Corrosion And Its Prevention

Objective

- What is corrosion
- Classification of corrosion
- Mechanism of corrosion
- Types of corrosion
- Corrosion prevention methods





Corrosion and Degradation of Materials











Engineer finds corrosion in collapsed bridge at North Carolina speedway (2000)





Introduction

- Corrosion is defined as unintentional destruction of a solid body by chemical or electrochemical reactions starting from the surface.
- Non-Metals corrode by chemical reactions & metals mostly by electrochemical reactions.
- Metals are at high energy levels & hence there is natural tendency to go to the low energy state i.e. they try to form oxides, hydroxides, carbonates, sulphides etc. depending on the type of environment to which they are exposed.

Chemical vs. Electrochemical Reactions

- Chemical reactions are those in which elements are added or removed from a chemical species
- Electrochemical reactions are chemical reactions in which not only elements may be added or removed from a chemical species but at least one of the species undergoes a change in the number of valance electron
- Corrosion processes are electrochemical in nature

Classification of corrosion

• Dry corrosion

• Wet corrosion

Dry corrosion

- Dry corrosion occurs when the metals are exposed to gaseous environment
- The extent of corrosion & protective values depends on the following factors
- 1. Chemical affinity between the environment & the metal.
- 2. Protective value of film.
- 3. Nature of film formed.
- 4. Adhesion between the film & the metal surface.
- 5. For non ferrous film, the extent of corrosion depends on the electronic & ionic conductivities of the film.

Pilling & Bedworth Rule

• This rules gives the idea about the nature of the film formed i.e. whether the film is porous or nonporous.

Volume of oxide

• Pilling & Bedworth Ratio =

Volume of equivalent amount of metal consumed during oxidation

= Md/mD

Formation & Growth Of Film

- The formation & growth of films occur by three successive stages
- 1. Adsorption
- 2. Chemisorptions
- 3. Growth of film
- 3.1 Growth of non porous film
- 3.2 Growth of porous film

Wet corrosion

- Wet corrosion occur when a metal or an alloy comes in contact with an aqueous solution of salt, acid or alkali by an electrochemical type of reaction.
- When a metal is immersed in an aqueous electrolyte, it dissolve / dissociate into metal ion + electron.
- This tendency of metal is called as electrolytic pressure or solution pressure (p)
- The dissolved ion from the solution tend to deposit on the immersed metal surface& oppose the solution pressure of metal. This tendency is called as osmotic pressure of metal ion (p)
- When these forces become equal, equilibrium is reached and under this condition, a definite number of electrons accumulate on the metal surface & a definite potential will be developed on the metal piece.

	Oxidation (corrosion) reaction	Electrode potential, E° (volts vs. standard hydrogen electrode)
+	$Au \rightarrow Au^{3+} + 3e^{-}$	+ 1.498
(10.51) (1.5 (1.5 (1.5 (1.5 (1.5 (1.5 (1.5 (1.5	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	+ 1.229
terminal and the second s	$Pt \rightarrow Pt^{2+} + 2e^{-}$	+1.200
More cathodic	$Ag \rightarrow Ag^+ + e^-$	+0.799
	$2Hg \rightarrow Hg_2^{2+} + 2e^-$	+0.788
(less tendency to corrode)	$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$	+0.771
	$4(OH)^- \rightarrow O_2 + 2H_2O + 4e^-$	+0.401
	$Cu \rightarrow Cu^{2+} + 2e^{-}$	+0.337
	$Sn^{2+} \rightarrow Sn^{4+} + 2e^{-}$	+0.150
e print de la constitue de la c	$Pb \rightarrow Pb^{2+} + 2e^{-}$ Sn \rightarrow Sn ²⁺ + 2e ⁻	- 0.126 - 0.136
	$Ni \rightarrow Ni^{2+} + 2e^{-}$	- 0.250
Moro gnodio	$Co \rightarrow Co^{2+} + 2e^{-}$	-0.277
More dilodic	$Cd \rightarrow Cd^{2+} + 2e^{-}$	-0.403
(greater tendency to corrode)	$Fe \rightarrow Fe^{2+} + 2e^{-}$	-0.440
	$Cr \rightarrow Cr^{3+} + 3e^{-}$	-0.744
	$Zn \rightarrow Zn^{2+} + 2e^{-}$	-0.763
	$AI \rightarrow AI^{3+} + 3e^{-}$	- 1.662
	$Mg \rightarrow Mg^{2+} + 2e^{-}$	- 2.363
*	$Na \rightarrow Na^+ + e^-$	-2./14

TABLE 12.1 Standard Electrode Potentials at 25°C*

* Reactions are written as anodic half-cells. The more negative the half-cell reaction, the more anodic the reaction is and the greater the tendency for corrosion or oxidation to occur.

	Galvanic Scale		
	or metals in Sea Water		
	NOTE: Potentials vary with the actu	ıal	
composition of the material.			
	Material	Potential	
(Magnesium and its Alloys	1.50	
s Noble	Zinc	-1.03	
	Aluminum and its Alloys	-0.75	
	Cast Iron	0.61	
es	Carbon Steel	-0.61	
C	Type 430 Stainless (Active)	0.57	
ive	Type 304 Stainless (Active)	0.53	
\ct	Type 410 Stainless (Active)	0.52	
0	Silicon Bronze	0.40	
or	Copper	-0.36	
Σ	Yellow Brass—268	0.36	
1	Red Brass—230	0.33	
Τ	Aluminum Bronze	0.32	
	Tin Bronze—(G & M)	-0.31	
	Admiralty Brass	0.29	
+	Copper-Nickel		
	90–10	0.28	
ble	80-20		
Vol	70–30	-0.25	
r l	Nickel—200		
6	Silver Solder	0.20	
siv	Inconel—600		
as	Monel		
D	Stainless Steel (Passive)		
ore	Silver/Silver Chloride half cell (Refere	nce) 0.00	
M	Graphite (note sign chan	nge) $+0.20$	

What is the voltage difference between Zinc (Zn) and Copper (Cu)?

An. 0.67v

What is more noble than Stainless Steel (Passive)?

An. Graphite

Mechanism Of Wet Corrosion

• The reaction at anode is always oxidation reaction & is associated with the dissolution of metal i.e.

Metal — Metal ions + electron

- The reaction at cathode is always a reduction reaction with no corrosion of cathode & varies depending on the nature of electrolyte in contact
- 1. Hydrogen evolution :
- 2. Oxygen absorption :

1.Hydrogen evolution :

- The hydrogen evolution occurs at the cathode in concentrated acidic environment (pH < 4) usually iron surface is covered with oxide at least at few points or it may difference in hydrogen over potential from point to point
- Due to this some areas act as cathode with respect to other areas which behaves as anode of the cell & galvanic corrosion occurs.
- At the anode : Fe Fe⁺⁺ + 2e
- At the cathode : $2H^+ + 2e = H_2$
- it is clear from the reaction that hydrogen evolution type of corrosion occurs by simple displacement of hydrogen ion from acidic solution by metal ion.

continue



2. Oxygen Absorption

- Oxygen absorption mechanism of corrosion occurs in mild acidic or alkaline environment (pH > 4)
- The above process for the rusting of iron taking an electrolyte of aqueous solution of sodium chloride.
- The area which are not covered with the oxide become anodic with respect to the areas covered with the oxide which become cathodic & corrosion occurs by the following reactions :
- Reaction at anode :Fe \rightarrow Fe⁺⁺ + 2e & Fe⁺⁺ + 2Cl⁻ \rightarrow FeCl₂
- Reaction at cathode : $4e + O_2 + 2H_2O \rightarrow 4OH^-$
- $OH^- + Na + \longrightarrow NaOH$
- Both the anodic product FeCl2 & cathodic product NaOH are soluble in water & diffuse towards each other.

continue....

- When both meet ferrous hydroxide is formed. In the presence sufficient dissolved oxygen, ferrous hydroxide is further oxidized to ferric hydroxide which has very little solubility in water & precipitate out as yellow rust.
- It is clear that there is no concentration polarization at both the electrode.

of sodium chloride.

firm taking an electrolyte of aqueous



Fig. 6.11 : Oxygen absorption mechanism of corrosion. areas which are not covered with the oxide become anodic with respect to

Types Of Corrosion

- General corrosion
- Pitting corrosion
- Crevice corrosion
- Intergranular corrosion
- Stress corrosion cracking
- Erosion corrosion
- Cavitation corrosion
- Corrosion fatigue
- Hydrogen blistering
- High temperature corrosion

• General / Uniform Corrosion



- Corrosion proceeds at the same rate throughout the area exposed to the environment & there is no clearly defined anode & cathode areas.
- the extent of corrosion can be expressed by loss in weight per unit area or by average penetration depth

Pitting Corrosion





 Pitting corrosion is a localized accelerated corrosion resulting in the formation of cavities around which the metal is relatively unattacked.

- Small anodic area & large cathodic areas results in high anodic current density leading to rapid corrosion of small anodic areas forming pit or pinholes
- This results in rapid perforation of metal sharply reducing the mechanical properties of of the component.
- Pitting has more effect on fatigue strength
- Pitting corrosion can occur under following situations:
- 1. Due to break in the protective coating
- 2. Due to destruction of passive layer at few points under certain environmental conditions.
- 3. Differential aeration corrosion may lead to pitting corrosion

continue...

 Crevice corrosion, corrosion take place in crevices bcz solutions retained at this place and takes longer time to dry out. When this occurs, the severity of attack is more severe at crevices. Crevices are formed bcz of the metal contact with another piece of the same or other metal or with a nonmetallic material. Corrosion in crevice is due to deficiency of O2, Acidity changes,

- Crevice Corrosion
 - narrow crevice filled with ionized solution
 - Oxygen-rich on the outside, oxygen-poor on the inside
 - metals oxidize with salt anions FeCl₂ and pH rises in cathodic zone
 - H⁺ may destroy passivity

Intergranular Corrosion



 This types of corrosion occurs at the grain boundaries or at the region adjacent to the grain boundaries due to precipitation of some phase at the grain boundaries

- The precipitate phase makes the material sensitive to corrosion
- The grain boundary phase or the region adjacent to grain boundary become anodic & get preferentially corroded
- This type of corrosion can occur even without the precipitation of phase at the grain boundaries, this is because the grain boundary regions being high energy region will get preferentially corroded due to their low electrode potential compared to the electrode potential of grain
- E.g. Corrosion of Austenitic stainless steels due to precipitation of complex chromium carbide along grain boundaries.
- Weld decay.

Stress corrosion cracking



- This type of corrosion occurs due to presence of stresses in the material
- The stresses area become anodic with respect to the other areas & get corroded by forming stress cell.
- It has been observed that if the stresses are tensile, it leads to cracking of the material in due course of time when exposed to certain environmental conditions & hence the phenomenon is known as SCC.
- The static tensile stress present in the material may be residual (internal) or applied (external).
- Internal stresses are developed due to cold working processes, or due to rapid cooling, poor design, precipitation of second phase.
- External stresses are produced due to application of external load on the components.

Erosion – Corrosion



- Erosion corrosion type of corrosion occurs by the simultaneous effect of corrosion & erosion produced by the turbulent flow of electrolyte, & also by the rubbing action of solid particle over a metal surface.
- This type of corrosion can occur in any metal & alloy.
- In many cases, it has been observed that the damage to the metal is due to the breaking of protective coating of corrosion product & coating is not get repaired due to turbulence flow of electrolyte.
- This type of corrosion is usually occurs in the regions where the flow of electrolyte is disturbed e.g. bend in pipes, condenser tube, valve seat in in water fitting etc.

Corrosion prevention Methods

Inhibitors

- Inhibitors is a substance which effectively decreases the corrosion rate of a metal when added in small amount to the corrosive environment.
- These substances control the anodic or cathodic reactions reducing the corrosion of metals.
- 1. Anodic Inhibitors
- 2. Cathodic Inhibitors

Anodic Inhibitors

- Anodic inhibitors when added to the electrolyte combine with the newly form metal ions at the anode & form a precipitate.
- This precipitate deposit on the anode surface forming a protective layer which stops or reduce the corrosion
- Thus the local anode areas get polarized i.e. increase In potential occurs at these areas.
- Anodic inhibitors work effectively when they are added in sufficient amount.

Cathodic Inhibitors

- Cathodic inhibitors reduce the corrosion by stopping the cathodic reaction
- In acidic electrolyte, cathodic reactions is of hydrogen evolution type
- In such case, corrosion can be reduced by reducing the diffusion of hydrogen ion to the cathode or by increasing the over potential of hydrogen.
- The diffusion of hydrogen ion is reduced by using certain organic compounds.
- hydrogen over potential is increased by adding salts of As, Sb & Bi.

Protective Coatings / Wrapping

- Provide barrier between metal and environment.
- Coatings may act as sacrificial anode or release substance that inhibit corrosive attack on substrate.
- Metal coatings :
 - Noble silver, copper, nickel, Cr, Sn, Pb on steel.
 Should be free of pores/discontinuity coz creates small anode-large cathode leading to rapid attack at the damaged areas.
 - Sacrificial Zn, Al, Cd on steel. Exposed substrate will be cathodic & will be protected.
 - Application hot dipping, flame spraying, cladding, electroplating, vapor deposition, etc.

Surface modification – to structure or composition by use of directed energy or particle beams. E.g ion implantation and laser processing.

- Inorganic coating : cement coatings, glass coatings, ceramic coatings, chemical conversion coatings.
- Chemical conversion anodizing, phosphatizing, oxide coating, chromate.
- Organic coating : paints, lacquers, varnishes. Coating liquid generally consists of solvent, resin and pigment. The resin provides chemical and corrosion resistance, and pigments may also have corrosion inhibition functions.
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- Paints, pigments are also widely used for the protection of metallic component.
- 3. Anodized Coating (Chemical Conversion Coating)
- In atmospheric conditions Al, Al alloys, Ti, Ti alloys form a thin film of oxide on their surfaces.
- This thin film of oxide provides a good resistance to further corrosion of the above materials.
- However, under the normal atmosphere conditions the thickness of oxide layer is very small & does not protect the metal from corrosion under severe condition of exposure.
- to make this materials highly corrosion resistant, the naturally existing film of oxide is increased in thickness by electrolysis.

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- The electrolysis process used for increasing thickness of oxide film is called anodizing.
- The metal is not coated by any other material as is done in the previous method, but the surface of metal is converted into oxide & hence they can called as chemical conversion coating.

Anodic Protection (Cathodic coating)

- Here the metal get protect anodic by the application of coating of cathodic material.
- Coating of Ni & Cr on Fe & steel, Coating of Au, Ag on brasses or bronzes.
- When the coating is dense, non porous & continuous, the electrolyte does not come in contact with the component & hence the component does not corrode.

Cathodic protection (Anodic Coating)

- Here the metal get protect cathode by the application of coating of anodic material.
- Coating of Zn & Cd on iron & steel
- When the coating is dense, nonporous & continuous, the electrolyte does not come in contact with the component & hence the component does not corrode.
- The coating metal completely separate the electrolyte from metal.
- Such coating completely prevent the component from corrosion even in the presence of discontinuous or breaks.



DESIGN for Corrosion



⁽i) Use wear plates to minimize corrosive wear

- Avoid sharp corners paint tends to be thinner at sharp corners and often starts to fail.
- Provide for easy drainage (esp tanks) avoid remaining liquids collect at bottom. E.g steel is resistant against concentrated sulfuric acid. But if remaining liquid is exposed to air, acid tend to absorb moisture, resulting in dilution and rapid attack occurs.
- Avoid hot spots during heat transfer operations localized heating and high corrosion rates. Hot spots also tend to produce stresses – SCC failures.
- Design to exclude air except for active–passive metals and alloys coz they require O_2 for protective films.
- Most general rule : AVOID HETEROGENEITY!!!

Intermolecular Forces and Potential Energy Surfaces

Different States of matter



Types of Forces of Interactions

Intermolecular forces: Interactions between molecules. Intramolecular forces: Within the same molecule.

Intramolecular forces are also of three types:

- 1. Ion-ion interactions (ionic bond)
- 2. Covalent interactions (Covalent bond)
- 3. Co-ordinate covalent interactions (co-ordinate covalent bond)

Types of Intermolecular Forces

- 1. Ion-Dipole interactions
- 2. Ion-Induced Dipole Interactions
- 3. Dipole-Dipole Interactions
- 4. H-Bonding

5.Instantaneous dipole-Induced Instantaneous dipole Vander Waals Forces (London or Dispersion Forces)

Ion-Dipole interactions

Ion-Dipole Forces

Attractive forces between an ion and a polar molecule



Ion-Dipole interactions

• Ion-Dipole interactions: Forces between ion and dipole



Ion-Dipole interactions



Ion-Induced Dipole Interactions

 Ion-Induced Dipole Interactions: Forces between ion and induced dipole



Permanent Dipole

 All polar molecules have permanent dipoles due to electronegativity difference of bonded atoms



Dipole-Dipole Interactions

Dipole-Dipole Interactions: Forces between opposite dipole of polar molecules.



Dipole-Dipole Interactions



Effect of Dipole-Dipole Interactions on boiling points

- CO and N₂ are both diatomic molecules with masses of about 28 amu. Since CO is a polar molecule, it experiences dipole-dipole attractions.
- Whereas N₂ is non polar, its molecules cannot exhibit dipoledipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between non polar N₂ molecules, so CO is expected to have the higher boiling point.
- Similar ICI and Br₂ have similar masses (~160 amu). ICI is polar and thus also exhibits dipole-dipole attractions;
- Br₂ is non polar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICI will have the higher boiling point.

Hydrogen-Bonding

- Hydrogen-Bonding: Hydrogen bonding is a dipole-dipole attractive force between two polar molecules, containing a hydrogen atom covalently bonded to an atom of F, O or N.
- This attraction between hydrogen and electron negative
 O, F or N element is called Hydrogen Bond.



Effects of Hydrogen Bonding

- Nitrosyl fluoride (ONF, molecular mass 49 amu) is a gas at room temperature. Water (H₂O, molecular mass 18 amu) is a liquid, even though it has a lower molecular mass. Both molecules have about the same shape and ONF is the heavier and larger molecule.
- Molecules with F-H, O-H, or N-H moieties are very strongly attracted to similar moieties in nearby molecules, a particularly strong type of dipoledipole attraction called hydrogen bonding.



Vander Waals Forces

The electrons of an atom or molecule are in constant motion at any moment in time, an atom or molecule can develop a temporary, **instantaneous dipole** if its electrons are distributed asymmetrically.

The presence of this dipole can, in turn, distort the electrons of a neighboring atom or molecule, producing an **induced dipole**.



Effect of Shape of molecule on strength of Forces

- The shapes of molecules also affect the magnitudes of the dispersion forces between them.
- For example, boiling points for the isomers *n*-pentane, isopentane, and neopentane are 36 °C, 27 °C, and 9.5 °C, respectively.
- This is because the surface area decreases with branching of the chain from
- *n*-pentane to isopentane and for neopentane.



Effect of strength of forces on physical state

- The Vander Waals forces are week forces and the strength depends on mass and shape of the molecule.
- Generally larger and heavier atoms and molecules exhibit stronger dispersion forces than do smaller and lighter atoms and molecules.
- F₂ and Cl₂ are gases at room temperature (Due to weaker attractive forces); Br₂ is a liquid, and l₂ is a solid (Due to stronger attractive forces).
- Trends in observed melting and boiling points for the halogens clearly demonstrate this effect.

Trends in melting points of Halogen Family

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F ₂	38 g/mol	72 pm	53 K	85 K
chlorine, Cl ₂	71 g/mol	99 pm	172 K	238 K
bromine, Br ₂	160 g/mol	114 pm	266 K	332 K
iodine, I ₂	254 g/mol	133 pm	387 K	457 K
astatine, At ₂	420 g/mol	150 pm	575 K	610 K

Melting and Boiling points

The relative magnitude of these forces can also be used to explain trends in melting points and boiling points.

It must be remembered that both melting point and boiling point tend to increase with increasing molar mass, all other factors being equal.

Compd	Mol. Wt.	Boil Point
N ₂	28	-196 °C
co	28	-192 °C
Br ₂	160	59 °C
ICI	162	97 °C

Ion-Ion Interactions (Ionic bond)

Na⁺ — Cl⁻ in salt. These are the strongest forces. Lead to solids with high melting temperatures. NaCl, mp = 800 °C



Metallic Bonding



Strength of Intermolecular Forces

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Nonbonding (Inte	ermolecular)			
Ion-dipole	••••••	Ion charge- dipole charge	40-600	Na+·····O
H bond –	δ ⁻ δ ⁺ δ ⁻ -A—H······:B-	Polar bond to H– dipole charge (high EN of N, O,	10-40 , F)	:Ö—Н;Ö—Н Н Н
Dipole-dipole	_	Dipole charges	5-25	I-CI
Ion-induced dipole	•••••	Ion charge- polarizable e ⁻ cloud	3-15	Fe ²⁺ O ₂
Dipole–induced dipole	9	Dipole charge- polarizable e ⁻ cloud	2-10	H—CI····CI—CI
Dispersion (London)		Polarizable e ⁻ clouds	0.05-40	F-FF-F

Kinetic Molecular Theory Deductions

Postulates

Evidence/deduction

 Gases are tiny molecules in mostly empty space. 	The compressibility of gases.
2. There are no attractive forces between molecules.	Gases do not clump.
3. The molecules move in constant, rapid, random, straight-line motion.	Gases mix rapidly.
4. The molecules collide classically with container walls and one another.	Gases exert pressure that does not diminish over time.
5. The average kinetic energy of the molecules is proportional to the Kelvin temperature of the sample.	Charles' Law

Features of gases

- Gases are always miscible
- Gases are compressible
- Gases exert pressure
- Gases are mostly nothing: less than 0.1 % of the volume is occupied by molecules (contrast 70 % for solids and liquids)
 - The ideal gas law assumes molecules occupy zero percent

Diffusion: mixing of gases Effusion: escape through a small opening



The four variables

- Pressure (P)
- Volume (V)
- Temperature (T in Kelvin)
- Number of molecules (n in moles)

Temperature

• Always use absolute temperature (Kelvin) when working with gases.


- **Boyle's Law:** Its state that at constant pressure the volume of a given mass of gas is inversely proportional to its partial pressure.
- Mathematically, $V \alpha 1/P$ or PV = K (constant)

Therefore $P_1V_1 = P_2V_2$







Molar Volume at STP



Charle's Law

- Charle's Law: Its state that at constant pressure the volume of a given mass of gas is directly proportional to absolute temperature.
- Mathematically
 - $V \alpha T$ At constant pressure



V/T = constant or

 $V_{1}/T_{1} = V_{2}/T_{2}$





Charles' Law

• Relationship between volume and temperature of gases.



Avogadro's Law

- Pressure and temperature constant
- Increase the amount, the volume increases



Avogadro's Principle

- Equal volumes of gases contain equal numbers of moles
 - at constant temp & pressure
 - true for any ideal gas



Mathematical form of Avogadro's Law

- The volume of an ideal gas varies directly with its molar amount at constant T and P
- Vαn
- V/n = constant
- The same volume of any gas contains the same number of moles at constant T,P
- The standard molar volume at 273 K and 1 atm is
 22.414 L

Volume of gas at STP

- Standard conditions of pressure and temperature
- T = 0 °C (273 K)
- Pressure: 1 atm
- PV = nR*T*
- V = 1mol(0.0821 L*atm/K*mol)(273 K)/(1 atm)
- V = 22.4 L
- This means that equal volumes of gases under identical conditions of temperature and pressure contain equal number of molecules

Molar volume of Gases

- The standard molar volume of 22.41 L can be compared with the experimental values of common real gases
- Agreement shows that these ideal gas laws can be widely applied for real gases





Combining all gas laws



Ideal Gas Law

PV = nRT

- UNIVERSAL GAS CONSTANT
 - R=0.08206 L·atm/mol·K
 - R=8.315 dm³·k Pa/mol·K

Dalton's Law of Partial Pressures

The total pressure of a mixture of gases

equals the sum of the partial pressures

of the individual gases.



 $P_{total} = P_1 + P_2 + \dots$

Dalton's Law of Partial Pressures



The Ideal gas

- The ideal gas is defined as follows
 - Interactions between molecules are nonexistent
 - Volume occupied by molecules is zero

Deviations from Ideal Behavior of Gases

- Deviation from ideal behavior is large at high pressure and low temperature
- At lower pressures and high temperatures, the deviation from ideal behavior is typically small, and the ideal gas law can be used to predict behavior with little error.



Deviation from ideal behavior as a function of temperature

 As temperature is decreased below a critical value, the deviation from ideal gas behavior becomes severe, because the gas CONDENSES to become a LIQUID.



Effect of intermolecular attractions on on gas pressure



Effect of molecular volume on volume of gas



free volume ≈

Vander Waals Equation

- Correction on pressure
- P_{obs} = observed pressure
- P' = pressure expected from the ideal

gas law

- $P_{ideal \ pressure} = P' + P_a$
- P_a = the inward force exerted on molecules about to strike the walls of container
- (Correction Factor) $p = an^2/v^2$

Vander Waals Equation

- Correct for the volume:
 - The actual volume of a real gas is
 - V nb
 - V = volume of the container
 - n = # moles of gas particles
 - b = constant, determined using experimental results

Real Gases: Vander Waal's equation

 $(P + an^2/V^2)(V-nb) = n RT$

an²/V² corrects for intermolecular attractions

nb corrects for the real volume of molecules

Isotherms for Carbon Dioxide

- The liquefaction of a gas takes place when the intermolecular forces of attraction become high so that they bind the gas molecules together to form the liquid state.
- The intermolecular forces of attraction can be increased either by increasing the pressure so that the molecules come close together or by cooling the gas so that the kinetic energy of the molecules decreases and they become slower.
- The plots showing the effect of pressure on the volume of CO₂ at different constant temperatures are called isotherms.

Isotherms for Carbon Dioxide

- At the lowest temperature i. e. 13.1°C, at low pressure, CO₂ exist as a gas, as shown at the point A.
- As the pressure is increased, the volume of the gas decreases along the curve.
- The point at which liquefaction of the gas starts, volume decreases rapidly liquid has much less volume than the gas.
- Once the liquefaction is complete, the increase in pressure has very little effect upon volume because liquids are very little compressible.



Isotherms for Carbon Dioxide

- As the temperature is increased, horizontal portion becomes smaller and smaller and at 30.98°C, it is reduced to a point E.
- Above 30.98°C, the gas cannot be liquefied at all, however high pressure may be applied. Thus 30.98°C is the critical temperature.
- Critical Temperature: The critical temperature is the temperature above which gas cannot be liquefied even so high pressure may be applied.





- I. Introduction
 - **A. Spectroscopy** is the study of the interaction of matter with the electromagnetic spectrum
 - 1. Electromagnetic radiation displays the properties of both particles and waves
 - 2. The particle component is called a *photon*
 - 3. The energy (E) component of a photon is proportional to the frequency. Where **h** is Planck's constant and v is the frequency in Hertz (cycles per second)

E = hv

 The term "photon" is implied to mean a small, massless particle that contains a small wave-packet of EM radiation/light – we will use this terminology in the course

- I. Introduction
 - 5. Because the speed of light, *c*, is constant, the *frequency, v*, (number of cycles of the wave per second) can complete in the same time, must be inversely proportional to how long the oscillation is, or *wavelength*:

$$\mathbf{v} = \frac{c}{\lambda} \qquad \qquad \therefore \mathbf{E} = h\mathbf{v} = \frac{hc}{\lambda}$$
$$c = 3 \times 10^{10} \text{ cm/s}$$

- 6. Amplitude, *A*, describes the wave height, or strength of the oscillation
- 7. Because the atomic particles in matter also exhibit wave and particle properties (though opposite in how much) EM radiation can interact with matter in two ways:
 - Collision particle-to-particle energy is lost as heat and movement
 - Coupling the wave property of the radiation matches the wave property of the particle and "couple" to the next higher quantum mechanical energy level

- I. Introduction
 - 8. The entire electromagnetic spectrum is used by chemists:



- I. Introduction
 - C. The IR Spectroscopic Process
 - 1. The quantum mechanical energy levels observed in IR spectroscopy are those of *molecular vibration*
 - 2. We perceive this vibration as heat
 - 3. When we say a *covalent bond* between two atoms is of a certain length, we are citing an average because the bond behaves as if it were a vibrating spring connecting the two atoms
 - 4. For a simple diatomic molecule, this model is easy to visualize:



Vibration of a Diatomic Molecule Approximates an Oscillating Spring

I. Introduction

- C. The IR Spectroscopic Process
 - 5. There are two types of bond vibration:
 - Stretch Vibration or oscillation along the line of the bond









out of plane

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- C. The IR Spectroscopic Process
 - 8. When a wave of infrared light encounters this oscillating EM field generated by the oscillating dipole of the same frequency, the two waves couple, and IR light is absorbed
 - 9. The coupled wave now vibrates with twice the amplitude



IR beam from spectrometer

- D. The IR Spectrum
 - 1. Each stretching and bending vibration occurs with a characteristic frequency as the atoms and charges involved are different for different bonds



- E. The IR Spectrum The detection of different bonds
 - 7. As opposed to chromatography or other spectroscopic methods, the area of a IR band (or peak) is not *directly* proportional to concentration of the functional group producing the peak
 - 8. The intensity of an IR band is affected by two primary factors: *Whether the vibration is one of stretching or bending*

Electronegativity difference of the atoms involved in the bond

- For both effects, the greater the change in dipole moment in a given vibration or bend, the larger the peak.
- The greater the difference in electronegativity between the atoms involved in bonding, the larger the dipole moment
- Typically, stretching will change dipole moment more than bending

- II. Infrared Group Analysis
 - A. General
 - 1. The primary use of the IR is to *detect functional groups*
 - 2. Because the IR looks at the interaction of the EM spectrum with actual bonds, it provides a unique qualitative probe into the functionality of a molecule, as functional groups are merely different configurations of different types of bonds
 - 3. Since most "types" of bonds in covalent molecules have roughly the same energy, i.e., C=C and C=O bonds, C-H and N-H bonds they show up in similar regions of the IR spectrum
 - 4. Remember all organic functional groups are made of multiple bonds and therefore show up as multiple IR bands (peaks)
Infrared Spectroscopy

Unsaturated Systems – substitution patterns

- The substitution of aromatics and alkenes can also be discerned through the outof-plane bending vibration region
- However, other peaks often are apparent in this region. These peaks should only be used for reinforcement of what is known or for hypothesizing as to the functional pattern.



Infrared Spectroscopy

Effects on IR bands

1. Conjugation – by resonance, conjugation lowers the energy of a double or triple bond. The effect of this is readily observed in the IR spectrum:



 Conjugation will lower the observed IR band for a carbonyl from 20-40 cm⁻¹ provided conjugation gives a strong resonance contributor





Strong resonance contributor

Poor resonance contributor (cannot resonate with C=O)

 Inductive effects are usually small, unless coupled with a resonance contributor (note –CH₃ and –Cl above)

Infrared Spectroscopy

Effects on IR bands

2. Steric effects – usually not important in IR spectroscopy, unless they reduce the strength of a bond (usually π) by interfering with proper orbital overlap:

- Here the methyl group in the structure at the right causes the carbonyl group to be slightly out of plane, interfering with resonance
- **3. Strain effects** changes in bond angle forced by the constraints of a ring will cause a slight change in hybridization, and therefore, bond strength

 As bond angle decreases, carbon becomes more electronegative, as well as less sp² hybridized (bond angle < 120°)

Effects on IR bands

4. Hydrogen bonding

- Hydrogen bonding causes a broadening in the band due to the creation of a continuum of bond energies associated with it
- In the solution phase these effects are readily apparent; in the gas phase where these effects disappear or in lieu of steric effects, the band appears as sharp as all other IR bands:

1-Butanol

Gas phase spectrum of 1-butanol Steric hindrance to H-bonding in a di-*tert*-butylphenol $\frac{1}{2}$

NICOLET 20SX FT

• H-bonding can interact with other functional groups to lower frequencies



Spectroscopic Techniques

 Spectroscopy: It is the measurement and interpretation of electromagnetic radiations absorbed or emitted when the molecule or atom or ion of a sample move from one energy state to another. Theses changes may be from ground sate to excited state or vice versa.





Electromagnetic Radiations (EMR)

Two characteristics of electromagnetic radiation are particularly important for understanding remote sensing. These are the wavelength and frequency.

Wave length (λ) is the length of one wave cycle, which can be measured as the distance between successive wave crests. Wavelength is measured in metres (m)

Frequency (f) refers to the number of cycles of a wave passing a fixed point per unit of time. Frequency is normally measured in hertz (Hz), equivalent to one cycle per second, and various multiples of hertz



Remember ! Two are inversely related to each other. The shorter the wavelength, the higher the frequency. The longer the wavelength, the lower the frequency





Absorption and Emission Spectra



• Electromagnetic Spectrum





Effect of electromagnetic radiations on Molecules



Electronic, Vibrational and Rotational energy levels





- Highly valuable technique for identifying C-H framework and even entire structure of a molecule.
- Determination of structure of natural product, proteins, enzymes, etc. help in designing the drug molecule.
- Important tool for physicists, chemists, pharmacists, biologists and others.
- Excellent application of NMR spectroscopy in medicine today is Magnetic Resonance Imaging (MRI).

Introduction to NMR

- Pauli observed that certain atomic nuclei have the properties of spin and magnetic moment in 1920s.
- Exposure of nuclei to a magnetic field leads to splitting of their energy levels.
- Purcell and another scientist independently demonstrated that nuclei absorb electromagnetic radiation (EMR) in a strong magnetic field in 1940s.
- First NMR spectrometer was designed by Varian Associate in 1953.

Nuclear Spin Quantum Number

 The nuclear spin quantum number of a nucleus is the resultant spin quantum numbers of neutrons and protons and it depends upon the number of neutrons and protons. E.g. Spin Quantum numbers (I) of some elements

Atomic	Mass	Spin Quantum	Examples of
Number	Number	Number (I)	Elements
Even	Even	0	₂ He ⁴ , ₆ C ¹² , ₈ O ¹⁶
Odd	Even	1, 2, 3	₇ N ¹⁴ , ₅ B ¹⁰ , ₁ D ²
Odd or Even	Odd	1⁄2, 3/2, 5/2	₁ H ¹ , ₉ F ¹⁹ , ₁₁ Na ²³

Number of energy Levels

- The number of nuclear energy levels associated with a particular nucleus can be calculated as:
- Number of nuclear energy levels = (2I+1)

Where I is spin nuclear quantum number

E.g. For hydrogen nucleus $I = \frac{1}{2}$ So

Number of nuclear energy levels:

(2X1/2 + 1) = 2











Interaction of Nuclei with EMR

- When the sample is subjected to a brief, intense pulse of EMR (radio frequency region), nuclei in the lower energy state can be promoted to higher energy state.
- When the nuclei return to original state, they emit signals whose frequency depends on the difference in energy between the two state.
- The NMR spectrometer display an NMR spectrum as a plot of frequency versus intensity.

NMR Spectrometer

Sample is lowered into the magnetic field here (there's a hole in the center of the magnet).

Big superconducting magnet, cooled in liquid helium. Source of the magnetic field (B_o).

Wooden chair, no magnetic metals allowed near the magnet!

Spectrum observed on computer monitor here.

Radio transmiter and receiver tuned to 300 MHz



Shielding and Deshielding

- All the protons do not experience the same applied magnetic field
- In an applied magnetic field, the electrons circulate about the nuclei and induce a local magnetic field that opposes the applied magnetic field.
- $B_{effective} = B_{applied} B_{local}$
- This means greater the electron density, greater B_{local} will be and more the proton will be shielded from the applied magnetic field.
- Proton will require lower frequency for resonance.

Low Resolution NMR Spectrum of CH₃CH₂OH







Low Resolution NMR Spectrum of CH₃CH₂OH



Acetaldehyde



Equivalent and non-equivalent protons





Information from NMR Spectra

 Number of Signals: The number of signals in an NMR spectrum determine the number of different types of Protons.

E.g. $CH_3^{a}-CH_2^{b}-OH^{c}$ $CH_3^{a}-CH_3^{a}$ $CH_3^{a}-CH_2^{b}-OH^{c}$ $CH_3^{a}COCH_3^{a}$ $CI^{a}CH^{b}_2-CH^{c}_2-OH^{d}$, $CH^{a}_3-CH^{b}-OH^{a}$ $CICH^{a}_2COCH^{b}_3$ $CI^{a}CH^{b}_2-CH^{c}_2-OH^{c}_3$ $CH^{b}_3-CH^{b}-OH^{a}_3$ $CICH^{a}_2COCH^{b}_3$ $CI^{a}CH^{b}_2-CH^{c}_2-OH^{c}_3$ $CH^{b}_3-CH^{b}-OH^{a}_3$ $CICH^{a}_2COCH^{b}_3$ $CI^{a}CH^{b}_3-CH^{b}_3$ $CH^{b}_3-CH^{b}-OH^{a}_3$ $CICH^{a}_3-CH^{b}-OH^{a}_3$ $CICH^{a}-OH^{a}-OH^{a}-OH^{a}-OH^{a}-OH^{a}-OH^{a}-OH^{a}-OH^{a}-OH^{a}-OH^{a}-OH^{a$







Number of Signals



Shielding and Deshielding



- Position of Signals: The signals in the NMR spectrum appear at different positions due shielding and deshielding of protons.
- Protons attached to an electronegative elements are deshielded, Whereas the protons attached to an electropositive elements are shielded.
Tetramethyl Silane as Reference (TMS)

The chemical shifts of different protons in different compounds

are measured relative to standard reference

compound tetramethyl Silane. $(CH_3)_4Si$ (TMS).

1. All the 12 protons are equivalent,

so show a sharp signal even at very low concentration

2. The protons are highly shielded due less electronegativity of

Silicon. The signal is very high field.

- 3. TMS is chemically inert and miscible with all solvents.
- 4. TMS has very low Boiling point so it can be removed easily

from the compound after taking the NMR spectrum.





Equivalent protons of TMS





Chemical shift

• The positions of the signals in an NMR spectrum are defined with

respect to reference compound (TMS).

 $\delta = \frac{vsample}{vTMS} \times 106$

v o

The advantage of the \Box scale is that the chemical shift of a given

nucleus is independent of the operating frequency.

Factors affecting Chemical shift

• (a) Inductive effect: A proton attached to an electronegative element is deshielded.

E.g.	CH ₃ -Cl	CH ₃ -F
	δ = 3.1	δ = 4.3
CH ₃ -CH ₂ ^a -CH ^b ₂ CI		$\delta_a < \delta_b$
More deshielding high δ value		

Effect of Electronegativity on δ value



Anisotropic effect



Induced circulation of pi electrons in the alkene



Induced local magnetic field of the pi electrons reinforces the applied field and provides part of the field necessary to bring a vinyl hydrogen into resonance.

Applied field, B₀

Induced flow of electrons in the pi system of alkyne



Induced local magnetic field of the pi electrons is against the applied field; it requires a greater applied field to bring an acetylenic hydrogen into resonance.

Applied field, B₀



Induced local magnetic field of the circulating pi electrons reinforces the applied field and provides part of the field necessary to bring aromatic hydrogens into resonance

Applied field





Hydrogen bonding

- The protons involved in hydrogen bonding is strongly deshielded and gives NMR signal at high δ value.
- Stronger the hydrogen bond greater will be the deshielding. e.g. –OH group in alcohol gives NMR signal at δ = 3.5-4.5. But –OH group in carboxylic acid gives at δ = 10-11

Typical values of chemical shift





Splitting of Signals

- Splitting of Signals: The signals of protons split due to spin-spin coupling into doublet, triplet, quartet or quintet and is multiplicity of a signal.
- Application: The splitting of signals of protons gives information about the number of protons on the neighboring carbon atoms.
- Multiplicity of signal = (2n+1) where n is number of protons on neighboring carbon atoms.





High resolution NMR Spectrum of CH₃CH₂OH



High resolution NMR Spectrum of CH₃CH₂OH



High resolution NMR Spectrum of CH₃CH₂OH











Ethyl acetate







Relative Peak ratio of peaks in quartet



Relative Peak ratio of peaks in quartet



Conditions for spin-spin coupling

1. Spin-spin coupling occur between the protons present on adjacent carbons e.g.

CH ^a -CH ^b	CH ^a -C-CH ^b

Coupling No Coupling

2. Protons must be non equivalent

CH ₂ ^a Cl-CH ₂ ^b Br	CH ₂ ^a Br-CH ₂ ^a Br
Coupling	No Coupling

Conditions for spin-spin coupling

¹H NMR—Spin-Spin Splitting

Three general rules describe the splitting patterns commonly seen in the 'H NMR spectra of organic compounds.

- 1. Equivalent protons do not split each other's signals.
- 2. A set of '**n**' non-equivalent protons splits the signal of a nearby proton into n + 1 peaks.
- Splitting is observed for nonequivalent protons on the same carbon or adjacent carbons.

If H_a and H_b are not equivalent, splitting is observed when:



Intensity of signals

 Intensity of signals: The intensity or relative height of signals indicate the number of protons of each type. E.g. If the NMR shows two signals and ratio of heights of those signals is 2:3, then there are two protons of one type and three protons of other type.

Relative ratio of multiplets



Coupling Constant

Coupling Constant: The distance

between two successive peaks of a

singlet is called coupling constant.

Applications of coupling constant:

- 1. To distinguish between a pair of singlet and a doublet
- 2. To distinguish between cis and trans isomer



Coupling Constant



Applications of NMR spectroscopy

1. Identification of structural isomer:

 $\begin{array}{c} \mathsf{CH}^{\mathsf{a}}_{3}\mathsf{-}\mathsf{CH}^{\mathsf{b}}_{2}\mathsf{-}\mathsf{CH}^{\mathsf{c}}_{2}\mathsf{-}\mathsf{OH}^{\mathsf{d}} & \mathsf{CH}^{\mathsf{a}}_{3}\mathsf{-}\mathsf{CH}^{\mathsf{b}}\mathsf{-}\mathsf{CH}^{\mathsf{a}}_{3} \\ & \mathsf{OH}^{\mathsf{c}} \\ \mathbf{4}\mathsf{-}\mathsf{Signals} & \mathbf{3}\mathsf{-}\mathsf{Signals} \\ \\ \mathsf{CH}^{\mathsf{a}}_{3}\mathsf{-}\mathsf{CH}^{\mathsf{b}}_{2}\mathsf{-}\mathsf{CH}^{\mathsf{c}}_{2}\mathsf{-}\mathsf{CI} & \mathsf{CH}^{\mathsf{a}}_{3}\mathsf{-}\mathsf{CH}^{\mathsf{b}}\mathsf{-}\mathsf{CH}^{\mathsf{a}}_{3} \\ & \mathsf{CI} \\ \\ & \mathbf{3}\mathsf{-}\mathsf{Signals} & \mathbf{2}\mathsf{-}\mathsf{Signals} \end{array}$

 Identification of cis and trans isomer: Because the protons involved in cis and trans isomer have different chemical shifts and coupling constant.



3. Detection of hydrogen bonding: Both intra and inter molecular bonding the absorption band for the proton involved down field.

Moreover intermolecular H-bonding is both concentration and temperature dependent.

 Detection of electronegative element: The presence of an electronegative atom causes deshielding and down field. 2. Prediction of aromatic protons: Since the aromatic protons appears at very low field (high δ value).

Determination of structures of Molecules on the basis of NMR signals.

- (a) The following molecules show only 1-S in their NMR spectrum propose a suitable structure
- (i) $C_2H_4Br_2$ (ii) C_3H_6 (iii) C_4H_6 (iv) C_2H_6O
- (b) The following molecules show only 2-S in their NMR spectrum propose a suitable structure

(i) $C_3H_6O_2$ (ii) C_3H_4

Relaxation processes

- Spin-spin Relaxation: In this process nucleus in upper state transfers energy to neighbouring nucleus in the ground state.
- Spin-lattice relaxation: In this process nucleus in upper state transfers energy to surrounding in the form of translational, rotational and Vibrational energy. This is also called longitudinal relaxation.
Magnetic Resonance Imaging (MRI)

- NMR has become an important tool in medical diagnosis as Magnetic Resonance Imaging (MRI).
- MRI machine is having a magnet large enough to accommodate an entire patient.
- Different tissue yield different signals. Most of the signals originate from the hydrogens of water molecule because these hydrogens are more abundant in tissues.
- The difference in the way water is bound in different tissues is what produces much of the signal variation among organs, as well as the signal variation between healthy and diseased tissue.

NMR and MRI use similar instruments







Carbon-13 NMR Spectroscopy

- The principle behind Carbon-13 NMR Spectroscopy is essentially the sane as Proton NMR spectroscopy.
- The chemical shift range over 220 ppm where the signals are less likely to overlap.
- All types of carbon may be observed as singlet.
- The signal can be split by nearby protons. However, the splitting is generally not observed because the spectra are recorded using spin decoupling .

Proton-Decoupled ¹³C NMR Spectrum



Distortionless Enhancement by Polarisation Transfer (DEPT)

- This technique is used to distinguish between CH, CH_2 , and CH_3 groups.
- DEPT spectrum does not show a signal for a carbon not attached with a proton.
- The spectrum is run under conditions that allows only signals resulting form either CH or CH_2 or CH_3 carbons.

Two-Dimensional Spectroscopy

- 2-D NMR technique allows to determine the structure of complex molecules.
- Important for biological molecules whose properties depends on how they fold in water.
- Recently 3-D NMR spectroscopy have been developed that can be used to determine the structures and orientations of very complex molecules.
- 2-D NMR spectra have two frequency axes and one intensity axis.
- The most common 2-D spectra involve ¹H-¹H, ¹³C-¹H and ¹³C-¹³C shift correlations.

2-D Spectra

- ¹H-¹H shift correlation spectroscopy (COSY) is used to identify protons that are coupled to each other.
- ¹³C-¹H heteronuclear correlation spectroscopy (HETCOR) indicate coupling between protons and carbons to which they are attached.
- ¹³C-¹³C correlation spectroscopy (incredible natural abundance double-quantum transfer experiment (INADEQUATE) used to identify directly bonded carbons.
- Other 2-D NMR are total correlation spectroscopy (TOCSY), nuclear Overhauser effect spectroscopy (NOESY), rotating-frame Overhauser effect spectroscopy (ROESY), heteronuclear multiple quantum coheherence (HMQC), etc.







The 3D structure of a protein (ECD1–CRF-R2β). (A)A ribbon diagram of the lowest energy conformer highlighting the β-sheets in cyan and the disulfide bonds in yellow. (B)Superposition of 20 conformers representing the 3D NMR structure.



Drug development

- More than 50% of the commercial drugs are chiral drugs.
- Less than half of these marketed in enantiomerically pure form.
- Only 10% of synthetic chiral drugs are available enantiopure.
- NMR proved to be an important tool in identifying pure enantiomers.
- Examples of different pharmacological response of two enantiomers are quite common.

Two enantiomers of a drug interact with its receptor site, which is chiral, differently and may lead to different effects.

(i) (S)-warfarin is six times as active as an anticoagulant as the R enantiomer.

(ii) (S)-propranolol introduced as a β -blocker for treatment of heart disease, but (R)-enantiomer acts as contraceptive, so enatiomeric purity is essential for clinical use.

- The alkaloid (-)-levorphanol is a powerful narcotic analgaesic with an activity 5-6 times stronger than morphine. Its enantiomer (+)-dextrophan is totally devoid of this activity, but is active as a cough supressant and is marketed as its methyl ether (dextromethorphan).
- The artificial sweetener aspartame, only one stereoisomer is sweet and other three are slightly bitter and must be avoided in the manufacturing process.

Drug thalidomide, both enantiomers have the desired sedative effect but only the (-) enantiomer causes foetal deformaties.

•

Therefore, synthesize, separate and evaluate all the possible isomers of a new product (or existing drug) before it is put to use.

Magnetic Resonance Imaging (MRI)

- NMR has become an important tool in medical diagnosis as Magnetic Resonance Imaging (MRI).
- MRI machine is having a magnet large enough to accommodate an entire patient.
- Different tissue yield different signals. Most of the signals originate from the hydrogens of water molecule because these hydrogens are more abundant in tissues.
- The difference in the way water is bound in different tissues is what produces much of the signal variation among organs, as well as the signal variation between healthy and diseased tissue.

NMR and MRI use similar instruments





THANKS

Organic Reactions and Synthesis of Drug Molecule

Types of organic Reactions

- 1. Addition Reactions
- 2. Substitution Reactions
- 3. Elimination Reactions
- 4. Condensation Reactions
- 5. Oxidation Reactions

Types of organic Reactions

- Substitution an atom (group) of the molecule is replaced by another atom (group)
- Addition π-bond of a compound serves to create two new covalent bonds that join the two reactants together
- Elimination two atoms (groups) are removed from a molecule which is thus cleft into two products
- Rearrangement atoms and bonds are rearranged within the molecule; thus, isomeric compound is formed

Types of Organic Reaction



Substitution Reactions

Nucleophilic Substitution

Electrophilic Substitution

Free radical Substitution

Reactive Intermediates

- Most of the organic reactions proceeds through following intermediates:
 - 1. Carbonium ions or Carbocations
 - 2. Carbanion
 - 3. Free radicals
 - 4. Carbenes

Covalent Bond

• **Covalent Bond: The bond formed by the sharing of electrons among the atoms is called covalent bond.**



Homolytic and Heterolytic cleavage



Bond Cleavage

Heterolytic Cleavage

$$A : B \longrightarrow A^{+} : B^{-} \qquad A^{-} : B^{+}$$

+^{vely} charged ion – Carbocation -^{vely} charged ion – Carbanion

Homolytic Cleavage

 $\bigcap_{A:B\longrightarrow A'+B'}$

Free radicals

Free Radical

 A Free Radical may be defind as an atom or group of atoms having unpaired electron.

Free Radical is produced by the **homolytic cleavage** of covalent bond.

$$\bigwedge_{CI-CI}^{\wedge} \longrightarrow CI + CI$$

Structure of Free Radical

Orbital structure

Alkyl free radical like carbocations are planar chemical species. The only difference being that in carboctions, the unhybridized p-orbital is empty while in the free radical, it contain the odd electron.



Classification of Free Radicals



Factors Affecting Stability of Free Radicals

- 1. Resonance Effect
- 2. Hybridization
- 3. Hyperconjugation

Conjugated and non-Conjugated Double bonds

"Conjugated" vs. non-conjugated dienes

1,3 hexadiene (conjugated π bonds)

1,4 hexadiene (*non* conjugated π bonds)

Resonance Effect

Greater Stability of Allyl and Benzyl Free Radical



Hyperconjugation



thermodynamic stability



3 Hyperconjugatable H s
Order of Relative Stability of free Radicals



Carbanions

Chemical species bearing a negative charge on carbon and possessing eight electrons in its valence shell are called carbanions,

 $HO^{-} + H^{-}CH_{2} - CHO \rightarrow H_{2}O + CHO$

and the second of the second second

Hydroxide ion Acetaldehyde ion Acetaldehyde carbocation

H₂N⁻

Amide ion Acetylene

 \dot{H} \dot{C} \equiv $C - H \rightarrow NH_3 + C \equiv C - H$

Types of carbanions



Orbital structure



Orbital structure of carbanions

Factors Affecting the stability of a Carbanion

- **1. The inductive effect:** Electronegative atoms adjacent to the charge will stabilize the charge.
- **2. Hybridization of the charge-bearing atom:** The greater the **s** -character of the charge- bearing atom, the more stable the anion.

3. The extent of conjugation of the anion: Resonance effects can

stabilize the anion. This is especially true when the anion is

stabilized as a result of aromaticity.



(a) Inductive effect

The stability of simple alkyl carbanions follow the order: $CH_3^- > 1^\circ > 2^\circ > 3^\circ$.



(b) Resonance effect

Allyl and benzyl carbanions are stabilized by resonance.

$$\dot{C}H_2 = CH - CH_2^2 \leftrightarrow CH_2 - CH = CH_2$$

(Allyl carbanion is stabilized by resonance)



(Benzyl carbanion is stabilized by resonance)

 $(C_6H_5)_3C^- > (C_6H_5)_2CH^- > C_6H_5CH_2$

Effect of Electron donating and Electron withdrawing groups on Stability of Carbanion

Electron-donating groups **destabilize** a Carbanion while electron-withdrawing groups **stabilize** it.



(c)s- Character

Stability of the carbanion increases with the increase in s- character of the carbon carrying the -ve charge.

$$R - C \equiv C$$
 > $R_2C = CH$ > $R - CH_2$

50% s- character

33% s- character

25% s- character

Carbocations

Chemical species bearing a positive charge on carbon and carrying six electrons in its valence shell are called carbocations or carbonium ions.



Orbital structure

The three sp²-hybridized orbitals of this carbon form three σ -bonds with monovalent atoms or groups lie in a plane are inclined to one another at an angle of 120°.



Types of carbonium ions



Stability

The stability of carbocations follow the order -

 $3^{\circ} > 2^{\circ} > 1^{\circ} > methyl.$

This order of stability can be explained on the basis of the following factors:

(a) Inductive Effect

(b) Resonance Effect

(c) Hyperconjugation Effect

(a) Inductive effect

More the number of alkyl group on the carbon atom carrying the +ve charge, greater would be the dispersal of the charge and hence more stable would be the carbocation. Thus, the stability of the carbocations decereases in the order: $3^{\circ} > 2^{\circ} > 1^{\circ} > ;$



(b) Resonance effect

Carbocations in which the +vely chared carbon atom is attached to a double bond or a benzene ring are stabilized by resonance.

$$CH_2 \stackrel{\frown}{=} CH \stackrel{\frown}{=} CH_2^+ \leftrightarrow CH_2 - CH = CH_2$$

(Allyl carbocations is stabilized by resonance)

More the number of phenyl group, greater is the stability.

 $(C_6H_5)_3C^+ > (C_6H_5)_2CH^+ > C_6H_5CH_2^+$

Benzyl and vinyl Carbonium ions



Hyperconjugation Effect

- Hyperconjugation is the interaction of the <u>electrons</u> in a <u>sigma</u> <u>orbital</u> (e.g. C–H or C–C) with an adjacent empty (or partially filled) non-bonding orbital.
- Spreading out charge by the overlap of an empty p-orbital with an adjacent σ bond is called hyperconjugation.



(c) Hyperconjugation effect

Tert – Butyl carbocation has nine α -hydrogens and hence nine hyperconjucation structures.



The stability of the various carbocations decreases in the order:



Nucleophile

- Nucleophile is a neutral or negatively charged Lewis base.
- Anions are usually more reactive than neutrals
- More basic nucleophiles react faster
- Better nucleophiles are lower in a column of the periodic table

Classification of Reagents

Nucleophilic Reagents (Nucleophiles)

• The negatively charged or electron rich species are nucleophilic.

e.g. OH^- , OCH_3^- , $-CN^-$, $-I^-$, $CH_3^ COO^-$, NH_2^- , CH_3^-

 $H_2O, NH_3, NH_3 - NH_2$

$$H_2 \ddot{O}, CH_3 - \ddot{O} - CH_3, C_2 H_5 - \ddot{O} H, \ddot{N} H_3,$$

• All nucleophiles are in general **Lewis bases**.

Classification of Reagents

Electrophilic Reagents (Electrophiles)

• All positively charged or electron deficient species are called electrophiles.

 H^{+} , CH_{3}^{+} , NO_{2}^{+} , CI^{+} , Br^{+} , Ag^{+}

Neutral Electrophiles

• Neutral reagents which contain an electron-deficient atom are also electrophiles.

AlCl₃, SO₃, BF₃, SOCl₂, POCl₃, FeCl₃, ZnCl₂

• All electrophiles are in general **Lewis acids**.

Leaving group



Rules for Using Curved Arrows

The nucleophilic site can be negative or neutral



Alkyl Halides

•Alkyl halides are organic molecules containing a halogen atom bonded to an *sp*³ hybridized carbon atom.

•Alkyl halides are classified as primary (1°), secondary (2°), or tertiary (3°), depending on the number of carbons bonded to the carbon with the halogen atom.

•The halogen atom in halides is often denoted by the symbol "X".



Other Types of Alkyl Halides

Other types of organic alkyl halides include:

•Alyllic halides have X bonded to the carbon atom adjacent to a C-C double bond.

•Benzylic halides have X bonded to the carbon atom adjacent to a benzene ring.

NOT ALKYL HALIDES

ring.

•Vinyl halides have a halogen atom (X) bonded to a C-C double bond.

• Aryl halides have a halogen atom bonded to a aromatic



vinyl halide

aryl halide



Nature of C-X Bond

 In alkyl haides caron halogen bond is polar due greater electronagtivity of halogen than carbon



SUBSTITUTION REACTIONS

One group takes the place of another.



 \mathbf{Y} takes the place of \mathbf{X} (Substitution)

Y "displaces" X

Nucleophilic Substitution Reaction

$$\overset{\delta+}{\mathbf{C}}\overset{\delta-}{-}\mathbf{X}$$



Elimination Reactions of Alkyl Halides

• Alkyl halides undergo elimination reactions with Brønsted–Lowry bases.



An Example of Nucleophilic Substitution Reaction



bromomethane

methanol

Types of Nucleophilic Substitution Reaction

1. Unimolecular Nucleophilic Substitution Reaction –

SN¹ Reaction

2. Bimolecular nucleophilic Substitution reaction- SN²
Reaction

Unimolecular Nucleophilic Substitution Reaction – SN¹ Reaction



он

Bimolecular nucleophilic Substitution SN² -Reaction

Substitution





Mechanisms of nucleophilic substitution reaction

There are two type of nucleophilic substitution reaction:

(i) S_N^1 Mechanism (unimolecular nucleophilic substitution) (ii) S_N^2 Mechanism (Bimolecular nucleophilic substitution)
(i) $\underline{S_N^1}$ Mechanism (unimolecular nucleophilic substitution)

IN this type, the rate of reaction depends only on the substrate (i.e., alkyl halide) and the reaction id of the first order change.

Rate ∞ [Substrate] or Rate = k [RX]

THIS TYPE OF REACTION PROCRRDS IN TWO STEP AS:

Steps involved in SN¹ Reaction



STEP 1. The alkyl halide undergoes heterolytic fission forming an intermediate, carbocation. This step is slow and hence is the rate determining step of the reaction.



STEP 2. The carbocation ion being a reactive chemical species, immediatrly reacts with the nucleophile [:Nu⁻] to give the substitution product. This step is fast and hence does not affect the rate of reaction.



Overall Mechanism of SN¹ reaction

The mechanism of an SN¹ reaction occurs in 2 steps:



- Reaction Steps ...
- 1. the slower, rate-limiting dissociation of the alkyl halide forming a C+ intermediate
- 2. a rapid nucleophilic attack on the C+

S_N1 : Unimolecular nucleophilic substitution

Example

Solvolysis of tert-butyl bromide to give tertiary butyl alcohol.



Mechanism

Step 1: the leaving group dissociates to form a carbocation



Step 2: reaction of the carbocation (an electrophile) with water (a nucleophile) gives an oxonium ion



Step 3: proton transfer completes the reaction



Factors affecting rate of SN¹ Reaction



Factors Affecting Rate of SN¹ Mechanism

- 1. The nature of the substrate (the alkyl halide)
- 2. The ability of the leaving group to leave
- 3. The nature of the solvent
- The rate is independent of the power of the nucleophile.
- 1.<u>The nature of the substrate</u>:



Nature of Alkyl Halide



Increasing rate of SN¹ reactions



Effect of nature of the leaving group on rate of SN¹ reactions

2. The nature of the leaving group:

- The nature of the leaving group has the same effect on both SN¹ and SN² reactions.
- The better the leaving group, the faster a C+ can form and hence the faster will be the SN¹ reaction.
- Groups which best stabilize a negative charge are the best leaving groups, i.e., the weakest bases are stable as anions and are the best leaving groups.
- Iodine (-I) is a good leaving group because iodide (I⁻) is non basic. The hydroxyl group (-OH) is a poor leaving group because hydroxide (OH⁻) is a strong base.

Bimolecular nucleophilic Substitution SN² -Reaction

 S_N2 Reaction: This is called bimolecular nucleophilic substitution and it is one-step process.



Kinetics of SN²

(ii) S_N^2 Machanism (Bimolecular nucleophilic subsititution): In This type, the rate of reaction depends on the concentration of both substrate (alkyl halide) and the nucleophilic; the reaction is said to be S_N^2 , the second order change

Rate ∞ [Substrate] [Nucleophile]

or

Rate = k [*R*X] [:Nu⁻]

Factors Affecting Rate of SN²

Steric Effect	
Nucleophile	
Solvent Effect	
Leaving Group	

Effect of nature of substrate on rate of SN² reactions



Me° >> 1° >> 2° >> 3°

decreasing rate of SN² reactions

Nature of Nucleophile

Negative charge is a stronger nucleophile than an analogous neutral species

 $(OH^{-} > H_2O) \& (NH_2^{-} > NH_3)$

- Nucleophilicity increase from left to right across the periodic chart (OH > F)
- Nucleophilicity increase down the periodic table
 - (I > Br > Cl > F)

Polar Protic solvents

Polar Protic Solvents		Dielectric constant	Dipole Moment	
:NH3	Ammonia	~25	1.4	D
СН ₃ н– <mark>Ӧ</mark> -Ċ-СН ₃ ĊН ₃	t-Butanol	12	1.7	D
H- <mark>Ö</mark> -CH ₂ CH ₂ CH ₃	n-Propanol	20	1.68	D
н− <mark>о</mark> -сн₂сн₃	Ethanol	25	1.69	D
H− <mark>Ö</mark> −CH₃	Methanol	33	1.70	D
<mark>о</mark> . н- <mark>ö</mark> -Ҁ-сн₃	Acetic acid	6.2	1.74	D
н-о-н	Water	80	1.85	D

Non Polar Aprotic Solvents

Nonpolar solve	ents	Dielectric constant	Dipole Moment
\sim	Pentane	1.8	0.00 D
\sim	Hexane	1.9	0.00 D
\bigcirc	Cyclohexane	2.0	0.00 D
\bigcirc	Benzene	2.4	0.00 D
CH ₃	Toluene	2.3	0.36 D

Polar Aprotic Solvents



Effect of Solvent



Effect of the solvent on rate of SN² reactions

• Nature of the solvent:

- **Protic solvents:** which contain -OH or $-NH_2$ groups. Protic solvents **slow down** $S_N 2$ reactions.
- Polar aprotic solvents: like acetone, which contain strong dipoles but no –OH or –NH₂ groups speed up $S_N 2$ reactions.
- Non polar solvents: e.g., hydrocarbons. S_N2 reactions are relatively slow in non polar solvents.

A solvated nucleophile has difficulty hitting the a-carbon.

$$\begin{array}{c} \delta^{+} \delta^{-} \\ H - OR \\ \delta^{+} \delta^{-} \\ RO - H - CR \\ \delta^{-} \delta^{+} \\ H - OR \\ \delta^{+} \delta^{-} \end{array}$$

Effect of the solvent on rate of S_N2 reactions

- Polar Aprotic Solvents: like acetone, acetone (CH₃COCH₃), dimethylformamide (DMF) (CH₃)₂NC=O, dimethyl sulfoxide, DMSO [(CH₃)₂SO], solvate the cation counterion of the nucleophile but not the nucleophile.
- Polar aprotic solvents solvate metal cations of nucleophile leaving the anion for attack.

$$\delta^{-} \delta^{+}$$

$$N \equiv C - CH_{3}$$

$$H_{3}C - C \equiv N : \cdots Na^{+} \cdots : N \equiv C - CH_{3}$$

$$N \equiv C - CH_{3}$$

$$N \equiv C - CH_{3}$$

$$\delta^{-} \delta^{+}$$

Nature of Leaving Group

The weakest bases (from strong acid) is the best leaving group

RELATIVE REACTIVITY
<< 1
1
200
10,000
30,000

Stereochemistry: All S_N^2 reactions proceed with backside attack of the nucleophile, resulting in inversion of configuration at a stereogenic center.



Inversion of Configration

 $S_{\rm N}{}^2$ reaction of optically active halides are concerted reactions and configuration of carbon is changed. This process is called as inversion of configuration, complete inversion takes place. This inversion of configuration is commonly known as Walden Inversion.



Example of SN² Reaction

Hydrolysis of methyl chloride is an example of S_N^2 reaction and high reaction concentration of the nucleophile (OH⁻) favours S_N^2 reaction. The chlorine atom present in methyl chloride is more electronegative than the carbon atom.

Therefore C — CI bond is partially polarized.



When the methyl chloride is attacked by OH⁻ strong nucleophile from the opposite side of the chlorine atom, a transition state results in which both OH and CI are partially bonded to carbon atom.



Comparison Between SN1 and SN2 reaction

PARAMETER	SN1	SN2
KINETIC	First order k[RX]	Second order <i>k</i> [RX][Nu:]
ALKYL HALIDE	3 > 2 > 1	CH3X > 1 > 2
LEAVING GROUP	Need good leaving group	Need good leaving group
NUCLEOPHILE	Weak nucleophile	Strong nucleophile

Reason of Electrophilic Substitution in Benzene

- Benzene does not undergo addition reactions like other unsaturated hydrocarbons, because addition would yield a product that is not aromatic.
- Substitution of a hydrogen keeps the aromatic ring intact.



Electrophilic Aromatic Substitution



Mechanism of Halogenation Reaction



Nitration and Sulfonation

• Nitration and sulfonation introduce nitro and sulfonic acid groups respectively into the aromatic ring.



Mechanism of Nitration Reaction

Step 1: Formation of the nitronium ion, NO2*

$$HO-SO_3-H + HO-NO_2 \longrightarrow H_2O + NO_2^+ + HSO_4^-$$

Step 2: Formation of an arenium ion as a result of electrophilic addition



Step 3: Loss of a proton gives the products



Mechanism of Sulfonation Reaction



Friedel-Crafts Alkylation and Friedel-Crafts Acylation

• In Friedel-Crafts alkylation, treatment of benzene with an alkyl halide and a Lewis acid (AlCl₃) forms an alkyl benzene.


Mechanism of Fridel – Craft Alkylation



Mechanism of Fridel – Craft Alkylation



Rearrangements can occur.



These results can be explained by Carbocation rearrangements.

Fridel-Crafts Acylation Reaction

- In Friedel-Crafts acylation, a benzene ring is treated with an acid chloride (RCOCI) and AlCl₃ to form a ketone.
- Because the new group bonded to the benzene ring is called an acyl group, the insertion of an acyl group to benzene is an acylation.



Electrophilic Substitution Reactions



Alkenes and alkynes are generally more reactive than alkanes due to the electron density available in their pi bonds.

Addition Reactions

 Unsaturated hydrocarbons undergo a number of different types of addition reactions across their double or triple bonds.



Symmetrical and Unsymmetrical Alkenes

• Symmetrical Alkene: Ethene



• Unsymmetrical Alkene: Propene



Electrophilic addition of HBr to Symmetrical Alkene



Orbital Structure of Ethylene

Ethylene



sigma bonding orbitals of ethylene

Electrophilic addition of HX to symmetrical Alkene

A reaction in which an atom or group of atoms is added to a molecule. divided into:



Electrophilic addition of HX to Unsymmetrical Alkene



Definitions

- **Regioisomers** two constitutional isomers that could result from an addition reaction.
- **Regiospecific** only one regiosisomer forms at the expense of the other.
- **Regioselective** both regioisomers are formed, but one is formed in preference.

Electrophilic addition of HBr to Unsymmetrical Alkene



Markovnikov's Rule

• This rule states that the addition of halogen acid takes place in such away that the negative part of the reagent attacks the carbon containing the less number of hydrogen across the double bond.

one hydrogen attached

 $CH_2 = CH - CH_3$

two hydrogens attached

three hydrogens but they are not attached to the double-bonded carbons

Mechanism of markovnikov's rule



Addition of HBr to 1-Butene



Addition of HBr to 2-Butene





Anti Markovnikov's Addition-Peroxide Effect

ANTI-MARKOVNIKOV'S RULE: FREE RADICAL ADDITION OF HYDROGEN BROMIDE

- When HBr is added to an alkene in the absence of peroxides it obey Markovnikov's rule.
- When HBr (not HCI or HI) reacts with unsymmetrical alkene in the presence of peroxides (compounds containing the O-O group) or oxygen, HBr adds in the opposite direction to that predicted by Markovnikov's rule.
- The product between propene and HBr under these conditions is 1-bromopropane and not 2-bromopropane.

CH₃CH=CH₂ + HBr → CH₃CH₂CH₂Br 1-bromopropane (major product) anti-Markovnikov's orientation

Peroxide Effect



MECHANISM FOR ANTIMARKOVNIKOV'S RULE





Peroxide Effect in Case of HCI and HI



- The last step shows that 2-bromopropane is obtained as the minor product.
- The peroxide effect is not observed in addition of HCl and HI. This may be due to the fact that the H–Cl bond being stronger than H–Br bond is not cleaved by the free radical, whereas the H–I bond is weaker and iodine free radicals combine to form iodine molecules instead of adding to the double bond.

Electrophilic addition reactions



Hydration: Addition of H₂O



Mechanism of Hydration



Addition of bromine(Br₂)



Mechanism of Addition of Br₂



Anti-Addition Stereospecific Reaction Anti-addition



 Alkyl halides undergo elimination reactions with Brønsted–Lowry bases. The elements of HX are lost and an alkene is formed.



Synthesis of Alkenes

1. Dehydrohalogenation of Alkyl Halides



2. Dehydration of Alcohols



3. Debromination of vic-Dibromides



Types of Elimination Reactions

In addition to substitution, alkyl halides can also undergo elimination reactions, which lead to the formation of alkenes.

As with substitution reactions, elimination reactions come in two mechanistic types: E1 eliminations (a two-step process involving an intermediate carbocation) E2 eliminations (a one-step process involving a concurrent abstraction of a proton, from an adjacent carbon, and extrusion of the leaving group)



Unimolecular Elimination Reaction

In this, two-step process, the rate of the reaction is dependent on the rate of ionization of the substrate (as was the case in the S_N1 reaction)



Unimolecular Elimination Reaction

Step 1: ionization of C-X gives a carbocation intermediate

 CH₃ slow, rate CH₃ determining CH₃ CH₃ + :Br:
CH₂-C-CH₃ determining CH₃-C-CH₃ + :Br:
Step 2: proton transfer from the carbocation of transfer from the carbocation of the carbocation of

$$\begin{array}{c} H & \begin{array}{c} CH_3 \\ \vdots O \\ H_3C \end{array} + H - CH_2 - C - CH_3 \\ H_3C \end{array} \xrightarrow{fast} \begin{array}{c} H \\ \vdots O \\ H_3C \end{array} + H - CH_2 = C - CH_3 \\ H_3C \end{array}$$

Satyzeff's Rule

In cases where more than one regioisomeric double bond is possible, the more substituted double bond may predominate (Zaitsev's Rule).



Bimolecular Elimination Reaction

Like the S_N^2 substitution, the E2 elimination is a one-step process. Like the S_N^2 substitution, the E2 elimination often requires stronger bases (nucleophiles for S_N^2).

Like the S_N2 substitution, the E2 elimination exhibits bimolecular kinetics.


Strong, less hindered bases (MeO', EtO', etc) generally give the most substituted alkene (Saytzeff's rule) as the major product.

Saytzeff product



Hofmann's Rule

Strong, bulky bases usually give the Hoffmann product (least highly substituted alkene) as the major product
 bulky bases often abstract a proton from a less hindered carbon

Saytzeff product

Hofmann product



Dehydration of Alcohols

Since hydroxide is a poor leaving group, it is common to first protonate the oxygen of the alcohol with a strong acid. The leaving group is thus the (neutral) water molecule as shown.



REACTIONS OF ALKENES

Catalytic hydrogenation:

- hydrogenation: addition of hydrogen to a double bond and triple bond to yield saturated product.

- alkenes will combine with hydrogen in the present to catalyst to form alkanes.



Catalytic Hydrogenation of Alkenes



Oxidation of alkenes

Oxidation of alkenes with Permanganate (Baeyer test)



Test for unsaturation



Oxidation of Alkenes

$$H_{2}C = CH_{2} + 4[O] \xrightarrow{Hot KMnO_{4}} H - C - OH \xrightarrow{[O]} H_{2}O + CO_{2}$$

Ethene Formic acid

$$CH_{3} - CH = CH_{2} + 4[O] \xrightarrow{Hot KMnO_{4}} CH_{3} - C - OH + HCOOH$$

Propene Acetic acid Formic acid

$$HCOOH \xrightarrow{[O]} H_{2}O + CO_{2}$$

Addition of halogen Acids to Alkenes



Addition of halogen Acids to Alkynes





Excess of halogen acid



Addition of HX in Presence of Peroxide

Anti-Markovnikov product is formed with a terminal alkyne.

$$CH_{3}-C \equiv C-H \xrightarrow{HBr} CH_{3}-C=C \xrightarrow{H} Br \xrightarrow{HBr} CH_{3}-C=C \xrightarrow{H} Br \xrightarrow{HBr} CH_{3}-C-C-H \xrightarrow{H} Br$$

Addition of halogen Acids to Alkynes

Alkynes undergo regioselective addition of either 1 or 2 moles of HX, depending on the ratios in which the alkyne and halogen acid are mixed

Mechanism of Addition of HX

 the intermediate in addition of HX is a 2° vinylic carbocation

$$CH_3C \equiv CH + H-Br$$
 \longrightarrow $CH_3C \equiv CH_2 + Br$
A 2° vinylic
carbocation

 reaction of the vinylic cation (an electrophile) with halide ion (a nucleophile) gives the product

$$CH_3C=CH_2 + Br \rightarrow CH_3C=CH_2$$

2-Bromopropene

- in the addition of the second mole of HX, Step 1 is reaction of the electron pair of the remaining pi bond with HBr to form a carbocation
- of the two possible carbocations, the favored one is the resonance-stabilized 2° carbocation



Addition of H₂O

In the presence of sulfuric acid and Hg(II) salts, alkynes undergo addition of water

 $\begin{array}{c} \mathsf{CH}_3 \, \mathsf{C} \equiv \mathsf{CH} + \mathsf{H}_2 \, \mathsf{O} & \underbrace{\mathsf{H}_2 \, \mathsf{SO}_4}_{\mathsf{Hg} \mathsf{SO}_4} & \bigcap_{1}^{\mathsf{I}} \mathsf{CH}_3 \, \mathsf{C} = \mathsf{CH}_2 & \longrightarrow \\ \mathsf{CH}_3 \, \mathsf{C} \equiv \mathsf{CH}_2 & \longrightarrow \\ \mathsf{CH}_3 \, \mathsf{C} = \mathsf{CH}_3 \, \mathsf{C} & \longrightarrow \\ \mathsf{CH}_3 \, \mathsf{C} = \mathsf{CH}_2 & \longrightarrow \\ \mathsf{CH}_3 \, \mathsf{C} = \mathsf{CH}_3 \, \mathsf{C} & \longrightarrow \\ \mathsf{CH}_3 \, \mathsf{C} = \mathsf{CH}_3 \, \mathsf{C} & \to \\ \mathsf{CH}_3 \, \mathsf{C} = \mathsf{CH}_3 \, \mathsf{C} & \to \\ \mathsf{CH}_3 \, \mathsf{C} = \mathsf{CH}_3 \, \mathsf{C} & \to \\ \mathsf{CH}_3 \, \mathsf{C} = \mathsf{CH}_3 \, \mathsf{C} & \to \\ \mathsf{CH}_3 \, \mathsf{C} = \mathsf{CH}_3 \, \mathsf{C} & \to \\ \mathsf{CH}_3 \, \mathsf{C} = \mathsf{CH}_3 \, \mathsf{C} & \to \\ \mathsf{CH}_3 \, \mathsf{C} = \mathsf{CH}_3 \, \mathsf{C} & \to \\ \mathsf{CH}_3 \, \mathsf{C} = \mathsf{CH}_3 \, \mathsf{C} & \to \\ \mathsf{CH}_3 \, \mathsf{C} = \mathsf{CH}_3 \,$

Reduction of Aromatic Compounds



Catalytic Oxidation of Alkanes

$$2CH_4 + O_2 \xrightarrow{Cu/523K/100atm} 2CH_3OH$$
 Methanol

$$CH_4 + O_2 \xrightarrow{MO_2O_3} HCHO + H_2O$$

 Δ Methanal

Combustion (Complete oxidation) of Alkanes

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

Methane
 $CH_3CH_2CH_3 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$
Propane

Oxidation of Benzene



Reduction of Carboxylic acid



Cyclization and Aromatization



Synthesis of Cycloalkanes





Catalytic Reforming

Alkanes are transformed into cycloalkanes and aromatic hydrocarbons by catalytic reforming.



The aromatic hydrocarbons produced by catalytic reforming are used as additives in gasoline and as starting materials for the petrochemical industry. Production of these aromatics is in the billions of pounds per year in the United States. **Periodic Properties**

Nuclear Charge

 The nuclear charge is the total charge of all the protons in the nucleus.

Generally, It increases with increase in atomic number across the period and down the group Only hydrogen's single electron experiences the full positive charge of its nucleus. For all other atoms, the nuclear charge that any given electron experiences is offset to some degree by other electrons.



Effective Nuclear Charge

- In a many-electron atom, electrons are both attracted to the nucleus and repelled by other electrons.
- Repulsion from other electrons reduces the attraction to the nucleus by a small amount giving rise to an "effective nuclear charge"
- The nuclear charge that an electron "feels" depends on both factors.
- Electrons in lower energy levels "shield" outer electrons from positive charge of nucleus.
- Effective nuclear charge: The net nuclear charge felt by an electron after shielding from other electrons in the atom is taken into account. $Z_{eff} = Z_{act} - Z_{shield}$.

Effective Nuclear Charge

The effective nuclear charge, Z_{eff} , is: $Z_{eff} = Z - S$

Where: Z = atomic number

S = screening constant, usually close to the number of inner (n-1) electrons.

For Na



Lithium has three protons and 1s²2s¹. The electron in the 2s orbital is shielded from the protons by the electrons of the 1s orbital. Thus, Z* felt by the 2s electron should be one rather than three. However, lithium's 2s electron does not behave as if it is experiencing exactly a +1 charge (Z* is 1.3 actually about charge units). The 2s orbital has two maxima in its radial probability function. and the lesser maxima penetrates within the maximum of the inner 1s electron. Although lithium's 2s electron spends most of its time in the outer lobe of that orbital feeling a nuclear charge of +1, some of the time it is inside the 1s orbital experiencing the full nuclear charge of +3. Thus, Z* is somewhat greater than +1.



Slater's Rules for Determining σ Z* = Z- σ

- The electronic structure of the atom is written in groupings as follows:
 (1s), (2s, 2p), (3s, 3p), (3d), (4s, 4p), (4d), (4f), (5s, 5p), (5d), (5f)...
- Electrons in higher groups than the electron you are considering (to the right on the list) do not shield electrons in lower groups.
- For **ns** or **np** electrons:
- Electrons in the same *ns, np* group contribute 0.35, except electrons in the *1s* orbital, where 0.30.
- Electrons in the *n-1* group(s) contribute **0.85**.
- Electrons in the *n*-2 or lower groups contribute **1.00**
- For nd and nf valence electrons:
 - Electrons in the same *nd* or *nf* group contribute 0.35.
 - Electrons in groups to the left contribute 1.00.



Calculation of Effective nuclear charge

Example: Calculate Z* for a 4s and a 3d electron in Zn

Determine the electron configuration for Zn

(1s)²(2s, 2p)⁸(3s, 3p)⁸(3d)¹⁰(4s)²

For a 4s electron:

Establish the screening constant for the 4s electron

 $\sigma = (2x0.30) + (1 \times 0.35) + (18 \times 0.85) + (10x1.00) = 26.55$

Calculate the effective nuclear charge

 $Z^* = Z - \sigma = 30 - 26.25 = 3.75$

For a 3d electron:

Establish the screening constant for the 3d electron

Calculate the effective nuclear charge



Z_{eff} and angular momentum

Penetration of orbitals: The ability of an electron to get close to the nucleus is called Penetration of electron.

- Electron in 2s orbital spends more time close to nucleus than electron in 2p
- 2s orbital lower in energy than 2p
- Shielding of 2s lower than 2p
- Shielding follows order: 3s>3p>3d
- Therefore the penetration of orbitals in a particular energy level (n) is given as under:

Allingood leiper Penetration Penetration Distance from the nucleus (b) Distance from the nucleus

s>**p**>**d**>**f**

• Uncertainty Principle: A small particle like electron, its location can not be exactly known and how it is moving.

• **De Broglie, Schrodinger and Heisenberg** believed that there is only the probability that electron can be found in certain volume in space around the nucleus. Orbital, Atomic orbital and Molecular orbital

- Orbital: It represents the probability of finding an electron in any one place around the nucleus.
- Atomic orbital: It may be defind as the region in space around the nucleus of the atom where the probability of finding the electron is maximum.
- Molecular orbitals: These are formed as a result from the overlap of two atomic orbitals, wherein a pair of electrons occupying.
Shapes of Atomic Orbitals

• Different atomic orbitals are denoted by letters. The **s** orbitals

are spherical, and **p** orbitals are dumbbell-shaped.



• Four of the five **d** orbitals have the same shape but different orientations in space.



Shapes of Bonding and Antibonding Molecular orbitals



Quantum Numbers

Quantum numbers can be used to describe the location of any one electron within an atom.

Four components:

1.Principal quantum number (n)

2.Azimuthal quantum number (I)

3.Magnetic quantum number (m)

4.Spin quantum number (m, or s)

1. Principal Quantum Number

Represented as "n".

n indicates the energy level.

n has a whole number value \geq 1.



2. Azimuthal Quantum Number

Represented as "I".

I indicates the orbital type.

I has a whole number value ≥ 0.
I = 0 represents the s-orbital
I = 1 represents the p-orbitals
etc.

3. Magnetic Quantum Number Represented as "m₁".

m is determined by the I value:

 $-l \le m_l \le +l$, where m_l are integers

Each m value represents a specific orbital.

Magnetic Quantum Number, m_/

Sublevel	1	m
S	0	0
р	1	-1,0,+1
d	2	-2,-1,0,1,+2
f	3	-3,-2,-1,0,+1,+2,+3

4. Spin Quantum Number

Represented as "s" or "m,".

Electrons spin in one of two directions.

s = +1/2 (up-spin) or s = -1/2 (down-spin)

Convention suggest up-spin electrons are placed in orbitals first.



Spin of electron Associated with magnetic field **Electronic Configration**

 Electronic Configration: It is the distribution of electrons in various orbitals of an atom on the basis of certain rules.

Filling Rules for Electron Orbitals

Aufbau Principle: Electrons are added in orbitals in order of increasing energy values. i. e. Orbital with lower energy is filed first;



Pauli Exclusion Principle

Pauli Exclusion Principle: An orbital can hold

a maximum of two electrons. To occupy the same orbital, two electrons must spin in opposite directions.

X	<u>1</u> 1s	<u> 11</u> 2 <i>s</i>
\checkmark	<u>↑↓</u> 1s	<u>↑↓</u> 2s

Hund's Rule

 Hund's Rule; Electron pairing in orbitals of same energy will not start until each orbital contains one electron





In the electronic configuration of nitrogen atom each p-orbital is singly filled.

Nitrogen:1s² 2s² 2p³



General rules for Electronic Configurations

General rules for writing electron configurations:

- 1. Electrons will reside in the available orbitals of the lowest possible energy.
- 2. Each orbital can accommodate a maximum of two electrons.
- 3. Electrons will not pair in degenerate orbitals if an empty orbital is available.
- 4. Orbitals will fill in the order indicated in the figure.



Electronic configuration of some elements



Condensed Electronic Configurations

Condensed Electron Configurations

- Neon (Z= 10) completes the 2p subshell. $1s^2 2s^2 2p^6$
- Sodium (Z = 11) marks the beginning of a new period. 1s² 2s² 2p⁶ 3s¹
- So, we write the condensed electron configuration for sodium as

Na: [Ne] 3s¹

- [Ne] represents the electron configuration of neon.
- **Core electrons:** electrons in [Noble Gas].
- Valence electrons: electrons outside of [Noble Gas].

Anomalous Electron Configurations

- A few exceptions to the Aufbau principles exist. Stable configuration:
 - half-filled d shell:

Expected	Actual
• Cr [Ar] 4S ² 3d ⁴	Cr has [Ar]4s ¹ 3d ⁵
• Mo [Kr] 5s ² 4d ⁴	Mo has [Kr] 5s ¹ 4d ⁵
filled d subshell:	
Expected	Actual
• Cu [Ar]4s ² 3d ⁹	Cu has [Ar]4s ¹ 3d ¹⁰
 Ag [Kr]5s²4d⁹ 	Ag has [Kr]5s ¹ 4d ¹⁰

• Exceptions occur with larger elements where orbital energies are similar.

Valence electrons

- When an atom undergoes a chemical reaction, only the outermost electrons are involved.
- These electrons are of the highest energy and are most away from the nucleus. These are the <u>valence electrons</u>.
- In K there is **one** valence electron



MODERN PERIODIC TABLE



PERIODIC PROPERTIES

- When elements are arranged in order of increasing atomic number, certain sets of properties recur periodically.
- (1) Effective Nuclear Charge
- (2) Atomic radius
- (3) Ionization energy
- (4) Electron affinities
- (5) Electronegativity

Variation of Effective Nuclear Charge in Group and Period

• Across Period: The effective nuclear charge (Zeff) increases from left to right due to addition of electrons in same energy



 Down the group: In a group from top to bottom the effective nuclear charge decrease due to addition of new energy shell and screening of outer most electron by the inner.



Atomic Radius

The atomic radius is one half of the distance between the nuclei of two atoms of the same element when the atoms are joined.



Classification of Atomic Radius

- We can classify atomic radius into three
- a) Covalent radius
- b) Metallic radius
- c) Van der Waals radius

Covalent Radius

• **Covalent Radius:** One half of the distance between the nuclei of two covalently bounded atoms of the same element in a molecule, is taken as covalent radius of the atom of that element.



Covalent radius

• Definition : half the length from one nuclei to another atom's nuclei bonded covalently.



Metallic radius

 Definition : half of the distance between the two adjacent metal atoms in the metallic lattice.



Vander Waals' Radius

• Vander Waals radius: It may be defind as one half of the distance between the nuclei of two adjacent identical atoms of two neighbouring molecules of an element in solid state.



Van der Waals radius

- Definition : half the distance between two neighbouring atoms which are not chemically bonded in solid state.
- Appear like touching, less attractive force.



Ionic Radius

 Ionic Radius: It may be defind as the distance from the nucleus of an ion upto which it has influence on its electron cloud. An *ion* is formed when an atom, or group of atoms, has a net positive or negative charge (why?).

If a neutral atom **looses** one or more electrons it becomes a cation.



If a neutral atom gains one or more electrons

it becomes an anion.





Cation is always **smaller** than atom from which it is formed. **Anion** is always **larger** than atom from which it is formed.



Relative Sizes of Some Atoms and Ions



Variation of atomic Radius

- In period: In general atomic radius decreases across the period from left to right.
- Cause: As we move from left to right the effective nuclear charge increases and addition of new electron takes place in the same energy shell. The greater the effective nuclear charge, the greater would be the force with which the electrons are pulled towards the nucleus. Hence the atomic radius decreases in the period.
- 1s²2s¹, 1s²2s², 1s²2s²2p¹, 1s²2s²2p², 1s²2s²2p³, 1s²2s²2p⁴, 1s²2s²2p⁵, 1s²2s²2p⁶,
- Addition of electron takes place in 2nd energy shell.

Variation of atomic Radius

- In Group: The atomic size increases in a group on moving from top to bottom.
- Cause: In a particular group the increase in atomic radius is due to addition of new energy shell. No doubt the nuclear charge also increases, which may decrease the size. But this increased nuclear charged is neutralized by the screen effect to some extent.
- 1s¹, 1s²2s¹, 1s²2s²2p⁶3s¹, 1s²2s²2p⁶3s²3p⁶4s¹, 1s²2s²2p⁶3s²
 3p⁶4s²3d¹⁰5s¹

	Increasing atomic radius							
	1A H 37	2A	3 A	4A	5A	6A	7A	8A He 31
S	Li 152	Be 112	B 0 85	C 0 77	N 0 70	0 © 73	F 0 72	Ne © 70
ic radiu	Na 186	Mg 160	AI 143	Si 118	P 110	S) 103	CI 99	Ar 98
atom	к	Ca	Ga	Ge	As	Se	Br	Kr
sing	227	197	135	123	120	117	114	112
creas	Rb	Sr	In	Sn	Sb	Te		Xe
Ĕ	248	215	166	140	141	143	133	131
	Cs	Ba	Т	Pb	Bi	Po	At	Rn
	265	222	171	175	155	164	142	140
Ionization Energy

 Ionization Energy: It may be defind as the amount of energy required to remove the electron from outer most energy shell of an isolated gaseous atom.



Successive Ionization Energies

- **First ionization energy:** The energy required to remove the first electron from an atom is called the first ionization energy.
- Second ionisation energy: The energy required to remove an electron from an ion with a 1+ charge is called the second ionization energy.
- $M_{(g)} + IE \longrightarrow M_{(g)}^{+} + e^{-}$ first ionization energy $M_{(g)}^{+} + IE \longrightarrow M_{(g)}^{2+} + e^{-}$ second ionization energy

$$||E_1| < ||E_2| < ||E_3|$$

- Effective nuclear charge
- Atomic size i.e. atomic radius
- Principle quantum number
- Shielding effect
- Half filled and completely filled orbitals
- Nature of orbitals
- The extent of penetration of valence electrons

- Atomic size: As the distance between the electron and the nucleus increases, i.e., as the size of the atom increases, the outermost electrons are less tightly held by the nucleus. Thus, it becomes easier to remove an outermost electron. Thus ionization enthalpy decreases with increases in atomic size.
- Effective nuclear charge: The greater the effective charge on the nucleus of an atom, the more difficult it would be to remove an electron from the atom because electrostatic force of attraction between the nucleus and the outermost electron increases. So greater energy will be required to remove the electron.

Penetration effect of orbitals: The penetration power of the electrons in various orbitals decreases in a given shell (same value of n) in the order: s>p>d>f. Since the penetration power of s-electron towards the nucleus is more, it will be closer to the nucleus and will be held firmly. Thus, for the same shell, the ionization enthalpy would be more to remove the s-electrons in comparison with the p-electron which in turn would be more than that for d-electron and so on. The order of energy required to remove electron from s, p, d-and f-orbitals of a shell is s>p>d>f.

Shielding or screening effect: Ionization enthalpy decreases when the shielding effect of inner electrons increases. This is because when the inner electron shells increases, the attraction between the nucleus and the outermost electron decreases. Screening effect results in decrease of force of attraction between the nucleus and the outermost electron and lesser energy is required to separate the electron. Thus the value of I.P. decreases.

- Stability of half-filled and fully-filled orbitals: If an atom has half-filled or completely filled sub-levels, its ionization enthalpy is higher than that expected normally from its position in the periodic table. This is because such atom, have extra stability and hence it is difficult to remove electrons from these stable configurations.
- According to Hund's rule the stability of half filled or completely filled degenerate orbitals is comparatively high. So comparatively more energy is required to separate the electron from such atoms.

Variation of ionization energy in period

- In Period: In general, the ionization energy increases as we move along a period from left to right.
- Cause: On moving across a period, the atomic size decreases and nuclear charge increases and therefore, the force of attraction exerted by the nucleus on electron in the outer most shell increases. Consequently, it becomes difficult to remove the electron and hence ionization energy increases.

Variation of ionization energy in Group

- In Group: In general, the ionization energy decreases as we move a group from top to bottom.
- **Cause:** On moving in a group, the atomic size increases and nuclear charge also increases which is neutralized by the screening effect. The overall effect of increase in atomic size and the screening effect is much more than the overall affect of increase in nuclear charge and therefore, the force of attraction exerted by the nucleus on electron in the outer most shell decreases. Consequently, it becomes easy to remove the electron and hence ionization energy decreases.

Electron Affinity

 Electron Affinity: It may be defined as the amount of energy released when an electron is added to neutral gaseous atom.

 $X_{(g)}$ + $e^- \longrightarrow X_{(g)}^-$ + Energy (EA)

Factors Affecting Electron Affinity

- Nuclear Charge: Higher the nuclear charge of the atom more strongly it will attract additional electron. Therefore electron affinity increases with increase in nuclear charge.
- Atomic Size: Smaller the size of atom lesser will be the distance between nucleus and the extra electron. Therefore, electrostatic force of attraction will be strong and hence electron affinity will be higher.
- Electronic Configurations: The stable electronic configurations (like half-filled and fully-filled) do not show much attraction for new electron so, have either zero or very low electron affinity.

Variation of Electron Affinity

- Across Period: On moving across a period, the atomic size decreases and nuclear charge increases.
 Consequently, force exerted by nucleus on new electron increases. i.e. the electron affinity increases as we move from left to right in a period.
- In Group: In a particular group from top to bottom the atomic size increases and nuclear charge also increases. However, the effective nuclear charge decreases due to screening effect. Consequently, atom will have less tendency to attract additional electron towards itself. Hence electron affinity decreases in group as we move from top to bottom.

Low Electron Affinity of F

On moving down the group Cl → Br → I, the electron affinity decreases. However the Fluorine has unexpectedly low electron affinity than Chlorine. It is due to the small size of Fluorine. The addition of an extra electron feels strong electron-electron repulsion in compact 2p subshell. Thus F has low electron affinity.

ELECTRONEGATIVITY

 Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons.



Electrons are equally attracted by atoms A and B as in H-H, CI-CI



Electrons are slightly more attracted To atom B than A as in **H-CI**



Electron are totally attracted by B and atom A has lost the control of electron as in **NaCl**

Factors Affecting Electronegativity

1. Charge on atom	HCIO +1,	HCIO ₄ +5
2. Hybridization	sp>sp²>s	p ³
3. Effect of substituent	CF ₃ I,	CH ₃ I

4. Effective nuclear charge $E_{zeff} \alpha EN$

Variation of Electronegativity

Electronegativity is the ability of an atom of an element to attract electrons when the atom is in a compound.

In general, electronegativity values decrease from top to bottom within a group due to decrease in effective nuclear charge. However in a period, electronegativity values increases from left to right in period due to increase in effective nuclear charge. **Coordination complex:** A compound in which central metal atom(usually a metal ion) bonded (coordinated) to a group of surrounding neutral molecules or ions is called coordination compound.

Ligand (ligare is Latin, to bind): A ligand is a molecule or ion that is directly bonded to a metal ion in a coordination complex

A ligand uses a **lone pair of electrons** (Lewis base) to bond to the metal ion (Lewis acid)





Ligands

- The molecules or ions coordinating to the metal are the ligands.
- They are usually anions or polar molecules.
- These must have lone pairs to interact with metal



The Interaction Between a Metal Ion and a Ligand Can Be Viewed as a Lewis Acid-Base Reaction



Types of Ligands

Ligand	Formula	Name
Fluoride ion	:F ⁻	Fluoro
Chloride ion	:Cl ⁻	Chloro
Nitrite ion	$:NO_2^-$	Nitro
	:ONO ⁻	Nitrito
Carbonate ion	$:OCO_2^{2-}$	Carbonato
Cyanide ion	:CN ⁻	Cyano
Thiocyanate ion	:SCN ⁻	Thiocyanato
	:NCS ⁻	Isothiocyanato
Hydride ion	:H ⁻	Hydrido
Oxide ion	$:O^{2-}$	Oxido
Hydroxide ion	:OH-	Hydroxo
Water	:OH ₂	Aqua
Ammonia	:NH ₃	Ammine
Carbon monoxide	:CO	Carbonyl
Nitrogen monoxide	:NO	Nitrosyl

Types of Ligands



Coordination Number





The number of these atoms is the coordination number.





Oxidation Number: The oxidation number of central atom in a complex is defined as charge it would carry if all the ligands are removed along with the electron pair that are shared with the central atom.

Calculation of Oxidation Number:

In the complex $[Co(en)_2Cl(ONO)]$ the charge on the complex is zero, whereas the charge on the central metal ion may be calculated as under :

[Co		$(en)_2$		Cl	(ONO)]
t		Ļ		Ļ	Ļ
x	+	2(0)	+	(- 1)	+(-1)=0
			r = +	2	

Similarly, in the complex ion $[Co(NH_3)_2Cl_4]^{2+}$ the charge on the cationic complex is + 2 and the charge on the central metal ion is

[Co	$(NH_3)_2$	Cl ₄] ²⁻
1	1	↓ ·
x +	2(0)	+4(-1) = -2
		x = +2

Oxidation number of the central metal ion.

$[Co(NH_3)_4 CI (NO_2)] K_3[Fe(CN)_6]$

x + 4(0) + 1(-1) + 1(-1) = 0 3(1) + x + 6(-1) = 0

x = + 2 x = + 3

Main features of valence bond theory

1. The central metal atom in complex makes available empty

orbitals equal to its coordination number.

Orbitals of Co ³⁺ ion	3d 11 11 11 1 1	4s Vacan	4p A t orbitals	4d
	Coordination nu	mber of	M (Co ³⁺) = 4	

2. The empty orbitals of metal hybridise to give a new set of equivalent hybridized orbitals with definite geometry.

Illustrative Example

Geometry of the compound $[Cr(CO)_6]$.

Solution



 $d^{2}sp^{3}$ hybridization = octahedral geometry

Crystal Field Theory

- 1. The interactions between the metal ion and the ligands are purely electrostatic (ionic).
- 2 The ligands are regarded as point charges.
- 3. If the ligand is negatively charged: ion-ion interaction.
- 4. If the ligand is neutral : ion-dipole interaction.
- 5. The electrons on the metal are under repulsive from

those on the ligands.





Tetrahedral and Octahedral crystal field Splitting

The splitting observed in a tetrahedral crystal field is opposite of splitting in octahedral complex.



Crystal field theory

The **spectrochemical series** places ligands in order of increasing field strength, with a somewhat arbitrary cutoff between those we consider to be generally strong field ligands and those we consider to be generally weak field ligands.

 $I^- < Br^- < CI^- < NO_3^- < F^- < OH^- < H_2O$

< py < NH_3 < NO_2^- < en < CN^- < CO

Geometry of $[PtCl_4]^{2-}$ and $[NiCl_4]^{2-}$.



 dsp^2 hybrid = square planar.





sp³ hybrid = tetrahedral.

 $[Co(NH_3)_6]^{3+}$ is diamagnetic and $[CoF_6]^{3-}$ is paramagnetic. Explain with the help of valence bond theory.

Solution





Vander Waal's Forces



Chemical bond

- Atoms, except those of **noble gases** do not exist free.
- Chemical Bond: It may be defined as the force of attraction that hold the atom in molecules together.
- This phenomenon of combination, called chemical bonding, involves bonding of two or more atoms either through transference of electrons or sharing of electrons among themselves so that all the atoms acquire stable electronic configuration.
Types of Chemical Bonds

• Covalent Bond: The bond formed by the sharing of electrons

among the atoms is called covalent bond.



 Covalency: The number of electrons that an atom contributes for sharing in a covalent bond. In H₂O molecule oxygen contributes two electrons , so its Covalency is two.



Ionic Bond

 Ionic bond: The electrostatic force of attraction between the oppositely charged ions formed by the transference of electrons is called ionic bond.



Generally, this type of bond formation takes place between the atoms out of which one has **low ionization energy** (i.e. high tendency to lose electron) and other has high **electron affinity** (high tendency to gain electron).

Coordinate bond

• **Coordinate bond:** The covalent bond in which both the electrons for sharing between atoms are contributed by one atom only is called coordinate covalent bond.





Electronegativity Difference	δ+ δ- H-F 2.1 4.0	$ \frac{\delta^{+}}{H-Cl} $ 2.1 3.0
	1.9	0.9
	More ionic	More covalent
	than H-Cl	than HF

Polarization and Polarizability

- The bond in a compound like **X**⁺**Y**⁻ may be considered to be 100% ionic.
- It will always have some degree of covalent character.
- When two oppositely charged ions (X⁺ and Y⁻) approach each other, the cation attracts electrons in the outermost shell of the anion but repels the positively charged nucleus.



Region where electrons are "shared"

- This results in a **distortion**, **deformation or polarization** of the anion. If the degree of polarization is quite small, an ionic bond is formed, while if the degree of polarization is large, a covalent bond results.
- The ability of a **cation** to distort an anion is known as its **polarization power** and the tendency of the **anion** to become polarized by the cation is known as its **polarizability**.

Factors affecting the polarization

- Cation polarizing power increases with – small radius (increasing charge density)
 - large positive charge (increasing charge density)
- Anion polarizability increases with
 - large radius (outer electrons far from nucleus and shielded by inner shells)
 - increasing negative charge increases its size
- Increasing anion polarisation means increasing covalent character to the bonding
 - indicated by large difference between theoretical and experimental lattice energies



Covalent Character of Ionic Bond

- The polarizing power and polarizability that enhances the formation of covalent bonds is favoured by the following factors:
- Small cation: the high polarizing power stems from the greater concentration of positive charge on a small area. This explains why LiBr is more covalent than KBr (Li⁺ 90 pm cf. K⁺ 152 pm).
- Large anion: the high polarizability stems from the larger size where the outer electrons are more loosely held and can be more easily distorted by the cation. This explains why for the common halides, iodides, are the most covalent in nature (I⁻ 206 pm).
- Large charges: as the charge on an ion increases, the electrostatic attractions of the cation for the outer electrons of the anion increases, resulting in the degree of covalent bond formation increasing.

Hard and Soft Acids

- Acid: According to Lewis concept an acid is a substance which can accept electron. e. g. BF₃, AlCl₃, FeCl₃ etc.
- Base: According to Lewis concept an acid is a substance which can donate electron. e. g. NH₃, OH⁻, H₂O etc.
- Hard Acid: The metal ion with no or lesser number of d electrons or metal ions in higher oxidation states are classified as hard acids. e. g. Li⁺, Na⁺, Mg²⁺, Ca²⁺, Cr³⁺, Ti⁺, Th⁴⁺ etc.
- Soft acid: The heavier metals with nearly full d electrons or metals in lower oxidation states and metals with bigger size are classified as soft acids. e. g. Ag⁺, Cu⁺, Pd²⁺, Cd²⁺, Cl⁻, Br⁻ etc.

Hard and Soft Bases

- Hard Bases: The ligands with small ionic radii, weekly polarizable and prefer to form stable complexes with lighter metal ions are called Hard bases. NH₃, H₂O, RNH₂,OH⁻, F⁻ etc.
- Soft Bases: The ligands with bigger size, highly polarizable and prefer to make complexes with heavy metals are called soft acids. e. g. RSH, RS⁻, R₂S, I⁻, CN⁻, SCN⁻, S₂O₃⁻, R₃P, R₃As RNC, CO, C₂H₄, C₆H₆, R⁻,

Hard Acid and Hard Base

Hard Acid	Hard Base
Small ionic radii,	Large ionic radii,
High positive charge,	Low positive charge,
Strongly solvated,	Completely filled atomic orbitals
Empty orbitals in the valence	Cu+, Ag+, Au+, Hg+ , Cs+ , Tl+ ,
H ⁺ , Li ⁺ , Na ⁺ , K ⁺ , Be ²⁺ , Mg ²⁺ ,	Hg²+ Pd²+, Cd²+ , Pt²+
Ca ²⁺ , Sr ²⁺ , Sn ²⁺ Al ³⁺ , Ga ³⁺ ,	
In ³⁺ , Cr ³⁺ , Co ³⁺ , Fe ³⁺ , La ³⁺ ,	
Si ⁴⁺ , Ti ⁴⁺ , Zr ⁴⁺ , Th ⁴⁺ ,	

Soft Acid and Soft Base

Soft Acid	Soft Base
Small ionic radii,	Large ionic radii,
Highly electronegative,	Intermediate
Weakly polarizable,	electronegativity,
Strongly solvated,	highly polarizable
H ₂ O, OH ⁻ , F ⁻ , Cl ⁻ ,	RSH, RS- , R ₂ S, I ⁻ , CN ⁻ ,
CH ₃ COO ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ ,	SCN ⁻ , S ₂ O ₃ ^{2 -} , R ₃ P, R ₃ As
CO ₃ ²⁻ , NO ₃ ⁻ , CIO ₄ ⁻ , ROH,	$(RO)_3P$, RNC, CO, C_2H_4 ,
RO^{-} , $R_{2}O$, NH_{3} ,	C ₆ H ₆ , R- , H

HSAB Principle and its Applications

- HSAB Principle: According to this principle, hard acids prefer to combine with hard bases, whereas soft acids prefer to combine with soft bases.
- Stability of complex: Ag⁺ ion is a soft acid, forms stable complex (Agl₂⁻) with soft base I⁻. Whereas with F⁻ ion (hard base) forms unstable complex (Ag₂F⁻).

•	Ag+ +	2I⁻ →	Agl ₂ -
	Soft acid	Soft Base	Stable
•	Ag+ +	$2F^{-} \longrightarrow$	Ag ₂ F ⁻
	Soft Acid	Hard base	Unstable

2. Predicting of coordination of ambient ligands with metal: The ligands having two donor atoms and may bind to central metal atom through either of its two donor atoms are called ambient ligands. For example [SCN]⁻ is an ambient ligand ;it can coordinate through N or S.

With Co^{2+} metal it form complex $[Co(NCS)_4]$ binding through N as Co^{2+} is a hard acid and so prefers to bind through hard base N.

However **Pd**²⁺ metal (**soft acid**) forms complex [Pd(SCN)₄] binding through Soft Base **S**.

3. Predicting Feasibility of Reaction: Reaction between Lil and CsF always proceed to give LiF and CsI. it is an intresting example of preferential combination of **soft-soft** and **hard-hard** species.

Lil	+	CsF	\longrightarrow	LiF	+	CsI
hard-soft		soft-hard		hard-hard		soft-soft

 Recovery of Au: The softest metal ion Au⁺(aq) is recovered in mining operations by suspending it in a dilute solution of CN-, which dissolves the Au.

 $4 \operatorname{Au}(s) + 8 \operatorname{CN}^{-}(aq) + O_2(g) + 2 \operatorname{H}_2 O \longrightarrow 4[\operatorname{Au}(\operatorname{CN})_2]^{-}(aq) + 4 \operatorname{OH}^{-}$

5. Predicting the solubility of Compound in H₂O: Why is Agl(s) water-

insoluble, but Lil water-soluble?

Agl is a soft acid-soft base combination, while Lil is hard-soft.

The interaction between Li⁺ and I⁻ ions is not strong.

AgI(s) + H₂O(l) \longrightarrow essentially no reaction Lil(s) + H₂O(l) \longrightarrow Li+ (aq) + l⁻ (aq) 6. Hydrogen Bonding: The strong hydrogen bond is possible in cases of H₂O, NH₃ and HF, since the donor atoms (F, O & N) are HARD BASES and their interactions with partially positively charged H, which is a HARD ACID, are stronger.

7. Precipitation reactions:

The softer acids like Ag⁺, Hg⁺, Hg²⁺ etc., and border line acids like Fe²⁺,Ni²⁺, Cu²⁺, Zn²⁺, Pb²⁺ etc., can be precipitated as sulfides from their aqueous solutions since S²⁻ ion is a softer base. CuS, HgS, NiS, FeS, ZnS, PbS etc. But Ca²⁺ and Mg²⁺ hard acids appear as carbonates CaCO₃, MgCO₃

Postulates of VSEPR Theory

- 1. The shape of any covalent molecule depends on the **number** of pairs of **electrons** around the central atom.
- The electron pairs in the valence shell around the central atom of a molecule repel each other and arrange themselves as far apart from each other as possible to minimize the repulsions between them
- 3. There are two types of valence shell electron pairs viz., i) Bond pairs and
 ii) Lone pairs. The order of repulsion between different types of electron pairs is as follows:
- Lone pair Lone pair > Lone Pair Bond pair > Bond pair Bond pair
- When the valence shell of central atom contains only bond pairs, the molecule assumes symmetrical geometry due to even repulsions between them.
- 5. However the symmetry is distorted when there are also lone pairs along with bond pairs due to uneven repulsion forces.

Geometry of Molecules With 2 Bond Pairs

 In BeCl₂ molecule the central atom Be is surrounded by two Cl atoms. The two bond pairs occupy positions such that the distance between them is maximum and so minimum repulsion. Hence the bonds are at an angle of 180 degrees from each other.





Geometry of NH₃

Ammonia has four groups of electrons and so it has the same electronic geometry as other molecules like CH₄.

In case of NH_3 however, one group has an unshared pair of electrons, and as per VSEPR the four electron groups around a central atom will be directed towards the corners of tetrahedron to give maximum separation.

However due to greater Lone pair –bond pair repulsion than bond pair –bond pair . The bond pairs will move close to each other giving distorted tetrahedral geometry (trigonal pyramid) with bond angle 107^o



Geometry of PF₅

Determine the hybridization of P in PF₅



Trigonal Bipyramid





Axial F atoms are in a different environment to the equatorial F atoms The red lines outline a trigonal bipyramid. Black lines show the covalent bonds

Geometry of H₂O Molecule-V Shape or Bent



Geometry of SF₆







Organic compounds with an electronegative atom or an electron-withdrawing group bonded to a *sp*³ carbon undergo substitution or elimination reactions



Halide ions are good leaving groups. Substitution reaction on these compounds are easy and are used to get a wide variety of compounds

R



+

X⁻ + H**Y**

Elimination

SUBSTITUTION REACTION WITH HALIDES



SUBSTITUTION REACTION WITH HALIDES



MECHANISM OF SN2 REACTIONS

The rate of reaction depends on the concentrations of both reactants.

When the hydrogens of bromomethane are replaced with methyl groups the reaction rate slow down.

The reaction of an alkyl halide in which the halogen is bonded to an asymetric center leads to the formation of only one stereoisomer

Alkyl halide	Relative rate
H H ^{WW} Br H	1200
H ₃ C H ^{WW} H	40
H ₃ C H ^{ww} H ₃ C	1
H ₃ C H ₃ C ^{WW} H ₃ C	≈ 0

MECHANISM OF SN2 REACTIONS

Hughes and Ingold proposed the following mechanism:



Transition state

Increasing the concentration of either of the reactant makes their collision more probable.

MECHANISM OF SN2 REACTIONS



FACTOR AFFECTING SN2 REACTIONS

The leaving group

relative rate	s of reaction	<u>рК_а НХ</u>	
$HO^{-} + RCH_{2}I \longrightarrow$	RCH ₂ OH + I	30 000	-10
$HO^{-} + RCH_{2}Br \longrightarrow$	RCH ₂ OH + Br	10 000	-9
$HO^{-} + RCH_2CI \longrightarrow$	RCH ₂ OH + Cl	200	-7
$HO^{-} + RCH_2F \longrightarrow$	RCH ₂ OH + F	1	3.2

The nucleophile

In general, for halogen substitution the strongest the base the better the nucleophile.



SN2 REACTIONS WITH ALKYL HALIDES



SUBSTITUTION REACTIONS WITH HALIDES



1-bromo-1,1-dimethylethane



1,1-dimethylethanol

If concentration of (1) is doubled, the rate of the reaction is doubled.

If concentration of (2) is doubled, the rate of the reaction is not doubled.

Rate law:

rate = k [1-bromo-1,1-dimethylethane]

this reaction is an example of a SN1 reaction. S stands for substitution N stands for nucleophilic

1 stands for unimolecular

MECHANISM OF SN1 REACTIONS

The rate of reaction depends on the concentrations of the alkyl halide only.

When the methyl groups of 1-bromo-1,1-dimethylethane are replaced with hydrogens the reaction rate slow down.

The reaction of an alkyl halide in which the halogen is bonded to an asymetric center leads to the formation of two stereoisomers

Alkyl halide	Relative rate
H H ^{WW} H	≈ 0 *
H ₃ C H ^{ww} H	≈ 0 *
H ₃ C H ^{ww} H ₃ C	12
H ₃ C H ₃ C ^{WW} H ₃ C	1 200 000

* a small rate is actually observed as a result of a SN2

MECHANISM OF SN1 REACTIONS


MECHANISM OF SN1 REACTIONS



FACTOR AFFECTING SN1 REACTION

Two factors affect the rate of a SN1 reaction:

- The ease with which the leaving group dissociate from the carbon
- The stability of the carbocation

The more the substituted the carbocation is, the more stable it is and therefore the easier it is to form. As in the case of SN2, the weaker base is the leaving group, the less tightly it is bonded to the carbon and the easier it is to break the bond

The reactivity of the nucleophile has no effect on the rate of a SN1 reaction

COMPARISON SN1 – SN2

SN1	SN2
A two-step mechanism	A one-step mechanism
A unimolecular rate-determining step	A bimolecular rate-determining step
Products have both retained and inverted configuration relative to the reactant	Product has inverted configuration relative to the reactant
Reactivity order: $3^{\circ} > 2^{\circ} > 1^{\circ} > methyl$	Reactivity order: methyl > $1^{\circ} > 2^{\circ} > 3^{\circ}$



ELIMINATION REACTIONS



1-bromo-1,1-dimethylethane

Rate law:

rate = k [1-bromo-1,1-dimethylethane][OH⁻]

this reaction is an example of a E2 reaction. E stands for elimination 2 stands for bimolecular

THE E2 REACTION



THE E1 REACTION



PRODUCTS OF ELIMINATION REACTION



For both E1 and E2 reactions, tertiary alkyl halides are the most reactive and primary alkyl halides are the least reactive The greater the number of alkyl substituent the more stable is the alkene

COMPETITION BETWEEN SN2/E2 AND SN1/E1



- SN2 and E2 are favoured by a high concentration of a good nucleophile/strong base
- SN1 and E1 are favoured by a poor nucleophile/weak base, because a poor nucleophile/weak base disfavours SN2 and E2 reactions

COMPETITION BETWEEN SUBSTITUTION AND ELIMINATION SN2/E2 conditions:

In a SN2 reaction: $1^{\circ} > 2^{\circ} > 3^{\circ}$ In a E2 reaction: $3^{\circ} > 2^{\circ} > 1^{\circ}$



COMPETITION BETWEEN SUBSTITUTION AND ELIMINATION SN1/E1 conditions:

All alkyl halides that react under SN1/E1 conditions will give both substitution and elimination products (≈50%/50%)

UV VISIBLE Spectroscopy

- I. Introduction
 - A. UV radiation and Electronic Excitations
 - 1. The difference in energy between molecular bonding, non-bonding and anti-bonding orbitals ranges from 125-650 kJ/mole
 - 2. This energy corresponds to EM radiation in the ultraviolet (UV) region, 100-350 nm, and visible (VIS) regions 350-700 nm of the spectrum
 - 3. For comparison, recall the EM spectrum:



- 4. Using IR we observed vibrational transitions with energies of 8-40 kJ/mol at wavelengths of 2500-15,000 nm
- 5. For purposes of our discussion, we will refer to UV and VIS spectroscopy as UV

- I. Introduction
 - B. The Spectroscopic Process
 - 1. In UV spectroscopy, the sample is irradiated with the broad spectrum of the UV radiation
 - 2. If a particular electronic transition matches the energy of a certain band of UV, it will be absorbed
 - 3. The remaining UV light passes through the sample and is observed
 - 4. From this residual radiation a spectrum is obtained with "gaps" at these discrete energies this is called an *absorption spectrum*



- I. Introduction
 - C. Observed electronic transitions
 - 1. The lowest energy transition (and most often obs. by UV) is typically that of an electron in the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO)
 - 2. For any bond (pair of electrons) in a molecule, the molecular orbitals are a mixture of the two contributing atomic orbitals; for every bonding orbital "created" from this mixing (σ , π), there is a corresponding antibonding orbital of symmetrically higher energy (σ^* , π^*)
 - 3. The lowest energy occupied orbitals are typically the σ ; likewise, the corresponding anti-bonding σ^* orbital is of the highest energy
 - 4. π -orbitals are of somewhat higher energy, and their complementary antibonding orbital somewhat lower in energy than σ^* .
 - 5. Unshared pairs lie at the energy of the original atomic orbital, most often this energy is higher than π or σ (since no bond is formed, there is no benefit in energy)

- I. Introduction
 - C. Observed electronic transitions
 - 6. Here is a graphical representation



- I. Introduction
 - C. Observed electronic transitions
 - 7. From the molecular orbital diagram, there are several possible electronic transitions that can occur, each of a different relative energy:



- I. Introduction
 - C. Observed electronic transitions
 - 7. Although the UV spectrum extends below 100 nm (high energy), oxygen in the atmosphere is not transparent below 200 nm
 - 8. Special equipment to study *vacuum* or *far UV* is required
 - 9. Routine organic UV spectra are typically collected from 200-700 nm
 - 10. This limits the transitions that can be observed:

$$\sigma \rightarrow \sigma^*$$
alkanes150 nm $\sigma \rightarrow \pi^*$ carbonyls170 nm $\pi \rightarrow \pi^*$ unsaturated cmpds.180 nm $n \rightarrow \sigma^*$ O, N, S, halogens190 nm $n \rightarrow \pi^*$ carbonyls300 nm

- I. Introduction
 - D. Selection Rules
 - 1. Not all transitions that are possible are observed
 - 2. For an electron to transition, certain quantum mechanical constraints apply these are called "selection rules"
 - For example, an electron cannot change its spin quantum number during a transition – these are "forbidden" Other examples include:
 - the number of electrons that can be excited at one time
 - symmetry properties of the molecule
 - symmetry of the electronic states
 - 4. To further complicate matters, "forbidden" transitions are sometimes observed (albeit at low intensity) due to other factors

- I. Introduction
 - E. Band Structure
 - 1. Unlike IR (or later NMR), where there may be upwards of 5 or more resolvable peaks from which to elucidate structural information, UV tends to give wide, overlapping bands
 - It would seem that since the electronic energy levels of a pure sample of molecules would be quantized, fine, discrete bands would be observed – for atomic spectra, this is the case
 - In molecules, when a bulk sample of molecules is observed, not all bonds (read – pairs of electrons) are in the same vibrational or rotational energy states
 - 4. This effect will impact the wavelength at which a transition is observed very similar to the effect of H-bonding on the O-H vibrational energy levels in neat samples

- I. Introduction
 - E. Band Structure
 - 5. When these energy levels are superimposed, the effect can be readily explained any transition has the possibility of being observed



Instrumentation and Spectra

- A. Instrumentation
 - 1. The construction of a traditional UV-VIS spectrometer is very similar to an IR, as similar functions sample handling, irradiation, detection and output are required
 - 2. Here is a simple schematic that covers most modern UV spectrometers:



- IV. Structure Determination
 - A. Dienes
 - 1. General Features

The $\Psi_2 \rightarrow \Psi_3^*$ transition is observed as an intense absorption (e = 20,000+) based at 217 nm within the observed region of the UV

While this band is insensitive to solvent (as would be expected) it is subject to the bathochromic and hyperchromic effects of alkyl substituents as well as further conjugation

Consider:



IV. Structure Determination

A. Dienes

2. Woodward-Fieser Rules

Woodward and the Fiesers performed extensive studies of terpene and steroidal alkenes and noted similar substituents and structural features would predictably lead to an empirical prediction of the wavelength for the lowest energy $\pi \rightarrow \pi^*$ electronic transition

This work was distilled by Scott in 1964 into an extensive treatise on the Woodward-Fieser rules in combination with comprehensive tables and examples – (A.I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*, Pergamon, NY, 1964)

A more modern interpretation was compiled by Rao in 1975 – (C.N.R. Rao, *Ultraviolet and Visible Spectroscopy*, 3rd Ed., Butterworths, London, 1975)

- IV. Structure Determination
 - C. Aromatic Compounds
 - 2. Substituent Effects
 - a. Substituents with Unshared Electrons
 - pH can change the nature of the substituent group
 - deprotonation of oxygen gives more available *n*-pairs, *lowering* transition energy
 - protonation of nitrogen eliminates the *n*-pair, *raising* transition energy

	Primary		Seco	Secondary	
Substituent	λ_{max}	Е	λ_{max}	Е	
-H	203.5	7,400	254	204	
-OH	211	6,200	270	1,450	
-0-	235	9,400	287	2,600	
-NH ₂	230	8,600	280	1,430	
$-NH_3^+$	203	7,500	254	169	
-C(O)OH	230	11,600	273	970	
-C(O)O ⁻	224	8,700	268	560	

- IV. Structure Determination
 - C. Aromatic Compounds
 - 2. Substituent Effects
 - b. Substituents Capable of π -conjugation
 - When the substituent is a π -chromophore, it can interact with the benzene π -system
 - With benzoic acids, this causes an appreciable shift in the primary and secondary bands
 - For the benzoate ion, the effect of extra *n*-electrons from the anion reduces the effect slightly

	Primary		Seco	ndary
Substituent	λ_{max}	Е	λ_{max}	Е
-C(O)OH	230	11,600	273	970
-C(O)O ⁻	224	8,700	268	560

- V. Visible Spectroscopy
 - A. Color
 - 1. General
 - The portion of the EM spectrum from 400-800 is observable to humans- we (and some other mammals) have the adaptation of seeing color at the expense of greater detail



- V. Visible Spectroscopy
 - A. Color
 - 1. General
 - When white (continuum of λ) light passes through, or is reflected by a surface, those Is that are absorbed are removed from the transmitted or reflected light respectively
 - What is "seen" is the complimentary colors (those that are not absorbed)
 - This is the origin of the "color wheel"



- V. Visible Spectroscopy
 - A. Color
 - 1. General
 - Organic compounds that are "colored" are typically those with extensively conjugated systems (typically more than five)
 - Consider β-carotene





 λ_{max} is at 455 – in the far blue region of the spectrum – this is absorbed

The remaining light has the complementary color of orange

Water and its treatment

Water is one of the most basic and essential compound necessary for

the survival of animals, plants, human life and is also used in various

types of industries.

Only less than 1% of the earth's water is available as fresh water. So it is

necessary that the available water should be used most carefully and

economically.

Distribution of water on earth:			
Oceans:	97.23%		
Ice caps and Glaciers:	2.14%		
Ground water:	0.61%		
Fresh water Lakes:	0.01%		
Others:	0.01%		

Sources of water

The main sources of water are:

- a. Surface water
- b. Underground water

Surface water includes

- 1. Rain water
- 2. Lake water
- 3. River water
- 4. Sea water

Rain water: It is the purest form of water obtained by evaporation of surface

water and subsequent condensation. However during condensation it dissolves

some atmospheric gases like CO_2 , SO_2 and oxides of nitrogen etc.

Acid rain: The first seasonal rain containing some dissolved gases is called

acid rain.

Lake water: This water is stored for future use and contains less amount of

dissolved salts but high amount of organic matter.

River water: This water is fed by rain, melting of ice and spring water. As water from these sources flow over the surface of land and therefore dissolves soluble minerals present in the soil and finally falls in river.

Sea water: The different rivers are the sources of sea water. It is the most impure form of water. The main reasons for this are:

- 1. The continuous evaporation increases the concentration of dissolved salts.
- 2. Impurities thrown by river water

It contains on an average about 3.5 % of dissolved inorganic salts, out of which about 2.6% is NaCl

Underground water

It includes water from well and spring and a part of rain water which percolates into the earth.

During its downward flow through the soil, it

dissolves some of minerals present in soil.

However underground water generally clear in

appearance and free from organic impurities due

to the filtering action of soil.

Impurities in water

1. Dissolved impurities:

a. Dissolved salts: Salts like carbonates, bicarbonates, chlorides, sulphates of Ca, Mg, Fe, Al and Na are present in water.

- **b.** Dissolved Gases: $SO_2, CO_2, O_2, H_2S, NH_3$ and oxide of N_2
- Suspended matter: These impurities may be inorganic (like Clay and sand) organic (vegetable and decomposed animal and vegetable matter, fungi, algae bacteria) imparts turbidity, colour and odour to water.
- Collodial impurities: Products from organic waste, finely divided silica and clay collodial impurities are present in water.
- 4. Micro-organisms: They include bacteria, fungi and algae are added by animal and vegetable waste which causes various diseases. Therefore this water is not fit for human consumption.

Hardness of Water and Hard water

Hard water: The water which does not produce leather with soap, but forms a white precipitates is called hard water. It is due to the presence of some dissolved salts of Ca and Mg Soft water: Water which forms leather with soap easily is called soft water. It does not contain the dissolved salts of Ca and Mg

Hardness: It is the property of the water due which it does not forms leather with soap.

Types of hardness

i.Temporary hardness: It is due to the presence of dissolved bicarbonates salts of Ca, Mg and other heavy metals. It can be removed easily by boiling the water. It is also called carbonate hardness.



ii. **Permanent hardness:** It is due to the presence of dissolved chlorides, Sulphates salts of Ca, Mg and some other heavy metals. It can not be removed by the simple process of boiling. It is also called non-carbonate hardness.

Degree of hardness

Hardness of water is not only due to the salts of Ca and Mg but also due to soluble salts of some other heavy metals like AI, Fe, Sr and Mn. However $CaCO_3$ is used as reference to express the hardness in terms of equivalents of $CaCO_3$ due to the following reasons:

a.It is the most insoluble salt.

b.Its molecular weight is 100 which makes the calculations easy

```
Mass of hardness producing X 100 substance in mg / L
```

Equivalents of $CaCO_3 =$

Molecular weight of substance

A hard water sample contains 10 mg / L of MgCl₂. Calculate the Calcium carbonate equivalents.

Equivalents of CaCO₃ =
$$\frac{Mass of hardness producing X 100}{Molecular weight of substance}$$
Equivalents of CaCO₃ =
$$\frac{10 X 100}{95} = 10.52 \text{ mg/L}$$

Units of hardness

i. Parts per million(ppm): It may be defined as the number of parts by weight of CaCO₃ equivalent hardness present per million i.e. 10⁶ parts by weight of water.

1ppm = 1 part of CaCO₃ equivalent hardness in 10^6 parts of water

(ii) Degree Clarke (^oCl): It may be defined as the number of parts by weight of CaCO₃ equivalent hardness present per 70000 parts by weight of water.

 $1^{\circ}CI = 1$ part of CaCO₃ equivalent hardness in 70000 parts of water.

(iii) **Degree French** (0 **Fr**): It may be defined as the number of parts by weight of CaCO₃ equivalent hardness present10⁵ parts by weight of water.

 1° Fr = 1 part of CaCO₃ equivalent hardness in 10^{5} parts of water

 $1 \text{ ppm} = 1^{\circ}\text{Cl} = 1^{\circ}\text{Fr} = 1 \text{ mg} / \text{L}$

Specification of water for different industrial use

1.Boilers industry: The water used in boilers should be soft. Because hard water forms scale and sludges

- Which prevents efficient heat transfer.
- The untreated water can lead to corrosion
- · Some times explosion may take place
- Also reduces the efficiency of boiler
- Reduces the life time of boiler

Specification of boiler feed water

- It should be free from hardness
- It should be free from organic matter, oil and grease to avoid foaming
- It should have low alkalinity as alkaline

impurities causes corrosion of boiler material

• It should be free from dissolved gases

such as CO_2 , H_2S , O_2 to avoid corrosion

- It should be free from turbidity and sediments
- It should not contain iron and manganese salts as they get deposited in boilers

Textile industry

Textile industry: In textile industry water is used for dyeing the cloths. The water used in textile industry should free from:

• Hardness as hard water decreases the solubility of dyes

which resists the uniform dyeing of cloths.

- Presence of organic matter imparts foul smell
- Free from Fe, Mn, colour and turbidity which causes

uneven dyeing and produces stain on fibre.

Sugar industry

Sugar industry: The water is used in sugar industry in sugar refining and therefore it should be free from hardness as the hard water

- Produces deliquescent sugar
- Free from sulphates, carbonates and nitrates their

presence causes crystallization of sugar difficult

• Free from micro-organisms decomposes sugar

Beverage industry: Water used in beverage industry should not be alkaline as alkaline water causes the neutralizes of fruit acid and changes the taste and quality of product

Laundries: Water used in Laundry should free from hardness as

- Hard water causes the consumption of large amount of soap.
- Free from Fe and Mn salts which imparts grey or yellow shade to fabric

Cooling system: Free from dissolved gases as presence of gases causes

corrosion.

Pharmaceutical and Dairies industry: It requires ultra pure water i. e. water free from all types of impurities should be colourless, tasteless, odourless and microorganisms.

Cooking: The water used for cooking should be soft because:

- a. Fuel requirement will be high if hard water is used
- b. Hard water imparts unpleasant taste if is used for making coffee or tea
- c. Hard water increases cooking time

Paper industry: The water used in paper industry should be free from:

- a. SiO₂, as it produces cracks in paper
- b. Fe and Mn salts, as they affect brightness and colour of the paper
- c. Alkalinity, as it consumes alum and therefore increases cost production
- d. Hardness, as it increases the ash content of the paper

Specification of water for domestic use

- 1. It should be clean, colourless and odourless
- 2. It should have good taste
- It should be reasonably soft i.e. its total hardness should be less than 500 ppm
- 4. It should be free from disease producing micro-organism
- 5. It should be in the range of 7.0-8.5
- 6. Its turbidity should be less than 10 ppm
- 7. It should free from dissolved gases like H_2S
- 8. It should not contain the minerals such as Pb, As, Cr and manganese salts

Purification of water for domestic use

Purification of water involves the following steps:

- Screening: It involves the removal of large sized floating impurities like wood pieces and leaves by passing raw water through filters having big holes.
- Sedimentation: It is a process of removing suspending impurities by allowing the water to stand for few days undisturbed to settle down the suspended impurities due to gravitational force.

3. Sedimentation with coagulation: Finely divided colloidal charged particles of silica, clay and organic matter do not settle down easily due to mutual repulsion and hence can not be removed by simple sedimentation. So these can removed by a process called coagulation. This process involves the addition of certain chemicals called coagulants like

- a. Alum ($K_2SO_4.AI_2(SO_4)_3.24H_2O$
- b. Sodium Aluminate (NaAlO₂)

These chemicals provides Al³⁺ ions which neutralize the negative charge of the colloidal particles which then settle down easily and thus can be removed.

Filtration

- **4. Filtration:** This process involves the removal of insoluble impurities by passing through a bed of proper sized granular material. The following types of filters are commonly used.
- a. Gravity sand filters
- b. Pressure filters





Sterilization or disinfection

5. **Sterilization or disinfection:** This process involves the removal of disease producing micro-organisms and pathogenic bacteria's.



- Boiling: Boiling kills all disease causing germs and bacteria's. Although this method is efficient and rapid, But this method is expensive for municipal supply of water.
- 2. Chlorination: It is a process of addition of chlorine to drinking water for



disinfection.

By using Chlorine gas

 By using Chlorine gas: Chlorine can be employed directly as a gas or in the form of concentrated solution in water. It forms hydrochloric acid (HCl) and Hypochlorous acid (HOCl) as;

> $Cl_2 + H_2O \longrightarrow HCI + HOCI$ HOC1 \longrightarrow HC1 + O nascent oxygen germs + O \longrightarrow germs are oxidized

 The effectiveness of chlorine disinfection depends upon the concentration, temperature, pH of water and amount of microorganism

Advantages and disadvantages of Cl₂ disinfectant

• Advantages:

- 1. It is effective and economical
- 2. It is stable and does not deteriorates on storing.
- 3. It can be used at high as well as low temperature
- 4. It does not introduce any impurity to water
- Disadvantages:
- If excess of chlorine is added it imparts unpleasant odour and taste to water
- 2. It is not effective at high PH

By using bleaching powder

 Bleaching powder: Bleaching powder also reacts with water and produces Cl₂ which in turn produces HCl and HOCl. The HOCl after dissociation produces oxygen nascent which oxidizes the germs.

 $CaOCl_{2} + H_{2}O \longrightarrow Ca(OH)_{2} + Cl_{2}$ $Cl_{2} + H_{2}O \longrightarrow HCl + HOCl$ $HOCl \longrightarrow HCl + O \text{ nascent oxygen}$ $germs + O \longrightarrow germs are oxidized$

- Disadvantages of bleaching powder:
- 1. It increases the hardness of water
- 2. If used in excess, imparts unpleasant taste and odour to water
- 3. It unstable, so can not be stored for long time
- **De-chlorination:** The excess of chlorine can removed by using adding small

amounts of reducing substances like SO_2 and Na_2SO_3 .

 $SO_2 + CI_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCI$ $Na_2SO_3 + CI_2 + H_2O \longrightarrow Na_2SO_4 + 2HCI$

Ozonization

Ozone is a powerful disinfectant when used for disinfection of

water. Ozone is very reactive and unstable. So when it is passed

through raw water, it decomposes to produce nascent oxygen which

oxidizes the germs.

 $O_3 \longrightarrow O_2 + O$ germs + $O \longrightarrow$ germs are oxidized Advantages: Ozone in addition to disinfection of water also acts as

- bleaching agent
- It also removes the organic matter
- It improves the taste of water
- Its excess is not harmful, Since it is unstable and decomposes into oxygen

Disadvantage: It is an expensive method can not be used for municipal

water supply.

By using Chloramine

Chloramine is prepared by mixing Chlorine with ammonia in the ratio 2:1 by volume. This process is called Chloramination.

 $Cl_2 + NH_3 \longrightarrow CINH_2 + HCI$ $CINH_2 + 2H_2O \longrightarrow HOCI + NH_4OH$ $HOCI \longrightarrow HCI + O$ nascentoxygen germs + $O \longrightarrow$ germs are oxidized

Advantages and disadvantages of Chloramine

Advantages:

i. It removes irritating smell by consuming excess of chlorine

ii. It imparts good taste to water

iii. It is much more lasting than chlorine

Disadvantage: The cost is very high

By using UV Radiations

Ultra-violet radiations are very effective to destroy
microorganisms present in water. For this purpose uv lamps
(enclosed in quartz bulb) are used. This method is used for
disinfection of swimming pool water because it does not
require any chemicals to be mixed with water.

- Aeration: In this method the water is passed through a perforated pipe at high pressure. As water spray into air, it comes into contact with oxygen of air and uv radiation of the sun light. This kills bacteria and the oxygen oxidizes the organic matter.
- Advantage: Most simple method for disinfection of water
- **Disadvantage:** Since exposure time is too small, So this method is not much effective.
- Ideal Disinfectant: Chlorine is most ideal disinfectant as:
- It is effective and economical
- Stable and therefore easy to store
- Does not introduce any impurity to water

Break point Chlorination

Break point Chlorination: It is the addition of sufficient amount of Cl₂ to oxidize organic matter and reducing substances leaving behind mainly free chlorine available for destroying the pathogenic bacterias.
Mechanism of Break-point chlorination:

Stage (I) : At this stage there is no free residual Cl_2 since all the added Cl_2 gets consumed for oxidation of reducing substances present in water

Stage II : With further addition of Cl_2 , the amount of residual Cl_2

increases due to formation of chloro-organic compounds.

Stage III: At this stage the destruction of chloro-organic compounds and chloramines takes place till minima in curve is obtained. (Breakpoint chlorination)

Stage IV : After break point chlorination the added Cl2 is not used in any reaction and is called free Cl2 which kills the pathogenic bacteria in water



Significance of break point chlorination

- It ensures complete destruction of organic matter, which imparts colour, bad odour and unpleasant taste to water.
- 2. It completely destroys all the disease-producing bacteria.
- 3. It prevents the growth of any weeds in water.
- 4. It prevents the presence of excess of chlorine which may impart unpleasant taste to water.

Boiler feed water

- **Boiler:** A boiler is a device which used to convert water under pressure into steam by supplying the heat.
- Specifications for boiler feed water:
- 1. It should be free from soluble salts of Ca and Mg
- 2. It should be free from turbidity and organic matter
- 3. It alkalinity should be 0.45-1 ppm
- It should be free from dissolved gases like oxygen and carbon dioxide
Boiler problems

 In a boiler, water is continuously converted into steam which increases the concentration of dissolved salts. A stage is reached that when ionic product of these salts exceeds their solubility product and they precipitate out in the form of sludge and scale.

Sludge and Scale

- Sludge: It is a soft, loose and slimy precipitate formed the boiler .Formation of sludge: These are formed by the substances like MgCO₃, MgCl₂,CaCl₂ and MgSO₄ in colder part of boiler because of their less solubility in cold water as compared to hot water.
- Scales: These are hard deposits firmly sticking to the inner part of boiler.

Formation of Scales

1. Deposition of Calcium sulphate: The solubility of CaSO₄

decreases with increase in temperature. Therefore at high temperature $CaSO_4$ gets precipitated in the form of scale.

2. Presence of silica: Silica if present in very small amount, it may deposit as Calcium silicate (CaSiO₃) or Mg(SiO₃)

3. Decomposition of
$$Ca(HCO_3)_2$$

$$Ca(HCO_3)_2 \xrightarrow{Heat} \downarrow CaCO_3 + H_2O + \uparrow CO_2$$

4. Hydrolysis of Magnesium salts

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCI$$

Disadvantages of scale formation

• Wastage of fuel: Scales have poor thermal conductivity so the rate of heat transfer from boiler to inside water will reduce so it will cause increase in fuel consumption.

Thickness of scale (mm)	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150%

• Lowering of boiler safety: Due to scale formation over-heating of boiler is required for a steady supply of steam. It makes boiler material weak and soft.

- Decrease in efficiency: Scales get deposited in the valves and condensers of the boilers, thereby chocking partially. It results in decrease in efficiency of the boiler.
- Danger explosion: Sometimes at high temperature, the scales crack and water comes in contact with overheated iron plates. This results in formation of large amount of steam suddenly which may cause explosion.
- Corrosion: Due to scale formation excessive heating of boiler material take place. At such high temperature corrosion of boiler material occurs at high rate.

Difference between scale and sludge

- 1. Sludges are soft, loose and slimy precipitate
- 2. They are no-adherent deposit and can be easily removed
- They are formed by substances like, CaCl₂, MgSO₄, MgCl₂ and MgCO₃ etc.
- 4.They are formed at colder parts of boiler.
- 5. They decrease the efficiency of boiler but are less dangerous
- 6. They can be removed by blowdown process

- 1. Scales are hard deposit.
- They stick very firmly to the inner surface of boiler and difficult to remove.
- 3. They are formed by like, $CaSO_4$, Mg(OH)₂, CaCO₃ and CaSiO₃ etc.
- 4. They are formed at hot of the boiler.
- They decrease the efficiency of boiler and chances of explosion are there.
- They can not be removed by blow-down process

Treatment of Boiler feed water

- Raw water can not be used directly in boilers as it can lead a large number of problems such as scale and sludge formation.
- So water is given following two types of treatment before using in the boilers
- 1. Internal treatment
- 2. External treatment

Internal treatment

- 1. Internal treatment: In this method treatment water is carried out inside the boiler and is achieved by adding certain chemicals to the boiler water for conditioning of water.
- Colloidal conditioning: Scale formation can be avoided by adding chemicals like kerosene, agar-agar etc. which get adsorbed over the scale forming precipitates and prevent their coagulation. So these salts remain loose and non sticky which can be removed by blow-down process.

Carbonate conditioning

 Carbonate conditioning: In this method Sodium carbonate is added to water converts scale forming salt calcium sulphate into sludge forming salt calcium carbonate.

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$

Drawback of carbonate conditioning: In high pressure boilers, hydrolysis of $CaCO_3$ and Na_2CO_3 to their hydroxide may take place which may cause caustic embrittlement

Phosphate conditioning

 Phosphate conditioning: In this method scale formation is prevented by adding sodium phosphate which reacts with Ca and Mg salts and forms their phosphates that can be easily removed by blowdown process.

$$3MCI_2 + 2Na_3PO_4 \longrightarrow M_3(PO_4)_2 + 6NaCI$$

 $3MSO_4 + 2Na_3PO_4 \longrightarrow M_3(PO_4)_2 + 3Na_2(SO_4)$

Calgon conditioning

 Calgon conditioning: In this method, Calgon (sodium hexametaphosphate) is added to boiler water which converts scale forming salts into soluble complex that remain soluble in water without causing any harm to boiler

$$Na_{2}(Na_{4}(PO_{3})_{6} \longrightarrow 2Na^{+} + (Na_{4}(PO_{3})_{6})^{2-}$$

$$2^{-}$$

$$CaSO_{4} + Na_{4}(PO_{3})_{6} \longrightarrow (Ca_{2}(PO_{3})_{6})^{2-} + 2Na_{2}SO_{4}$$

EDTA conditioning

• EDTA conditioning: This method involves the addition of 1.5% alkaline solution of EDTA to boiler feed water forms complexes with scale forming cations which remain soluble in water. Moreover, this treatment also prevents the deposition of iron oxide.

External treatment

- External treatment: This method involves the removal of impurities from the boiler feed water. The following methods are used to remove the soluble impurities;
- 1. Lime-Soda Process
- 2. Ion exchange method
- 3. Zeolites Process
- Softening of water: The process of removal of hardness causing salts from water is called softening of water

Lime-Soda process

- Lime-Soda process: This method involves the treatment of hard water with lime (Ca(OH)₂) and Soda (Na₂CO₃) which react with Ca and Mg salts to form insoluble precipitates. This process can be carried out either in cold or in hot conditions.
- a. Cold Lime-soda process
- b. Hot Lime-soda process

Cold Lime-soda process

 Cold Lime-soda process: In cold lime process measured quantity of chemical (lime, soda and coagulant) and raw water are added from the top of the container into the inner vertical chamber which is fitted with a stirrer. Vigorous stirring and mixing causes precipitation of soluble salt due reaction with lime and soda. The coagulants entraps fine particles (precipitates) of $CaCO_3$ and $Mg(OH)_2$ and thus helps in the formation of coarse particles which settles at the bottom of chamber



Hot lime-soda process

• Hot lime-soda process: In this process hard water is treated lime and soda at a temperature 94°-100°C in a reaction tank which has three inlets, each for hard water, chemicals and superheated steam. From the reaction tank, the contents go to sedimentation tank in which sludge settles down and the water passes through a sand filter. The sand filter has three layers of sand which removes the sludge from the soft water.



Advantages of lime-soda process

- Lime-soda process is economical as compared to other processes.
- 2. It removes not only hardness causing salts but also other minerals.
- 3. Treated water is alkaline and therefore corrosive.
- 4. Iron and Mn salts are also removed to some extent which imparts colour to water.
- Alkaline nature of water amount of bacterias is reduced

Disadvantages of lime-soda process

- 1. It requires careful operation and skilled operation for economical and efficient softening.
- 2. Sludge disposal is difficult and poses problem.
- Soft water contains some soluble salts like sodium sulphate and can not be used in high pressure boilers

Difference between hot and cold lime-soda process

- 1.Cold lime-soda is carried out at room temperature.
- 2. It is a slow process.
- 3. Coagulants are used
- 4.Soft water has hardness around 60 ppm
- 5.Dissolved gases are not removed
- 6.Softening capacity is low
- 7.Filtration is not easy due high viscosity of water

- 1.Hot lime-soda is carried out at high temperature.
- 2. It is a fast process.
- 3. Coagulants are not used
- 4.Soft water has hardness around 15-30 ppm
- 5.Dissolved gases are also removed
- 6. Softening capacity is high
- 7.Filtration is easy due low viscosity of water

Reactions involved in lime-soda process

$$Ca(HCO_{3})_{2} + Ca(OH)_{2} \xrightarrow{\Delta} 2 CaCO_{3} + H_{2}O \qquad 1L$$

$$Mg(HCO_{3})_{2} + Ca(OH)_{2} \xrightarrow{\Delta} MgCO_{3} + 2 H_{2}O + CaCO_{3}$$

$$MgCO_{3} + Ca(OH)_{2} \xrightarrow{\Delta} Mg(OH)_{2} + CaCO_{3}$$

$$Mg(HCO_{3})_{2} + 2 Ca(OH)_{2} \xrightarrow{\Delta} Mg(OH)_{2} + 2 H_{2}O + 2 CaCO_{3}$$

$$MgCl_{2} + Na_{2}CO_{3} \xrightarrow{\Lambda} MgCO_{3} + 2NaCl$$

$$MgCO_{3} + Ca(OH)_{2} \xrightarrow{\Lambda} Mg(OH)_{2} + CaCO_{3}$$

$$1 L + 1 S$$

$$MgCl_{2} + Na_{2}CO_{3} + Ca(OH)_{2} \xrightarrow{\Lambda} Mg(OH)_{2} + CaCO_{3} + 2NaCl$$

$$CaCl_2 + Na_2CO_3 \xrightarrow{\Delta} CaCO_3 + 2NaCl 1S$$

$$CaSO_4 + Na_2CO_3 \xrightarrow{\Delta} CaCO_3 + Na_2SO_4 1S$$

$$2 \text{ HCI} + \text{ Ca}(\text{OH})_2 \xrightarrow{\Delta} \text{ CaCl}_2 + 2 \text{ H}_2\text{O}$$

$$\left. \begin{array}{c} 1\text{ L} + 1 \text{ S} \\ 1\text{ L} + 1 \text{ S} \\ 2 \end{array} \right\}$$

$$CaCl_2 + \text{ Na}_2\text{CO}_3 \xrightarrow{\Delta} \text{ CaCO}_3 + 2 \text{ NaCl} \right\} 2$$

2 NaHCO₃ + Ca(OH)₂
$$\xrightarrow{\Delta}$$
 CaCO₃ + H₂O + Na₂CO₃
1 L - 1S

Zeolite or Permutit Process

In this process hard water is passed through sodium zeolites, which are a group of hydrated crystalline aluminosilicates (Z = Al₂Si₂O₈.xH₂O) and are prepared by soaking the zeolites with concentrated NaCl solution which are designated as Na-Zeolite (Na₂Z). The loose Na⁺ ions are replaced by Ca²⁺ and Mg²⁺ ions present in hard water as;

 $CaSO_{4} + Na_{2}Z \longrightarrow CaZ + Na_{2}SO_{4}$ $CaCl_{2} + Na_{2}Z \longrightarrow CaZ + 2 NaCl$ $MgSO_{4} + Na_{2}Z \longrightarrow MgZ + Na_{2}SO_{4}$ $MgCl_{2} + Na_{2}Z \longrightarrow MgZ + 2 NaCl$

Regeneration of Zeolite bed

After long use, Zeolite is completely converted to Calcium and Magnesium zeolite. The zeolite bed can be regenerated passing the concentrated solution of chemicals such as NaCl, NaNO₃ and Na₂SO₄.

So when brine solution (NaCl) is passed through exhausted zeolite bed Ca²⁺ and Mg²⁺ ions present in zeolite bed gets exchanged with Na⁺ ion of brine solution

$$CaZ + 2 NaCI \longrightarrow CaCI_2 + Na_2Z$$

$$MgZ + 2 NaCI \longrightarrow MgCI_2 + Na_2Z$$

Advantage of zeolite process:

- 1. The hardness is nearly completely removed and soft water produced has hardness 10 ppm
- 2. It is quite clean and rapid process which requires less time for water softening.
- 3. No impurities are precipitated, so removal of sludge is no longer required.
- 4. Maintenance and operation is easy and requires no skilled workers.
- 5. The process automatically adjusts itself to water of different hardness.
- 6. The equipment used is compact and occupies less space

Disadvantage of zeolite process:

- 1. Acidic water can not be softened as it destroys zeolite bed.
- 2. Turbid and water containing suspended can not softened by this method as pores of bed get clogged.
- 3.Water to be softened should not be hot as the zeolite tends to dissolve in hot water.
- The water should not contain large amounts of Fe²⁺ and Mn²⁺ ions as Manganese and Iron zeolites are difficult regenerate.
- 5. The anions such as Cl⁻ SO₄²⁻ and HCO₃⁻ are not removed by this process.
- 6. The installation cost is high

Zeolite process

- 1. Installation cost is high
- 2.Operating cost is less as zeolites can be regenerated with cheaper NaCl
- The treatment plant is compact and so requires less space
- 4.Treated water contains large amount of sodium salts
- Acidic water can not be softened as it decomposes zeolite bed

Lime-soda process

- 1. Installation cost is low
- 2.Operating cost is higher as

costly chemicals are used

- 3. The treatment plant is bulky
 - and so requires large space
- 4.Treated water contains less dissolved sodium salts
- 5. Acidic water can be softened

6. The water should be freefrom turbidity as thesuspended impurities blockthe pores of zeolites

- 7. No sludge is formed, so no problem of sludge disposal
- Treated water contains
 more NaHCO3 which can not
 be used in boiler
- It automatically adjusts itself
 to water samples having
 different hardness

- 6. Turbid water can be softened
- 7. Large quantity of sludge is formed
- 8. Treated water is free from NaHCO $_3$ and is suitable for boilers
- Frequent control and adjustment of reagents is required, So skilled workers are required

Ion-exchange process

 Ion-exchange resin: The ion exchange resins are cross-linked, high molecular weight organic polymers in which functional groups attached to polymeric chains contains exchangeable ions.

Ion exchange resins are of following two types:

- (i) Cation exchange resins
- (ii) Anion exchange resins

- (i) Cation exchange resins: These resins have acidic functional groups like –SO₃H or –COOH which can exchange cations of hard water with their H⁺ ions. Therefore they are called cation exchangers.
 - When hard water is passed through the cation exchange resin RH, the H+ ions of exchanger are replaced by cations of the hard water.

$$2RH + Ca^{2+} \longrightarrow R_2Ca + 2H^+$$
Cation exchanger
$$(2RH + Mg^{2+} \longrightarrow R_2Mg + 2H^+)$$
Cation exchanger

(ii) Anion exchanger: These resins have basic functional groups such as quaternary ammonium or quaternary phosphonium groups. These resins after treatment with dil. NaOH solution become capable to exchange its OH⁻ ions with the anions of hard water. These are also called anion exchangers.

When hard water is passed through the anion exchange resin R'OH the OH⁻ ions of the anion exchanger are replaced by anions of hard water in the following way

$$\begin{array}{c} \mathsf{R'OH} + \mathbf{CI} \longrightarrow \mathsf{R'CI} + \mathsf{OH} \\ \hline \mathsf{Anion exchanger} \\ \hline \mathsf{2R'OH} + \mathsf{SO}_4^{2^-} \longrightarrow \mathsf{R'}_2\mathsf{SO}_4 + \mathbf{OH} \\ \hline \mathsf{Anion exchanger} \end{array}$$

- Demineralised or deionised water: Water free from any type of dissolved minerals is called demineralised water and it is not suitable for drinking.
- Potable water: Water which can be used for drinking is called potable water.
- Conductivity water: The water which has no conductivity is called conductivity water.

- **Brackish water:** Water containing large amount of dissolved salts having brackish taste called brackish water.
- Desalination of brackish water: The process used to remove soluble salts from brackish water is called desalination.

The following techniques are used for desalination:


- Distillation: In distillation brackish water on heating in a evaporator the water evaporates leaving salts behind. The desalinated vapours are then condensed in a separate container.
- Disadvantage: This method is very expensive and so can be used for the desalination of large amount of water.
- Freezing: In this method the water is cooled. On cooling the water salt is left in mother liquor and ice crystals are formed. These crystals are separated, washed and melted to get pure water

• Electrodialysis: This method is based on the principle that when potential difference is applied between two electrodes placed in a salty water the ion move towards oppositely charge electrodes.



• Osmosis: Osmosis is a phenomenon in which solvent molecules flows through a semipermeable membrane from a region of low concentration to high concentration when two solutions of different concentration are in contact with each other. However if a hydrostatic pressure more than osmotic pressure is applied on the region of high concentration the solvent molecules starts flowing from a concentrated solution to a dilute solution. This process is called reverse osmosis.

• **Reverse osmosis:** In this process a hydrostatic pressure more than osmotic pressure is applied on brackish water. The pure water flows through semipermeable membrane leaving the salts behind.



Advantages of reverse osmosis

- 1. It is simple and operated expenses are low.
- 2. It is effective in removing collodial matter also.
- 3. It removes both ionic and non ionic impurities.
- 4. It operates at low temperature.
- 5. The water obtained can be used in high pressure boilers
- 6. It is energy efficient.
- 7. It can be used for the desalination of large amount of water

Boiler of corrosion

- Boiler of corrosion: The decay of boiler material due the presence of some impurities present in water is called boiler corrosion.
- Impurities causing boiler corrosion:

(a) Dissolved oxygen: In boilers at high temperature the dissolved react with iron wall of boiler to form rust.

 $2 \operatorname{Fe} + 2\operatorname{H}_2 O + O_2 \longrightarrow 2 \operatorname{Fe}(O\operatorname{H})_2$ $4 \operatorname{Fe}(O\operatorname{H})_2 + O_2 \longrightarrow 2 (\operatorname{Fe}_2 O_3 \cdot 2\operatorname{H}_2 O)$

Prevention of corrosion due to oxygen

 Corrosion of boilers due oxygen can be prevented by removing the oxygen from the water and this can be done by adding certain chemicals like hydrazine, sodium sulphate and sodium sulphide.

 $N_{2}H_{4} + O_{2} \longrightarrow N_{2} + 2H_{2}O$ $2 Na_{2}SO_{3} + O_{2} \longrightarrow 2 Na_{2}SO_{4}$ $Na_{2}S + 2O_{2} \longrightarrow Na_{2}SO_{4}$

Corrosion due to dissolved CO₂

(b) Dissolved CO_2 : Carbondioxide dissolved in water forms carbonic acid which causes the boiler corrosion.

 $CO_2 + H_2O \longrightarrow H_2CO_3$

Source of CO_2 in water: CO_2 is present in boiler water in dissolved

form or it is contributed by the decomposition of bicarbonates of Ca and Mg.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$
$$Mg(HCO_3)_2 \longrightarrow MgCO_3 + H_2O + CO_2$$

Prevention of corrosion due to dissolved CO₂

Corrosion caused by the presence of dissolved CO_2 can be prevented by removing the CO_2 from Water. This can be done either by mechanical aeration or by adding ammonia.

 $NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2CO_3$

Corrosion by Mineral acid

(c) Mineral Acid: Hydrolysis of salts like MgCl₂ present in water forms HCI which causes boiler corrosion due to following reaction.

 $MgCl_{2} + 2H_{2}O \longrightarrow Mg(OH)_{2} + 2HCl$ $Fe + 2HCl \longrightarrow FeCl_{2} + H_{2}$ $FeCl_{2} + H_{2}O \longrightarrow Fe(OH)_{2} + 2HCl$ $4Fe(OH)_{2} + O_{2} + H_{2}O \longrightarrow 4Fe(OH)_{3}$

- Foaming: The formation of small bubbles at the surface of water in boilers due the presence some impurities like oils and alkalis is called foaming.
- Priming: Steam produced in boilers carries some droplets of water due to which it becomes wet. The formation of wet steam is called priming. It is caused by high steam velocity, presence of dissolved salts and sudden boiling.
- Prevention of Priming: It can be prevented by using soft water, steam purifiers and improving design of boilers