORROSION**: This type of corrosion is due to the direct chemical attack of metal surfaces by the atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen or anhydrous inorganic liquid, etc. The chemical corrosion is defined as the direct chemical attack of metals by the atmospheric gases present in the environment. Example: (i) Silver materials undergo chemical corrosion by Atmospheric H2S gas . (ii) Iron metal undergo chemical corrosion by HCl gas.

TYPES OF DRY or CHEMICAL CORROSION: 1. Corrosion by Oxygen or Oxidation corrosion 2. Corrosion by Hydrogen 3. Liquid Metal Corrosion

CORROSION BY OXYGEN or OXIDATION CORROSION:

Oxidation corrosion:-

- It is brought about by direct action of oxygen at low (or) high temperatures, usually in the absence of moisture.
- At high temperatures all metals are attacked by oxygen and are oxidized – except noble metals like Ag, Au, and Pt.
- At ordinary temp generally all the metals are slightly attacked. However alkali metals – Li, Na, K, Rb etc. and alkaline earth metals – Be, Ca, Sr etc. are attacked very rapidly and get oxidized readily.

The reactions in the oxidation corrosion are

$$2\,M + n/2\,O_2 \longrightarrow \underset{\text{Metal ions}}{2M^{n+}} + \underset{\text{oxide ions}}{2n\,O^{2-}}$$

$$2\,M \longrightarrow 2\,M^{n+} + 2n\,e^{-}$$

$$n/2\,O_2 + 2n\,e^{-} \longrightarrow nO^{2-}$$

$$2M + n/2\,O_2 \longrightarrow 2M^{n} + 2nO^{2-}$$

12. **Explain WET OR ELECTROCHEMICAL CORROSION**

Electrochemical corrosion involves:

The formation of anodic and cathodic areas or parts in contact with each other

ii) Presence of a conducting medium

iii) Corrosion of anodic areas only and

iv) Formation of corrosion product somewhere between anodic and cathodic areas. This involves flow of electron-current between the anodic and cathodic areas. At anodic area oxidation reaction takes place (liberation of free electron), so anodic metal is destroyed by either dissolving or assuming combined state (such as oxide, etc.). Hence corrosion always occurs at anodic areas.

Evolution of hydrogen: occurs

- In acidic environments.
- For eg in the corrosion of iron metal the anodic reaction is dissolution of Fe as ferrous ions with liberation of e^-s.

  $Fe \text{ ------> } Fe^{+2} + 2e^-$ oxidation.

- These electrons flow through the metal from anode to cathode (acidic region) where H^+ ions are eliminated as H_2 gas.

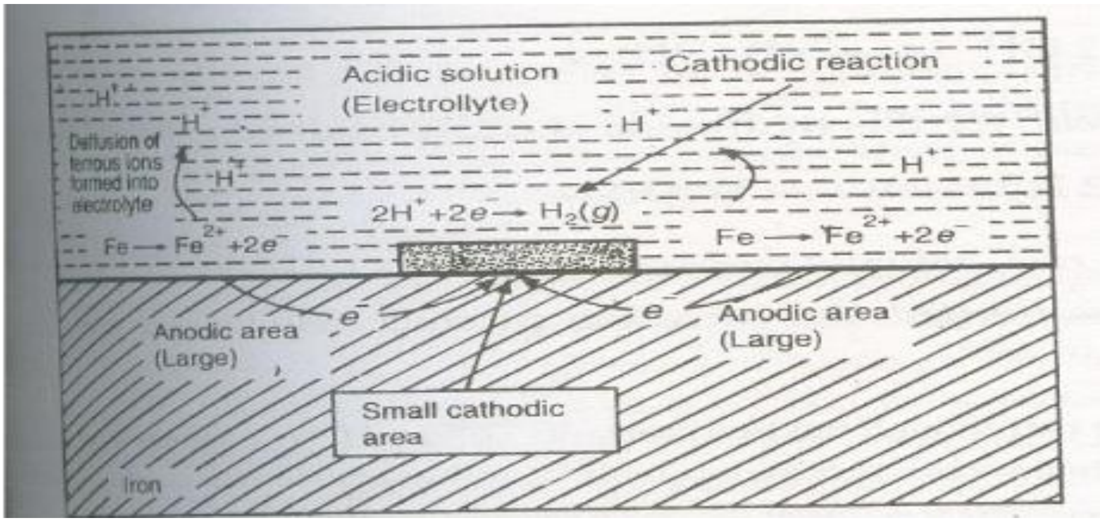
  $2H^+ + 2e^- \text{ ------> } H_2$ reduction.

- The overall reaction is

  $Fe + 2H^+ \text{ ------> } Fe^{2+} + H_2$

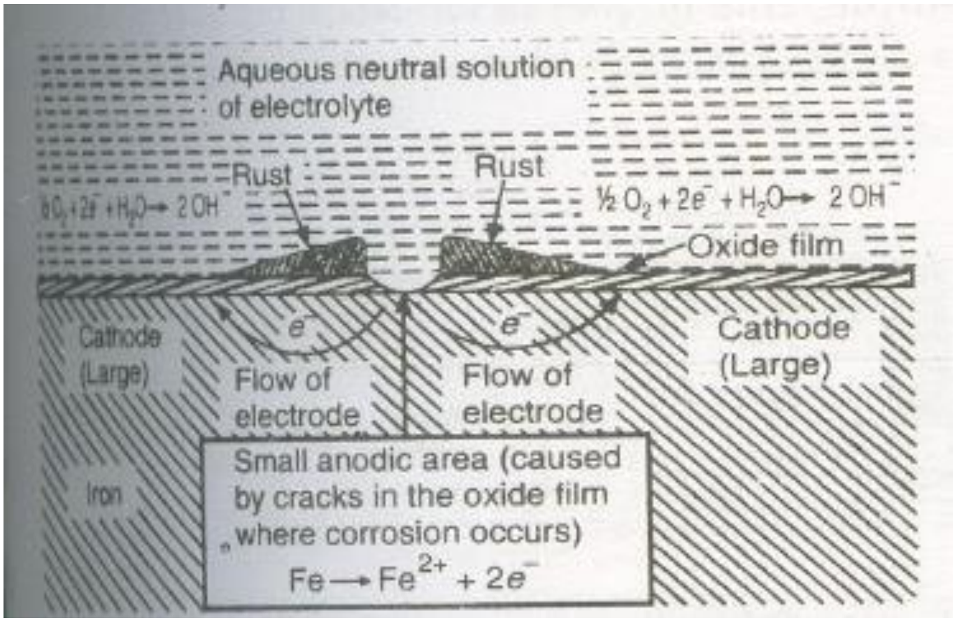
- This type of corrosion causes "displacement of hydrogen ions from the acidic solution by metal ions.

- In hydrogen evolution type corrosion, the anodes are very large areas, where as cathodes are small areas.
- All metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.



13. Fig: Mechanism of wet corrosion by hydrogen evolution

Absorption of oxygen type corrosion: Rusting of Fe in neutral aqueous solution of electrolytes like NaCl in the presence of atmospheric oxygen is a common example of this type of corrosion.



14.

15. Fig: Mechanism of wet corrosion by absorption of oxygen

16.

- The surface of iron will be usually coated with a thin film of iron oxide. However if this oxide film develops some cracks, anodic areas are created on the surface.
- While pure metal parts act as cathode.
- Thus anodic areas are very small surface parts.
- The rest of the surface of the metal forms cathodes.
- Thus at the anodic part iron metal dissolves as Fe^{+2} ions with the liberation of e^- s.

$$Fe \text{ ------> } Fe^{+2} + 2e^-$$

- The liberated e^- s flow from anodic to cathodic areas through iron metal during which they interact with dissolved oxygen and moisture.

$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$

- The Fe^{+2} ions and OH^- ions diffuse and form ferrous hydroxide precipitate when they meet with each other

$Fe^{+2} + 2OH^-$ ------> $Fe(OH)_2$

- If enough O_2 is present $Fe(OH)_2$ is easily oxidized to $Fe(OH)_3$ (ferric hydroxide)

$4 Fe(OH)_2 + O_2 + 2H_2O$ ------> $4Fe(OH)_3$

The product called yellow rust actually corresponds to $Fe(OH)_3.H_2O$.

- If the supply of O_2 is limited, the corrosion product may be even black anhydrous magnetite Fe_3O_4.

17. Explain Lewis concept of acids and bases.

Ans. Lewis Acids and Bases

In the Brønsted-Lowry definition of acids and bases, a base is defined as a compound that can accept a proton. However, *how* does it accept the proton?

One feature that Brønsted-Lowry bases have in common with each other is that they have an unshared pair of electrons. When a hydronium ion comes wandering by the molecule, sometimes the lone pairs will reach out and grab it.

A Lewis base is a compound that donates an electron pair to another compound (the ammonia in our example). A Lewis acid is a compound that accepts an electron pair (the H^+ ion in our example).

18. Discuss Zeolite process

Answer: Zeolites are naturally occuring hydrated sodium aluminium silicate, Na_2O. Al_2O . x SiO_2 yH_2O where x = 2 to 10 and y = 2 to 6. The synthetic form of zeolite is known as permutit. Synthetic zeolite is represented by Na_2Ze. The sodium ions which are loosely held in Na_2Ze are replaced by Ca^{2+} and Mg^{2+} ions present in the water. Natural zeolites are non-porous.

Synthetic zeolites are porous and gelly structure. They are prepared by heating together china clay, feldspar and soda ash. These zeolites are higher exchange capacity per unit weight than natural zeolites.

Process

In this process, the hard water is passed through a bed of sodium zeolite (Na_2 Ze). The hardness causing ions (Ca^{2+}, Mg^{2+}) in hard water is replaced by loosely held sodium ions in zeolite bed. The outgoing soft water contains only sodium ions.

$$Na_2Ze + Ca(HCO_3)_2 \rightarrow CaZe + 2NaHCO_3$$

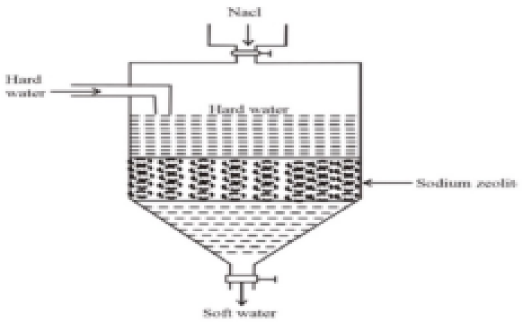
$$Na_2Ze + Mg(HCO_3)_2 \rightarrow MgZe + 2NaHCO_3$$

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

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

$$Na_2Ze + CaSO_4 \rightarrow CaZe + Na_2SO_4$$

$$Na_2Ze + MgSO_4 \rightarrow MgZe + Na_2SO_4$$



19.