

Salient features of CFT -

- Metal ion and ligands are considered point charges.
- These interact by ionic (electrostatic) bonding.
- Ligands can be either negative point charges or neutral dipoles.

Salient features of CFT

i) In a complex central **metal atom or ion** is **surrounded** by various **ligands**.

ii) **Ligands** are **negatively charged** ions or **neutral molecules**, having lone pair of electrons (i.e. H_2O , NH_3).

iii) **Metal ion & ligands** are considered **point charges**. Their interaction is **purely electrostatics (ionic)**.

iv) When ligands approach to central metal, degeneracy of d-orbitals in metal removed due to repulsion between metal & ligands & split into different energy levels (**t_{2g} or eg**). The **repulsion** is **more** if ligands approach **along the axis** of d-orbitals & acquire **higher energy** (eg in oh or t_{2g} in Td). While **repulsion** is **less** if ligands approach in **between the axis** of d-orbitals & acquire **less energy** (t_{2g} in oh or eg in Td). Thus difference between these splitted energy is called **crystal field stabilizing energy (CFSE)** & denoted by **10 Dq** or small delta. 10Dq Value depends on **geometry of complexes**.

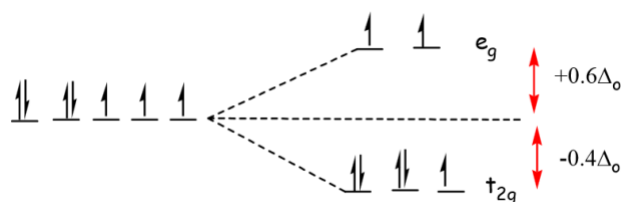
v) **Electrons** of metal are **filled** in splitted d-orbital. According to **Hund's rule** i.e. from lower energy levels.

vi) Since there is no orbital overlapping hence no covalent character in bonding.

vii) The magnitude of **CFSE** depends on **nature & number of ligands** & also **geometry** of complex.

If $\text{CFSE} > 0$ then stable complex, if $\text{CFSE} < 0$ then unstable complex.

Octahedral complex- splitting of d-orbitals- CFSE-High spin



$$\text{CFSE} = \Delta E = E_{\text{ligand field}} - E_{\text{isotropic field}} \quad \text{---(1)}$$

The energy of the isotropic field (Eisotropic field) is

$$\text{Eisotropic field} = 7 \times 0 + 2P = 2P$$

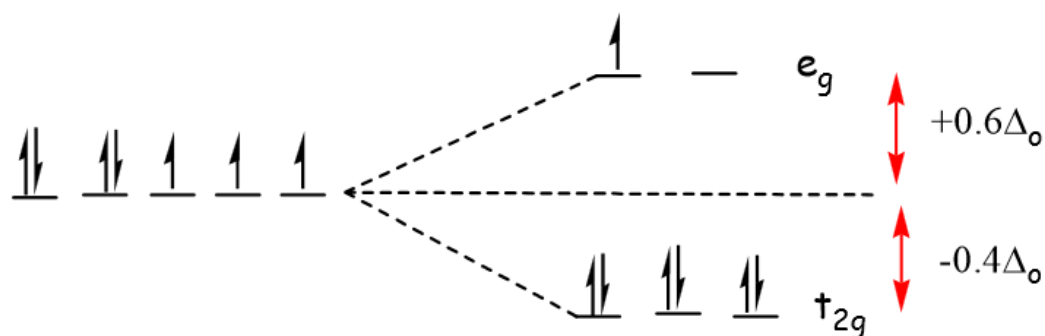
The energy of the octahedral ligand field $E_{\text{ligand field}}$ is

$$E_{\text{ligand field}} = (5 \times -2/5 \Delta_o) + (2 \times 3/5 \Delta_o) + 2P = -4/5 \Delta_o + 2P$$

So via Equation 1, the CFSE is

$$\text{CFSE} = E_{\text{ligand field}} - E_{\text{isotropic field}} = (-4/5 \Delta_o + 2P) - 2P = -4/5 \Delta_o$$

Octahedral complex- splitting of d -orbitals- CFSE-Low spin



The energy of the isotropic field is the same as calculated for the high spin configuration in Example 1:

$$E_{\text{isotropic field}} = 7 \times 0 + 2P = 2P$$

The energy of the octahedral ligand field $E_{\text{ligand field}}$ is

$$E_{\text{ligand field}} = (6 \times -2/5 \Delta_o) + (1 \times 3/5 \Delta_o) + 3P = -9/5 \Delta_o + 3P$$

So via Equation 1, the CFSE is

$$\text{CFSE} = E_{\text{ligand field}} - E_{\text{isotropic field}} = (-9/5 \Delta_o + 3P) - 2P = -9/5 \Delta_o + P$$

Calculation of CFSE for few Octahedral complexes

low spin if $\Delta_o > P$, and high spin if $\Delta_o < P$

The e_g orbitals are repelled by an amount of $0.6 \Delta_o$ orbitals are repelled by an amount of $0.6 \Delta_o$
The t_{2g} orbitals to be stabilized to the extent of $0.4 \Delta_o$

3d complexes are **high spin** with **weak field** ligands and **low spin** with **strong field** ligands.

High valent 3d complexes (e.g., Co^{3+} complexes) tend to be **low spin** (large Δ_o)

4d and 5d complexes are always low spin (large Δ_o)

e g - The higher energy set of orbitals (d_{z^2} and $d_{x^2-y^2}$) t2g - The lower energy set of orbitals (d_{xy} , d_{yz} and d_{xz})

Δ_o or $10 Dq$ - The energy separation between the two levels

Spectrochemical Series

An arrangement of ligands according to their ability to increase Δ for a given metal center

Weak – I⁻, Br⁻, SCN⁻, Cl⁻, N₃⁻, F⁻, H₂NC(O)NH₂, OH⁻, ox²⁻, O₂²⁻, H₂O, NCS⁻, py, NH₃, en, bpy, phen, NO₂⁻, CH₃⁻, C₆H₅⁻, CN⁻, CO – Strong

magnetic moment, μ

$$\mu = \sqrt{n(n+2)} \text{ BM}$$

N = no. of unpaired electron

Calculation of CFSE for few Octahedral complexes

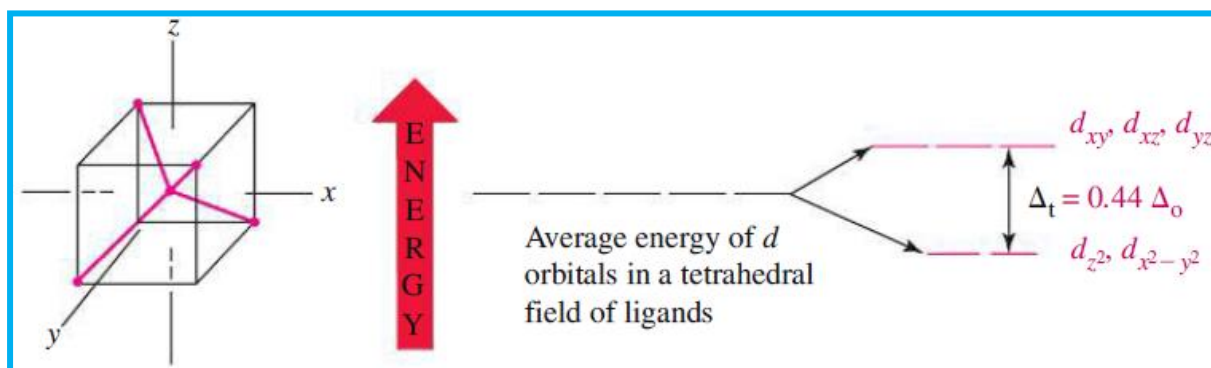
$$\Delta_{\text{tet}} = 4/9 \Delta_o$$

Magnetic moment for tetra hedral complex

Ni(II) electronic configuration = d⁸ (e⁴ t₂⁴) magnetic moment $\sqrt{8} = 2.83$ 3.7-4.0

K₃[Fe(CN)₆] has a magnetic moment of 1.73 B.M., which is a d⁵ low-spin complex with one unpaired electron

[Fe(H₂O)₆]³⁺ ions are high-spin with 5 unpaired electrons. It has a magnetic moment of 6 B.M.



- Imagine a tetrahedral molecule inside a cube with metal ions in the center of the cube. The ligands occupy the four alternate corners of the cube leaving the rest four corners empty.
- The two 'e' ($d_{x^2-y^2}$ and d_{z^2}) orbitals point to the center of the face of the cube while the three 't₂' (d_{xy} , d_{yz} and d_{zx}) orbitals point to the center of the edges of the cube.

- Thus, the t_2 orbitals are nearer to the direction of approach of the ligands than the e orbitals. (The ligands do not directly approach any of the metal d orbitals)

Isomerism in transition metal compounds

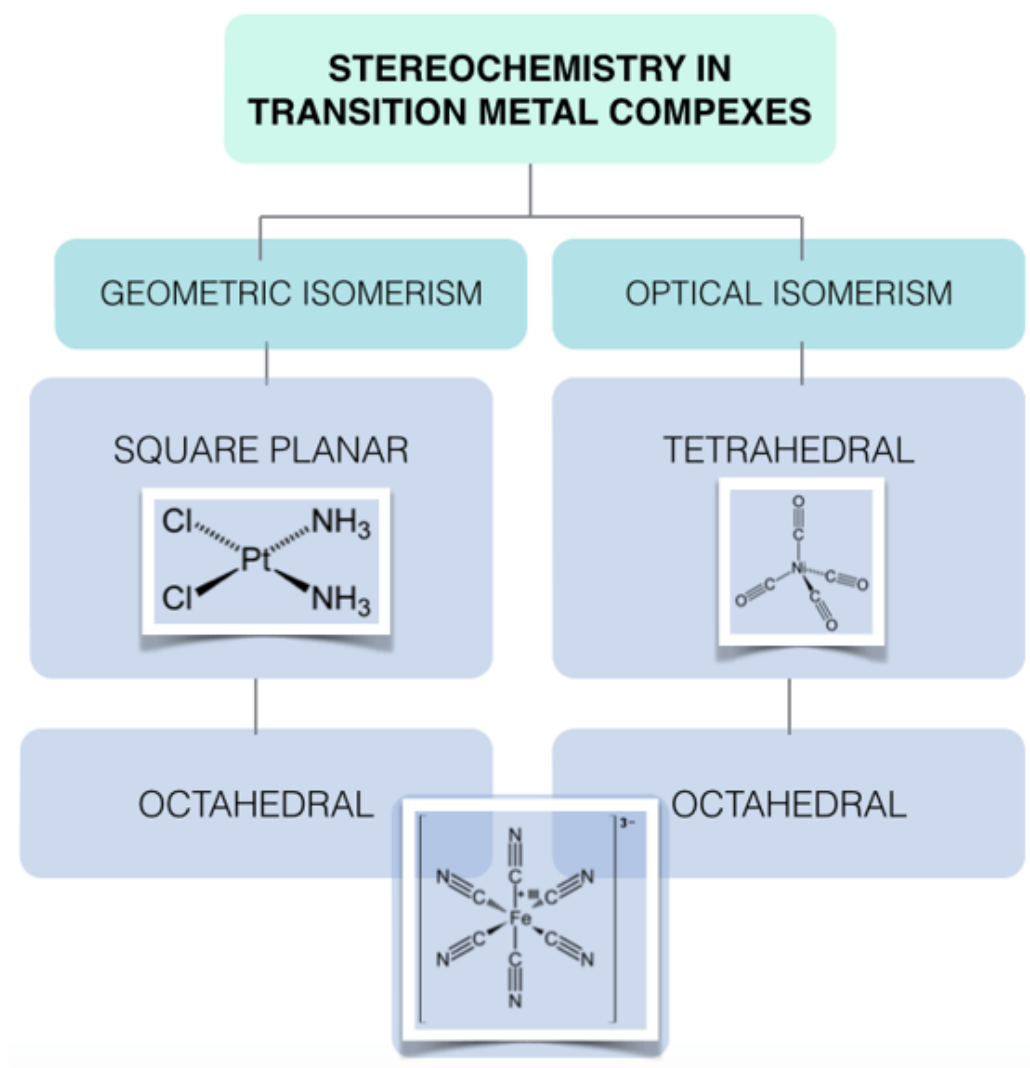
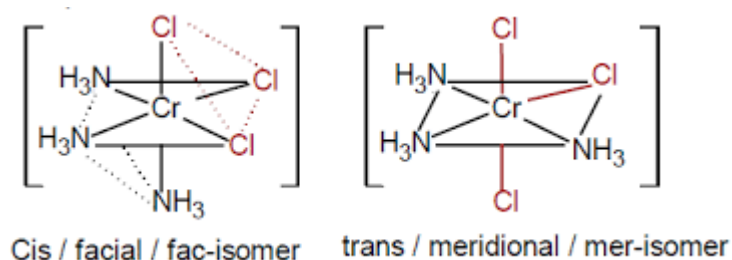
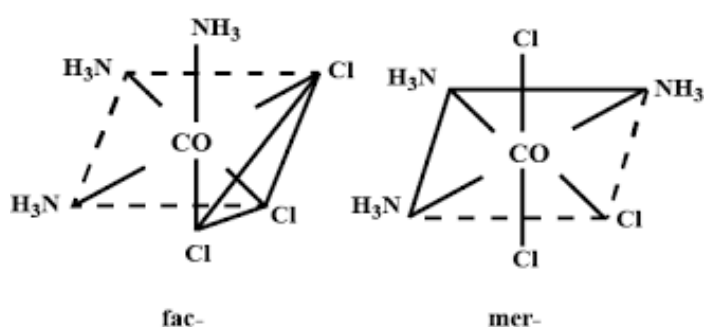
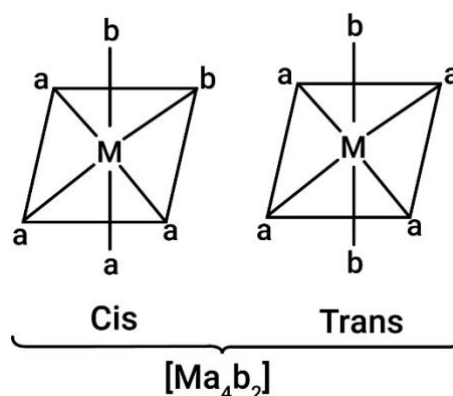
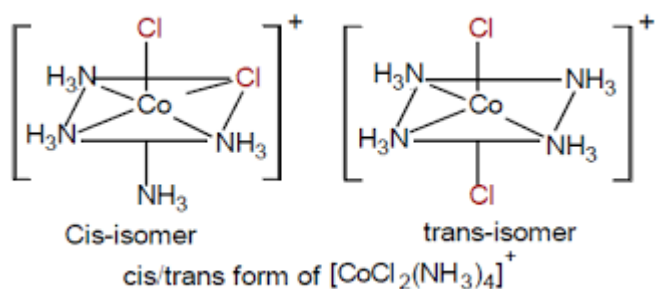


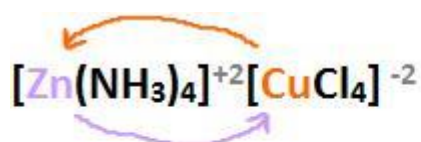
Fig 2: Stereochemistry Table

Geometrical Isomerism-Octahedral complex

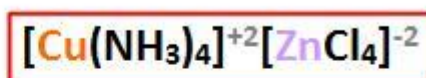


Structural Isomerism

Coordination isomerism occurs compounds containing complex anionic and cationic parts can be thought of as occurring by interchange of some ligands from the cationic part to the anionic part. Hence, there are two complex compounds bound together, one with a negative charge and the other with a positive charge. In coordination isomers, the anion and cation complexes of a coordination compound exchange one or more ligands

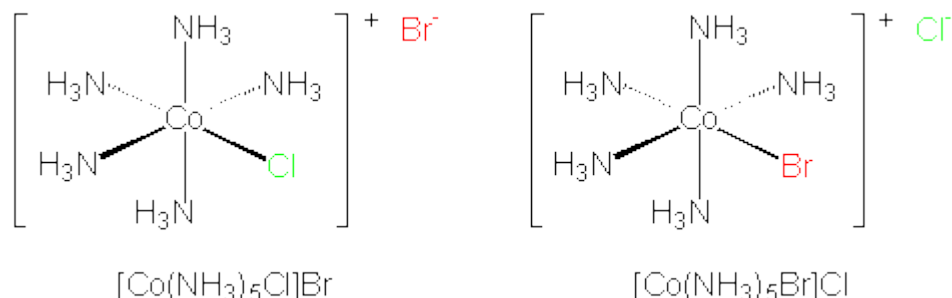


Tetraaminezinc(II)
TetrachloroCuprate(II)



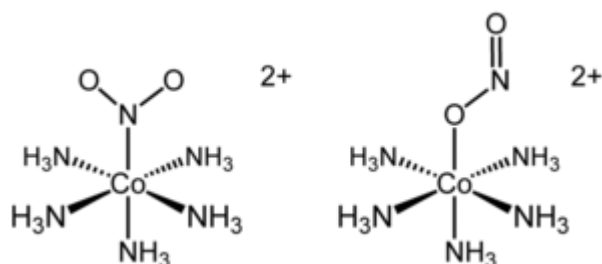
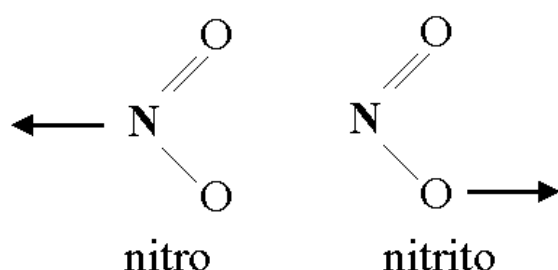
TetraamineCopper(II)
TetrachloroZincate(II)

Ionization isomers occur when a ligand that is bound to the metal center exchanges places with an anion or neutral molecule that was originally outside the coordination complex. The geometry of the central metal ion and the identity of other ligands are identical



A very similar type of isomerism results from replacement of a coordinated group by a solvent molecule (*Solvate Isomerism*), which in the case of water is called *Hydrate Isomerism*. The best known example of this occurs for chromium chloride ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) which may contain 4, 5, or 6 coordinated water molecules

- $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$: bright-green colored
- $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$: grey-green colored
- $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$: violet colored
- Linkage isomerism occurs with *ambidentate* ligands that are capable of coordinating in more than one way. The best known cases involve the monodentate ligands: $\text{SCN}^-/\text{NCS}^-$ and $\text{NO}_2^-/\text{ONO}^-$. The only difference is what **atoms the molecular ligands bind to the central ion**



Effective Nuclear Charge

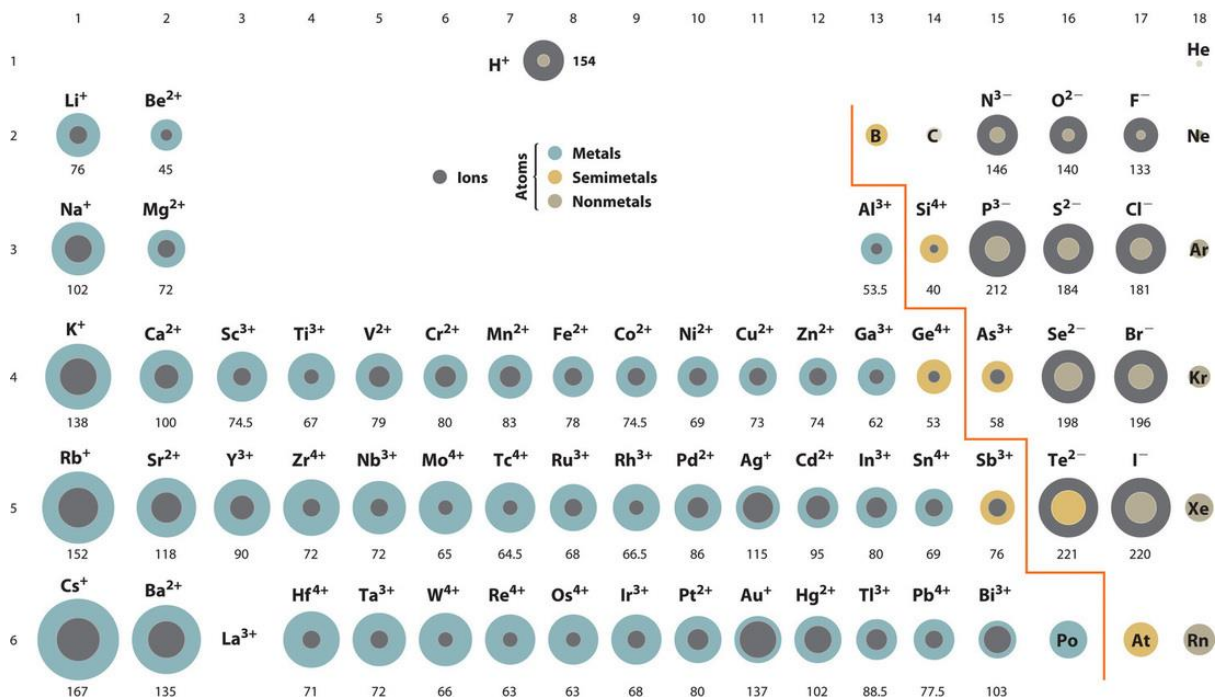
Z_{eff} can be calculated by subtracting the magnitude of shielding from the total nuclear charge and the effective nuclear charge of an atom is given by the equation

$$Z_{\text{eff}} = Z - S$$

Z is the atomic number (number of protons in nucleus) and S is the shielding constant

$$1s > 2s > 2p > 3s > 3p > 4s > 3d > 4p > 5s > 4d > 5p > 6s > 4f$$

Penetration describes the proximity to which an electron can approach to the nucleus



Groups include elements having the same electron configuration in their outer shell, which results in group elements sharing similar chemical properties

The periodic table lists elements by atomic number, which is the number of protons in every atom of that element

Elements in the periodic table are arranged in **periods** (rows) and **groups** (columns)

Ionization energy is the energy required to remove an electron from a neutral atom in its gaseous phase

The lower this energy is, the more readily the atom becomes a cation. Therefore, the higher this energy is, the more unlikely it is the atom becomes a cation

Another factor that affects ionization energy is electron shielding. Electron shielding describes the ability of an atom's inner electrons to shield its positively-charged nucleus from its valence electrons. When moving to the right of a period, the number of electrons increases and the strength of shielding increases. As a result, it is easier for valence shell electrons to ionize, and thus the ionization energy decreases down a group.

The ionization energy of the elements within a period generally increases from left to right. This is due to valence shell stability.

The ionization energy of the elements within a group generally decreases from top to bottom. This is due to electron shielding.

electron affinity is the ability of an atom to accept an electron.

electron affinity is a quantitative measurement of the energy change that occurs when an electron is added to a neutral gas atom. The more negative the electron affinity value, the higher an atom's affinity for electrons.

- Electron affinity increases from left to right within a period. This is caused by the decrease in atomic radius.
- Electron affinity decreases from top to bottom within a group. This is caused by the increase in atomic radius.
- Atomic radius decreases from left to right within a period. This is caused by the increase in the number of protons and electrons across a period. One proton has a greater effect than one electron; thus, electrons are pulled towards the nucleus, resulting in a smaller radius.
- Atomic radius increases from top to bottom within a group. This is caused by electron shielding.

UNIT-2

Hard soft acids and bases

Hard Lewis acids are characterized by small ionic radii, high positive charge, strongly solvated, empty orbitals in the valence shell and with high energy LUMOs.

Soft Lewis acids are characterized by large ionic radii, low positive charge, completely filled atomic orbitals and with low energy LUMOs.

Hard Lewis bases are characterized by small ionic radii, strongly solvated, highly electronegative, weakly polarizable and with high energy HOMOs.

Soft Lewis bases are characterized by large ionic radii, intermediate electronegativity, highly polarizable and with low energy HOMOs.

The **Borderline** Lewis acids and bases have intermediate properties.

Type of Acid/Base	CHARACTERISTICS	EXAMPLES
Hard acids	<ul style="list-style-type: none"> * Atomic centers of small ionic radii (<90 pm). * High positive charge. * Empty orbitals in their valence shells. * Low electronegativity (0.7-1.6) and low electron affinity. * Likely to be strongly solvated. * High energy LUMO. 	H^+ , Li^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Sn^{2+} Al^{3+} , Ga^{3+} , In^{3+} , Cr^{3+} , Co^{3+} , Fe^{3+} , Ir^{3+} , La^{3+} , Si^{4+} , Ti^{4+} , Zr^{4+} , Th^{4+} , U^{4+} , VO^{2+} , UO_2^{2+} $BeMe_2$, BF_3 , BCl_3 , $B(OR)_3$, $AlMe_3$
Soft acids	<ul style="list-style-type: none"> * Large radii (>90 pm). * Low or partial positive charge. * Completely filled orbitals in their valence shells. * Intermediate electronegativities (1.9-2.5) * Low energy LUMOs with a large magnitude of LUMO coefficients. 	Cu^+ , Ag^+ , Au^+ , Hg^+ , Cs^+ , Tl^+ , Hg^{2+} , Pd^{2+} , Cd^{2+} , Pt^{2+} Metal atoms in zero oxidation states BH_3
Borderline acids		Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , $B(CH_3)_3$, SO_2 , NO^+
Hard bases	<ul style="list-style-type: none"> * Small radii (around 120pm) & highly solvated. * electronegative atomic centres (3.0-4.0). * Weakly polarizable. * Difficult to be oxidized. * High energy HOMO. 	H_2O , OH^- , F^- , Cl^- , $CH_3CO_2^-$, PO_4^{3-} , SO_4^{2-} , CO_3^{2-} , NO_3^- , ClO_4^- , ROH , RO^- , R_2O , NH_3 , RNH_2 , N_2H_4
Soft bases	<ul style="list-style-type: none"> * Large atoms (>170 pm) with intermediate electronegativity (2.5-3.0). * High polarizability * Easily undergo oxidation. * Low energy HOMOs but large magnitude HOMO coefficients. 	S^{2-} , RSH , RS^- , R_2S , I^- , CN^- , SCN^- , $S_2O_3^{2-}$, R_3P , R_3As , $(RO)_3P$, RNC , CO , C_2H_4 , C_6H_6 , R^- , H^-
Borderline bases		Aniline, pyridine, N_3^- , Br^- , NO_2^- , SO_3^{2-} , N_2

Internal energy, Helmholtz free energy, Enthalpy, (Definition, expression & explanation)

S2

First law: Energy is conserved; it can be neither created nor destroyed.

Second law: In an isolated system, natural processes are spontaneous when they lead to an increase in disorder, or entropy.

internal energy, E , which is the sum of the kinetic and potential energies of the particles that form the system.

enthalpy (H), which is the sum of the internal energy of the system plus the product of the pressure of the gas in the system times the volume of the system.

$$H_{\text{sys}} = E_{\text{sys}} + PV$$

Helmholtz free energy is a thermodynamics concept in which, thermodynamic potential is used to measure the work of a closed system with constant temperature and volume

$$A = U - TS$$

A Helmholtz free energy

U=Internal Energy

T= Temperature

S= Entropy

Gibbs's free energy, Entropy (Definition, expression & explanation)

The Gibbs free energy of a system at any moment in time is defined as the enthalpy of the system minus the product of the temperature times the entropy of the system

$$G = H - TS$$

The change in the Gibbs free energy of the system that occurs during a reaction is therefore equal to the change in the enthalpy of the system minus the change in the product of the temperature times the entropy of the system

Gibb's – Helmholtz equation of free energy and its application

Fundamental equations - Differential forms of U, H, A, G

Start from definitions and re-express as differentials in terms of thermodynamic variables:

$H = U + PV$ method use $dU = dq + dw$ but recognize state function

$A = U - TS$ $dU = dq_{rev} + dw_{rev} = TdS - PdV$

$G = H - TS$ assume only P,V work

Take differentials:

$dH = dU + d(PV) = TdS - PdV + PdV + VdP = TdS + VdP$

$dA = dU - d(TS) = TdS - PdV - TdS - SdT = -SdT - PdV$

$dG = dH - d(TS) = TdS + VdP - TdS - SdT = -SdT + VdP$

Used a lot, called the fundamental equations:

$dU = TdS - PdV$

$dH = TdS + VdP$

$dA = -SdT - PdV$

$dG = -SdT + VdP$

Gibb's – Helmholtz equation of free energy and its application

Calculate ΔH_{rxn} from ΔG and its variation with the temperature at constant pressure

Calculate ΔG_{rxn} for a reaction at a temperature other than 298K

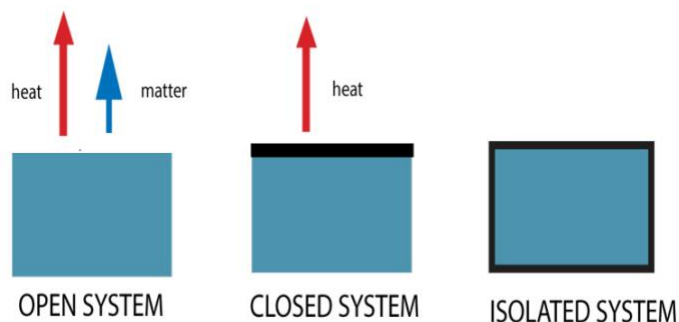
Calculate the effect of a temperature change on the equilibrium constant K_p

The standard state entropy change for a reaction, ΔS° , can be calculated from data in thermodynamic tables in a manner similar to changes in enthalpy and free energy. ΔS° for a chemical reaction is

$$\Delta S^\circ = \sum n S^\circ_{\text{products}} - \sum n S^\circ_{\text{reactants}}$$

System, Surroundings,

Homogeneous, Heterogeneous, open, closed



Open system:

For example boiling water without a lid

Heat escape into the air.

At the same time steam (which is matter) also escapes into the air

Closed system:

Example of a closed system – a pressure cooker

Example – A thermoflask is an isolated system

Electrochemical cells / galvanic cells, cell representation, cell potential, relationship between cell potential and free energy (no derivation)

An electrochemical cell is a device that can generate electrical energy from the chemical reactions occurring in it, or use the electrical energy supplied to it to facilitate chemical reactions in it. These devices are capable of converting chemical energy into electrical energy, or vice versa.

Galvanic Cell / Voltaic Cell

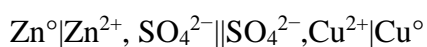
Chemical energy is transformed into electrical energy in these electrochemical cells.

The redox reactions that take place in these cells are spontaneous in nature.

In these electrochemical cells, the anode is negatively charged and the cathode is positively charged.

The electrons originate from the species that undergoes oxidation.

cell representation



The cell potential

$$E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} + E^\circ_{\text{oxidation}}$$

relationship between cell potential and free energy

In a galvanic cell, the Gibbs free energy is related to the potential by: $\Delta G^\circ_{\text{cell}} = -nFE^\circ_{\text{cell}}$.

If $E^\circ_{\text{cell}} > 0$, then the process is spontaneous (galvanic cell).

If $E^\circ_{\text{cell}} < 0$, then the process is nonspontaneous (electrolytic cell).

Nernst equation – Derivation

$$\Delta G = -nFE \quad (1)$$

with

n is the number of electrons transferred in the reaction (from balanced reaction),

F is the Faraday constant (96,500 C/mol), and

E is potential difference.

Under standard conditions, Equation 2 is then

$$\Delta G^\circ = -nFE^\circ \quad (2)$$

Hence, when E° is positive, the reaction is spontaneous and when E° is negative, the reaction is non-spontaneous. From thermodynamics, the Gibbs energy change under non-standard conditions can be related to the Gibbs energy change under standard Equations via

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (3)$$

Substituting $\Delta G = -nFE$ and $\Delta G^\circ = -nFE^\circ$ into Equation 3, we have:

$$-nFE = -nFE^\circ + RT \ln Q \quad (4)$$

Divide both sides of the Equation above by $-nF$, we have

$$E = E^\circ - \frac{RT \ln Q}{nF} \quad (5)$$

Equation 5 can be rewritten in the form of \log_{10} :

At standard temperature $T = 298 \text{ K}$, the $2.303RT/F$ term equals 0.0592 V and Equation 5 can be rewritten:

$$E = E^\circ - 0.0592 \log_{10} Q / n \quad (6)$$

Nernst equation applications-

Acid base, oxidation reduction

, Solubility equilibria

electrochemical methods provide a convenient way to determine the concentrations of very dilute solutions and the solubility products (K_{sp}) of sparingly soluble substances

the voltage of the concentration cell due to the difference in $[Ag^+]$ between the two cells is as follows:

$$E_{\text{cell}} = 0V - (0.0591V/1) \log([Ag^+]_{\text{dilute}}/[Ag^+]_{\text{concentrated}})$$

$$= -0.0591 \text{ V} \log(K_{sp}/1.0)$$

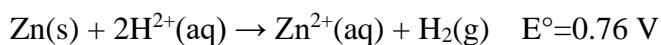
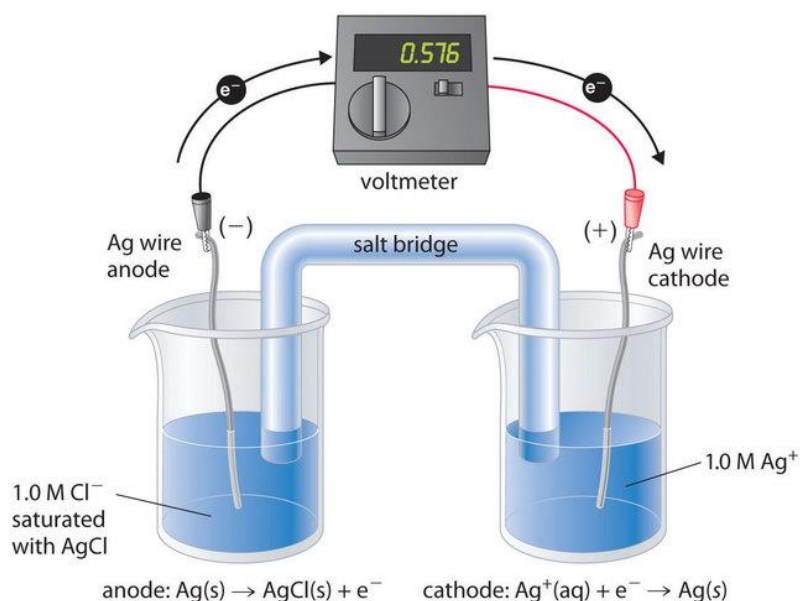
$$= -0.0591 \text{ V} \log K_{sp} \quad (1)$$

$$\log K_{sp} = -E_{\text{cell}}/0.0591 \text{ V} = -0.580 \text{ V}/0.0591 \text{ V} = -9.81$$

$$K_{sp} = 1.5 \times 10^{-10}$$

The solubility product of silver chloride

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$



E cell value is 0.26V

from Nernst equation

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591 \text{ V}) \log Q/n$$

we can calculate $[\text{H}^+]$ under nonstandard conditions

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591 \text{ V})/n \log ([\text{Zn}^{2+}]\text{P}_{\text{H}_2} / [\text{H}^+]^2)$$

$$0.26 = 0.76 \text{ V} - (0.0591 \text{ V}/2) \log ((1.0)(1.0)/[\text{H}^+]^2)$$

$$16.9 = \log(1/[\text{H}^+]^2) = \log[\text{H}^+]^{-2} = (-2) \log[\text{H}^+]$$

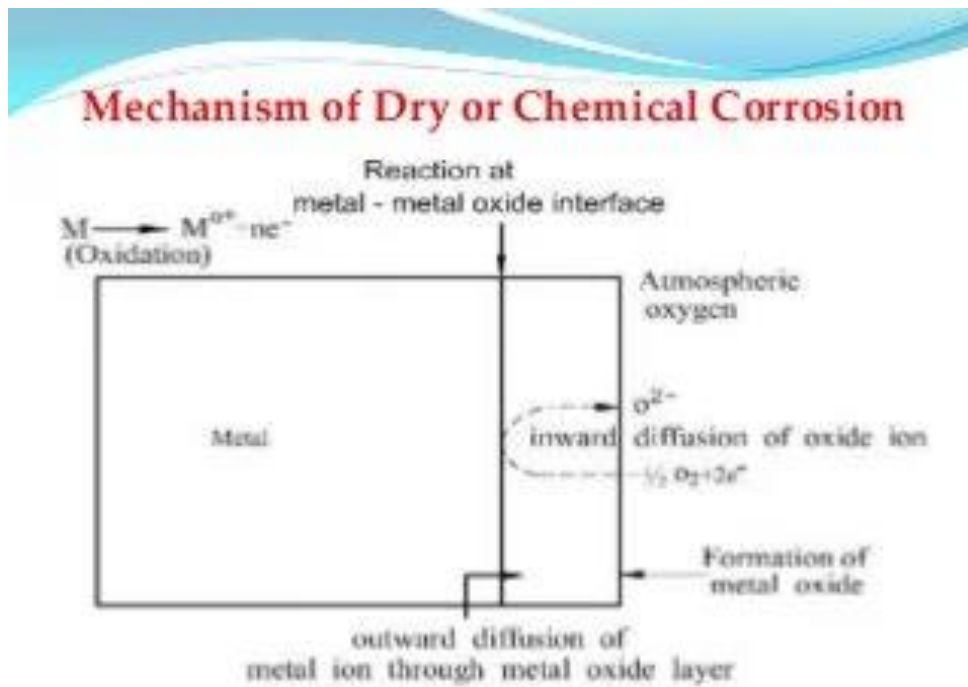
$$8.46 = -\log [\text{H}^+]$$

$$8.5 = \text{pH}$$

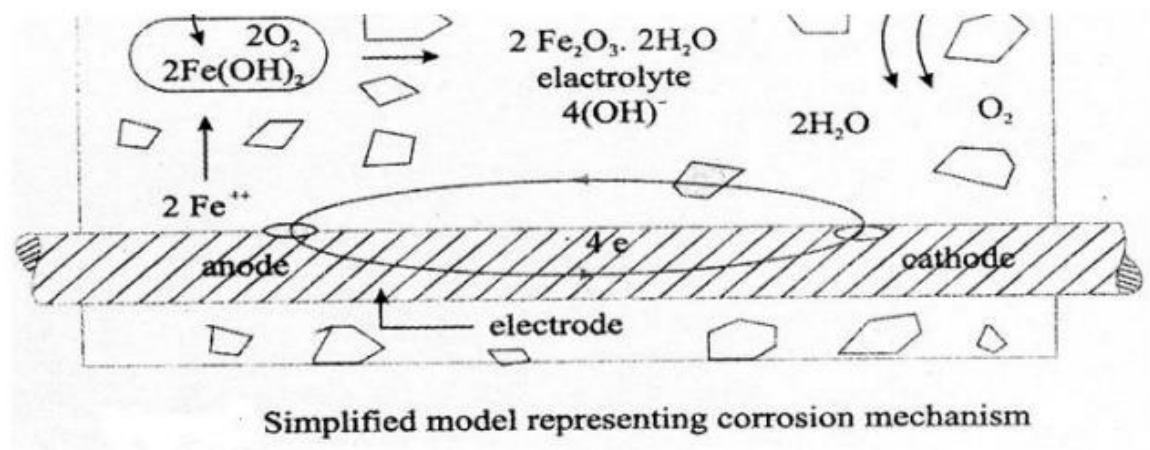
Definition, Types- Dry and Wet [Hydrogen evolution and Oxygen absorption types only]

Wet corrosion occurs in the presence of a liquid containing ions, an electrolyte. Problems with wet corrosion attacks in stainless steels occur in mineral acids, process solutions, seawater and other chloride containing media. Examples of wet corrosion forms are: Crevice corrosion



Dry corrosion or oxidation occurs when oxygen in the air reacts with metal without the presence of a liquid. Typically, dry corrosion is not as detrimental as wet corrosion, but it is very sensitive to temperature.



Wet Corrosion



Electrode potential expression for various electrodes

	$\text{F}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{F}^-(\text{aq})$	2.87	
	$\text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l})$	1.78	
	$\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$	1.51	
	$\text{Cl}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-(\text{aq})$	1.36	
	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^- \longrightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$	1.33	
	$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l})$	1.23	
	$\text{Br}_2(\text{l}) + 2 \text{e}^- \longrightarrow 2 \text{Br}^-(\text{aq})$	1.09	
	$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$	0.80	
	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	0.77	
	$\text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$	0.70	
	$\text{I}_2(\text{s}) + 2 \text{e}^- \longrightarrow 2 \text{I}^-(\text{aq})$	0.54	
	$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \longrightarrow 4 \text{OH}^-(\text{aq})$	0.40	
	$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Cu}(\text{s})$	0.34	
	$\text{Sn}^{4+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Sn}^{2+}(\text{aq})$	0.15	
	$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g})$	0	
	$\text{Pb}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Pb}(\text{s})$	-0.13	
	$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Ni}(\text{s})$	-0.26	
	$\text{Cd}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Cd}(\text{s})$	-0.40	
	$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Fe}(\text{s})$	-0.45	
	$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Zn}(\text{s})$	-0.76	
	$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	-0.83	
Weaker oxidizing agent	$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Al}(\text{s})$	-1.66	Stronger reducing agent
	$\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Mg}(\text{s})$	-2.37	
	$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$	-2.71	
	$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$	-3.04	

Free energy of a corrosion reaction – thermodynamics discussion

$$w = \Delta G = -nFE$$

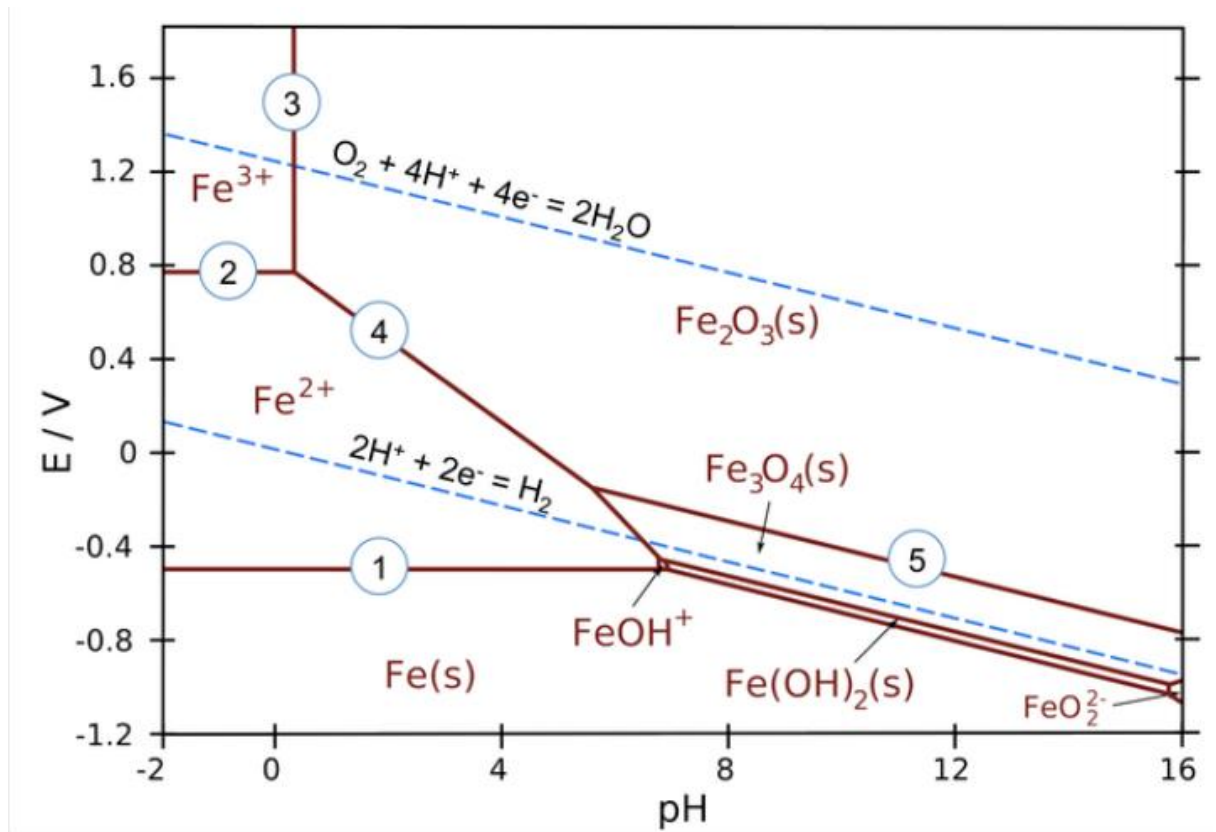
$$\Delta G^\circ = -nFE^\circ$$

Pourbaix diagram for Iron

Areas in the Pourbaix diagram mark regions where a single species ($\text{Fe}^{2+}(\text{aq})$, $\text{Fe}_3\text{O}_4(\text{s})$, etc.) is stable. More stable species tend to occupy larger areas.

Lines mark places where two species exist in equilibrium

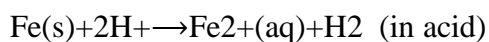
- **Pure redox** reactions are **horizontal** lines - these reactions are not pH-dependent
- **Pure acid-base** reactions are **vertical** lines - these do not depend on potential
- Reactions that are **both** acid-base and redox have a slope of $-0.0592 \text{ V/pH} \times \# \text{H}^+/\# \text{e}^-$



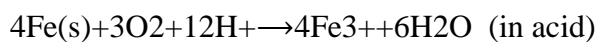
Examples of equilibria in the iron Pourbaix diagram (numbered on the plot):

1. $\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe(s)}$ (pure redox reaction - no pH dependence)
2. $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ (pure redox reaction - no pH dependence)
3. $2\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3(\text{s}) + 6\text{H}^+$ (pure acid-base, no redox)
4. $2\text{Fe}^{2+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3(\text{s}) + 6\text{H}^+ + 2\text{e}^-$ (slope = $-59.2 \times 6/2 = -178 \text{ mV/pH}$)
5. $2\text{Fe}_3\text{O}_4(\text{s}) + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{e}^-$ (slope = $-59.2 \times 2/2 = -59.2 \text{ mV/pH}$)

Below the H_2 line, water is unstable relative to hydrogen gas, and above the O_2 line, water is unstable with respect to oxygen. For active metals such as Fe, the region where the pure element is stable is typically below the H_2 line. This means that iron metal is unstable in contact with water, undergoing reactions:



Iron (and most other metals) are also thermodynamically unstable in air-saturated water, where the potential of the solution is close to the O_2 line in the Pourbaix diagram. Here the spontaneous reactions are:

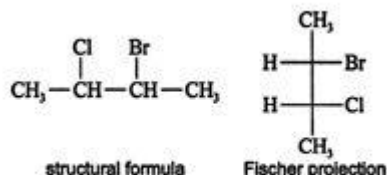


Immunity means that the metal is not attacked, while corrosion shows that general attack will occur. Passivation occurs when the metal forms a stable coating of an oxide or other salt on its surface, the best example being the relative stability of aluminium because of the alumina layer formed on its surface when exposed to air

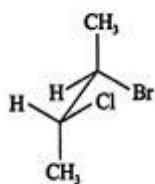
UNIT-3

Fischer, Sawhorse and Newmann projections - any one example for each

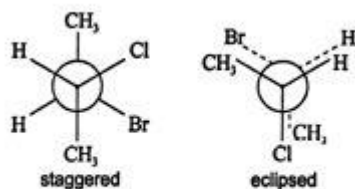
Fischer projection: The “backbone” atoms of a carbon chain are represented simply by a straight line, and the terminal carbons are written as groups. The atoms or groups bonded to the chain carbons are “attached” with perpendicular lines. Compare the structural formula and Fischer projection of 2-bromo-3-chlorobutane



In a sawhorse projection, the backbone carbons are represented by a diagonal line, and the terminal carbons are shown in groups, just as in the Fischer projection. You can see in the next illustration that the top carbon group of the Fischer projection of 2-bromo-3-chlorobutane has become the back carbon group of the sawhorse projection.



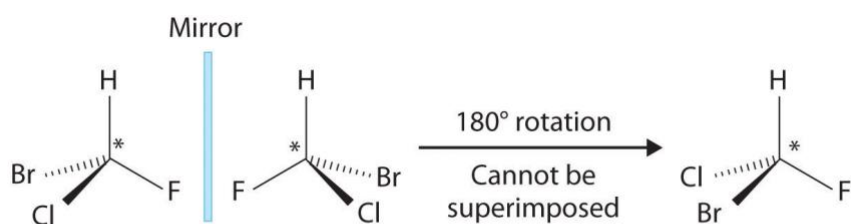
This type of projection is used mainly to show interaction leading to stress between atoms or groups in three-dimensional space due to steric crowding. In this representation, a molecule is viewed from one “end.” The “front” carbon of the backbone is represented by a dot, and the “back” carbon of the backbone is shown as a circle. Lines representing the bonds attaching the atoms and groups to the backbone carbons emanate from the dot and the circle at 120° angles. Compare the two conformations of 2-bromo-3-chlorobutane in the Newman projection to the previous sawhorse and Fischer projections.



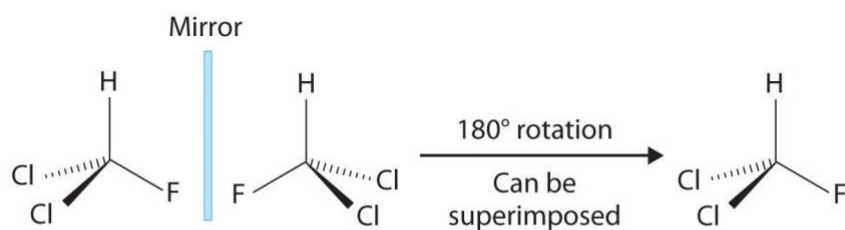
Structural isomers-Definition, types-chain, position, functional and metamerism with an example for each, Stereoisomers- enantiomers, diastereoisomers – definition with an example for each.

Stereoisomers contain different types of isomers within itself, each with distinct characteristics that further separate each other as different chemical entities having different properties

Enantiomers is the essential mirror-image, non-superimposable type of stereoisomer introduced in the beginning of the article. Figure 3 provides a perfect example; note that the gray plane in the middle demotes the mirror plane

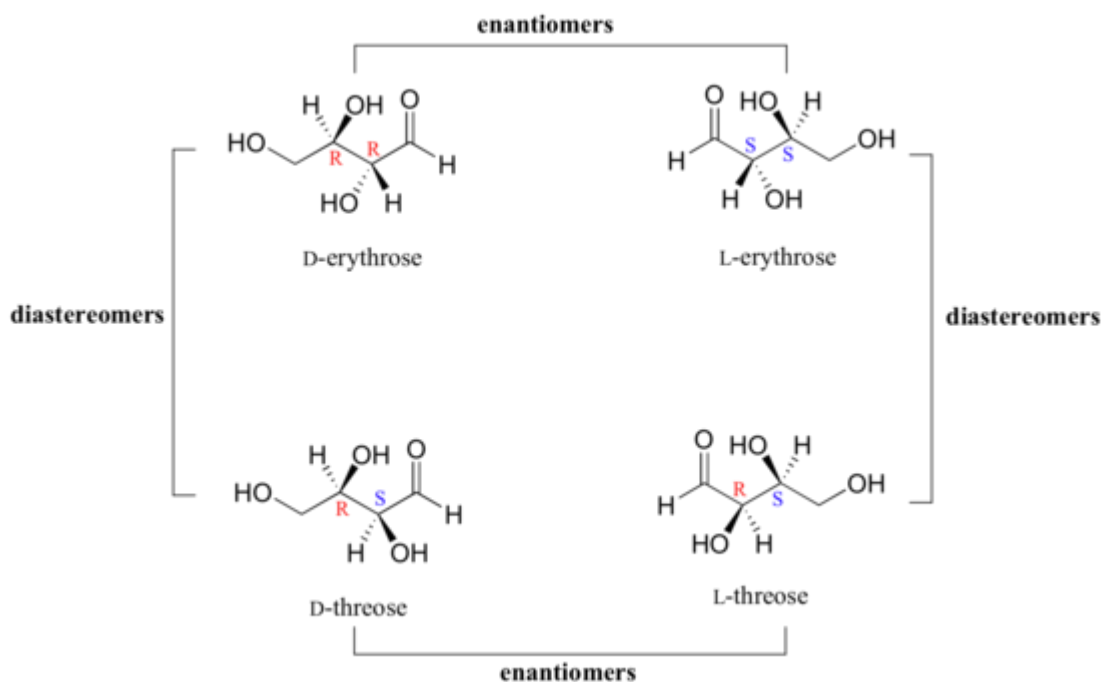


(a) Bromochlorofluoromethane



(b) Dichlorofluoromethane

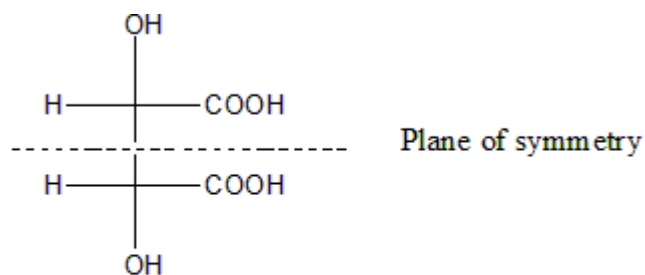
D-threose, is *not* a mirror image of erythrose. D-threose is a diastereoisomers of both D-erythrose and L-erythrose



Chirality essentially means 'mirror-image, non-superimposable molecules', and to say that a molecule is chiral is to say that its mirror image (it must have one) is not the same as it self

An **achiral object** is identical with (superimposable on) its mirror image

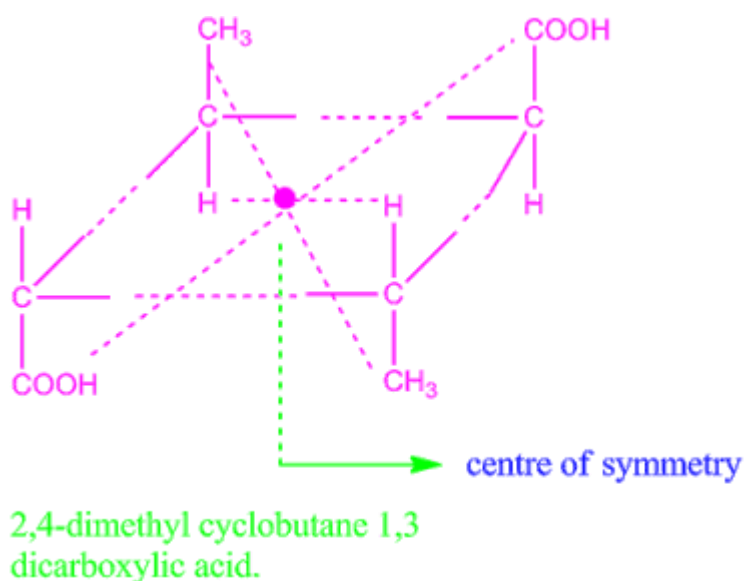
This molecule does have a plane of symmetry, and is therefore achiral. In general, any compound like this, having stereogenic carbons but also a plane of symmetry, is called a **meso compound**



Meso tartaric acid

An axis of symmetry is an imaginary axis around which by rotating through a minimum angle of rotation, the original compound is obtained

A **centre of symmetry** is an imaginary point in the molecules such that if a line is drawn from any group of the molecule to this point and then extended to an equal distance beyond the point, it meets the mirror images of the original group



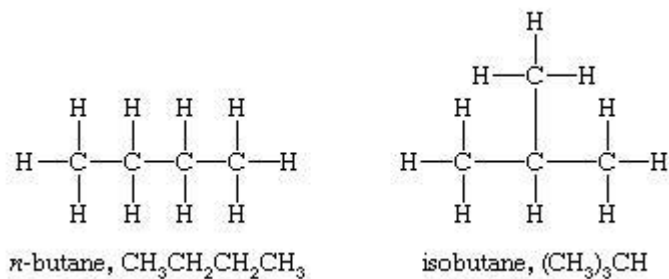
Structural isomers are molecules that have the same molecular formula but with the atoms connected in a different order.

There are three types of structural isomers.

1. Chain isomers

In chain isomers, the carbon atoms are connected in different orders.

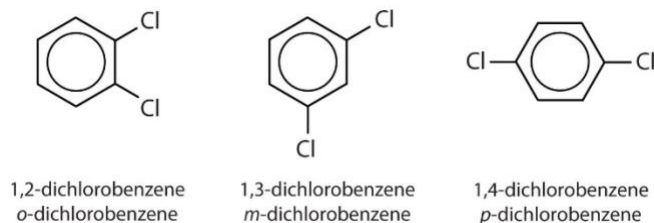
There are two isomers with the formula C_4H_{10} .



2. Position isomers

In position isomers, the carbon skeleton remains unchanged, but functional groups are moved around.

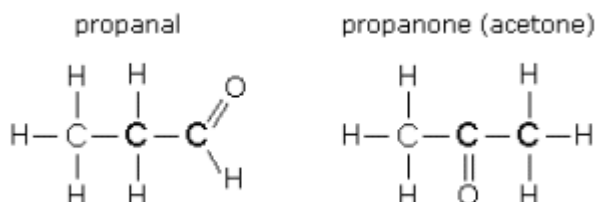
For example, there are two structural isomers with the molecular formula C_3H_7Br



3. Functional Group Isomers

In functional group isomers, the atoms are arranged to make different functional groups.

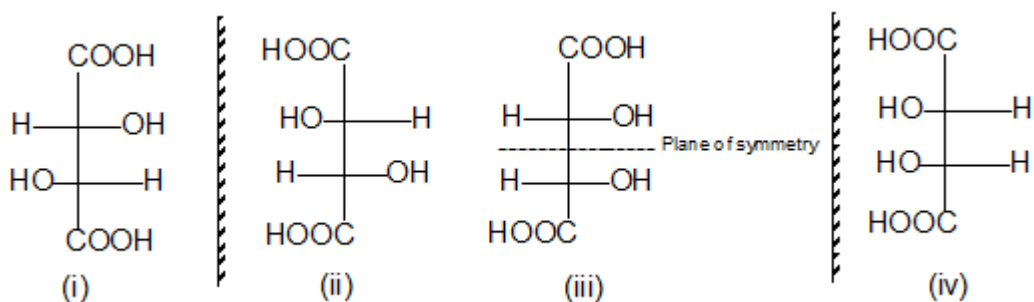
For example, a molecular formula C_3H_6O could be propanal (an aldehyde) or propanone (a ketone).



Optical activity

racemic, mesomers, dl isomers

The molecule contains two chiral carbon and the number of optical isomers should be $2^n=2^2=4$; but number of optical isomers reduces to 3 because one molecule has plane of symmetry.



III and IV are same

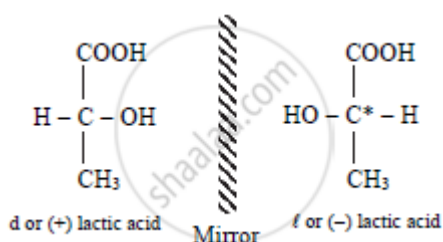
Rotation of IV by 180° yield III.

I and II are enantiomers

III is meso-form of tartaric acid.

A meso compound is one which is optically inactive although have more than one chiral carbons

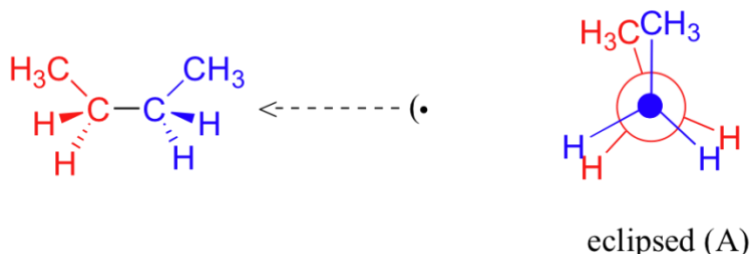
Optical Activity – Some substances have the property to rotate plane polarized light to the left or to the right. These substances are termed as optically active substance and this property is called Optical activity



Racemic mix. is always inactive (dl - form) due to external / internal compensation.
In case of lactic acid racemic mix. is inactive due to external compensation

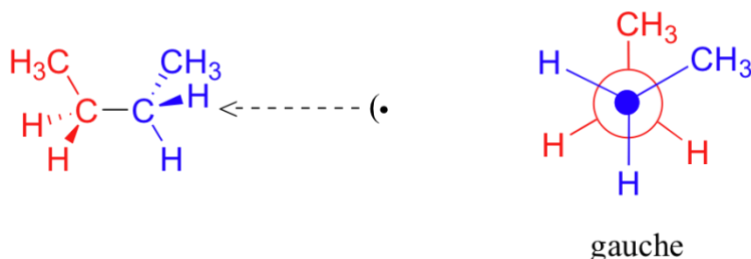
Conformational analysis- conformations of n-butane

There are now three rotating carbon-carbon bonds to consider, but we will focus on the middle bond between C₂ and C₃. Below are two representations of butane in a conformation which puts the two CH₃ groups (C₁ and C₄) in the eclipsed position



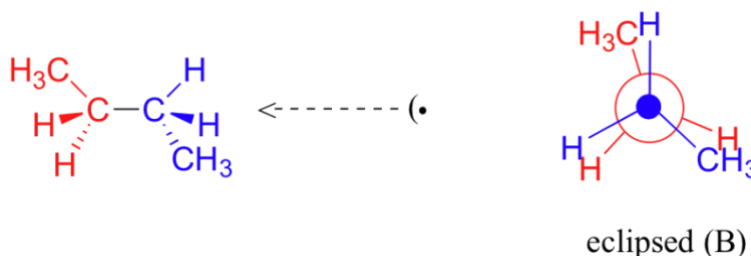
This is the highest energy conformation for butane, due to what is called '**van der Waals repulsion**', or '**steric repulsion**', between the two rather bulky methyl groups

Rotation of the front, (blue) carbon by 60° clockwise, the butane molecule is now in a staggered conformation



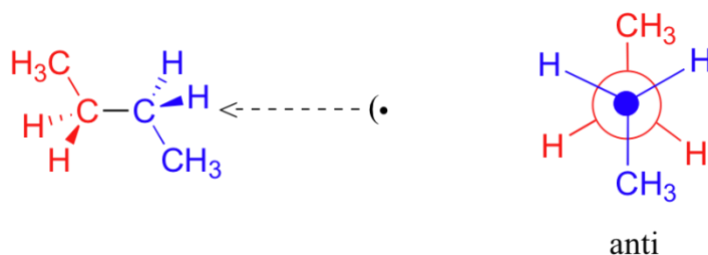
This is more specifically referred to as the '**gauche**' conformation of butane

A further rotation of 60° gives us a second eclipsed conformation (B) in which both methyl groups are lined up with hydrogen atoms



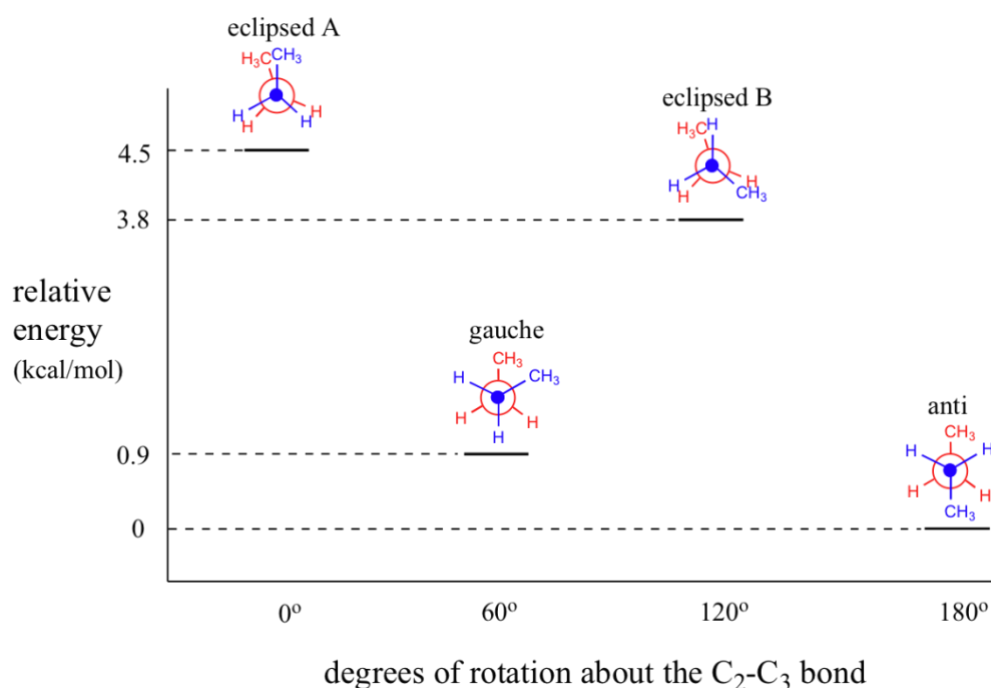
Due to steric repulsion between methyl and hydrogen substituents, this eclipsed conformation B is higher in energy than the gauche conformation. However, because there is no methyl-to-methyl eclipsing, it is lower in energy than eclipsed conformation A

One more 60° rotation produces the 'anti' conformation, where the two methyl groups are positioned opposite each other and steric repulsion is minimized



Anti form is the lowest energy conformation for butane

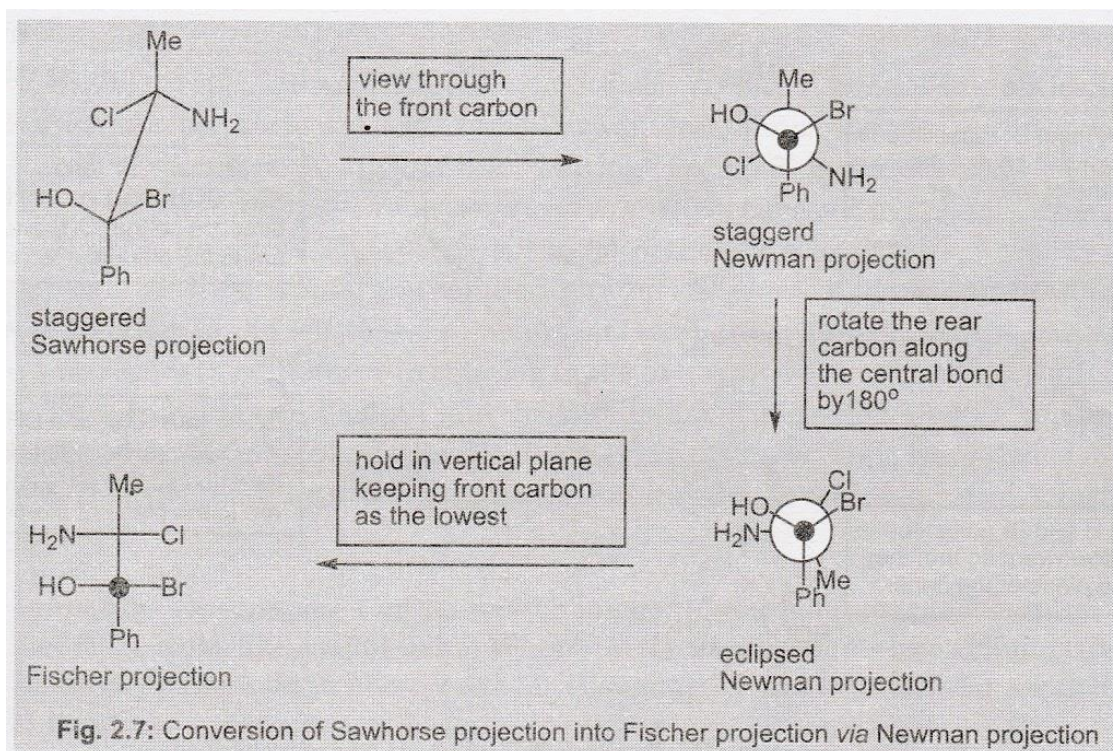
The diagram below summarizes the relative energies for the various eclipsed, staggered, and gauche conformations



Inter conversion of Sawhorse, Newman and Fischer projections with examples

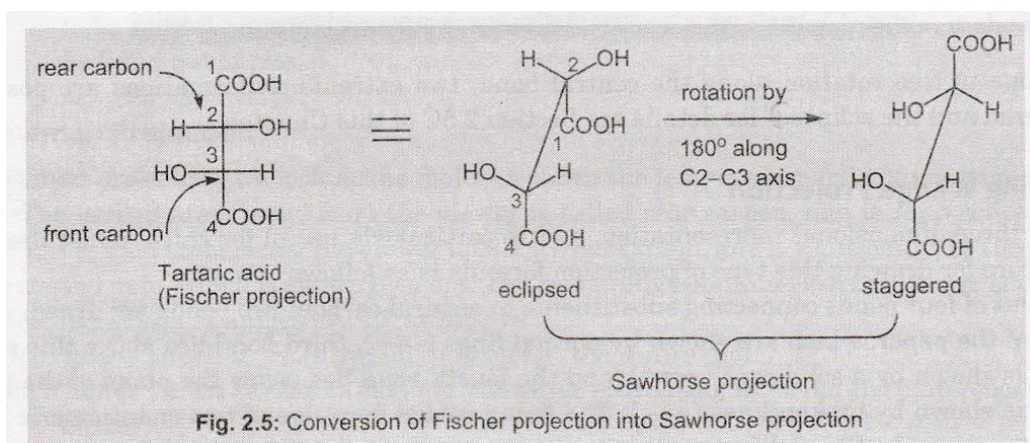
Sawhorse Projection to Newman Projection And then Fischer Projection

The molecule is viewed from front carbon (the central C-C bond being invisible) to get the staggered Newman projection. The rear carbon is rotated by 180° to get eclipsed Newman projection. Then, the molecule is held in the vertical plane, i.e. central bond is visible in the vertical plane in such a manner that front carbon is the lowest carbon



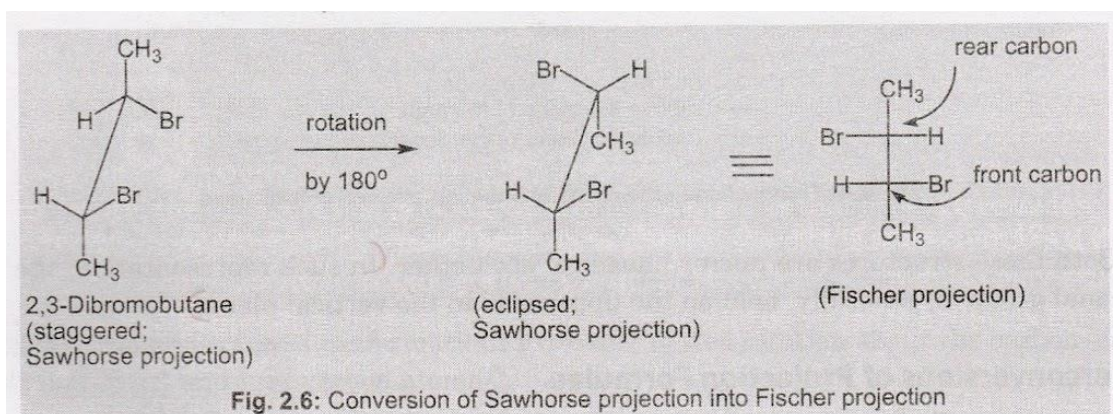
Fischer Projection to Sawhorse Projection

Fischer projection of a compound can be converted into Sawhorse projection; first in the eclipsed form (in Fischer projection the groups on neighbouring carbons are considered to be eclipsing each other), by holding the model in horizontal plane in such a way that the groups on the vertical line point above, and the last numbered chiral carbon faces the viewer. Then, one of the two carbons is rotated by an angle of 180° to get the staggered form (more stable or relaxed form).



Sawhorse Projection to Fischer Projection

First, the staggered Sawhorse projection is converted to an eclipsed projection. It is then held in the vertical plane in such a manner that the two groups pointing upwards are away from the viewer, i.e. both these groups are shown on the vertical line. Such a conversion for 2,3-dibromobutane is shown.



Brief account on Nucleophilic and Electrophilic substitution reactions with an example for each, explanation on S_N1 mechanism only taking an example.

- A **nucleophile** is an the electron rich species that will react with an electron poor species
- A **substitution** implies that one group replaces another.

Nucleophilic substitution reactions occur when an electron rich species, the **nucleophile**, reacts at an electrophilic saturated C atom attached to an electronegative group (important), the **leaving group**, that can be displaced as shown by the general scheme

S_N2 indicates a **substitution, nucleophilic, bimolecular** reaction, described by the expression rate = $k [\text{Nu}][\text{R-LG}]$.

This implies that the rate determining step involves an interaction between two species, the nucleophile and the organic substrate.

This pathway is a concerted process (single step) as shown by the following reaction coordinate diagrams, where there is simultaneous attack of the nucleophile and displacement of the leaving group



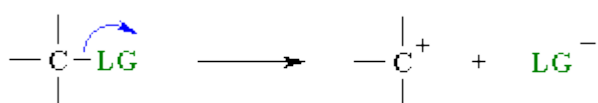
Reactivity order for S_N2 : $\text{CH}_3^- > \text{CH}_3\text{CH}_2^- > (\text{CH}_3)_2\text{CH}^- > (\text{CH}_3)_3\text{C}^-$

S_N1 indicates a **substitution, nucleophilic, unimolecular** reaction, described by the expression rate = $k [\text{R-LG}]$.

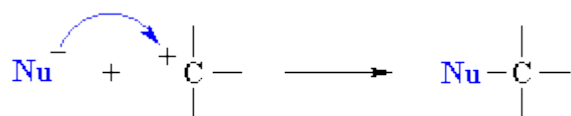
This implies that the rate determining step of the mechanism depends on the decomposition of a single molecular species.

This pathway is a multi-step process with the following characteristics

step 1: slow loss of the leaving group, LG, to generate a carbocation intermediate



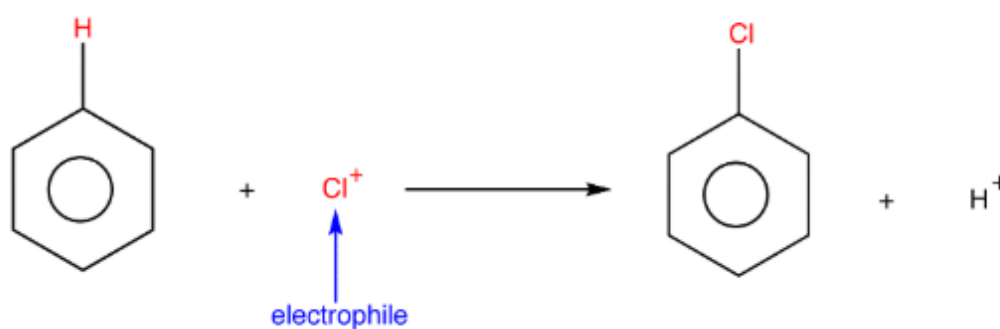
step 2 : rapid attack of a nucleophile on the electrophilic carbocation to form a new s bond



Reactivity order S_N1 : $(\text{CH}_3)_3\text{C}- > (\text{CH}_3)_2\text{CH}- > \text{CH}_3\text{CH}_2- > \text{CH}_3-$

Electrophilic substitution reactions

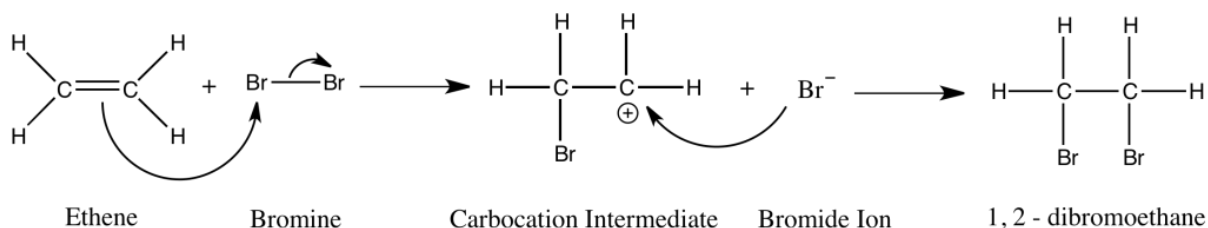
An electrophilic substitution reaction is a chemical reaction in which the functional group attached to a compound is replaced by an electrophile. The displaced functional group is typically a hydrogen atom.



Nucleophilic and Electrophilic and Free radical addition reactions

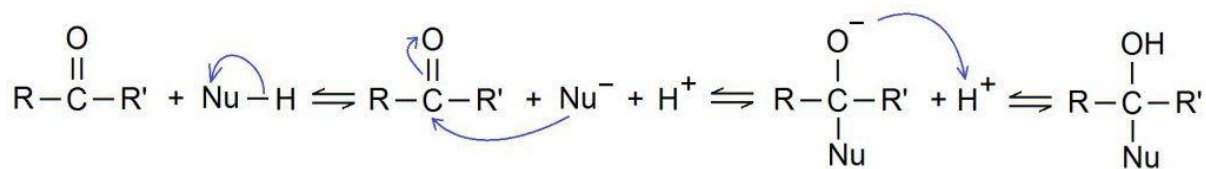
Electrophilic addition

An electrophilic addition reaction can be described as an addition reaction in which a reactant with multiple bonds as in a double or triple bond undergoes has its π bond broken and two new σ bonds are formed



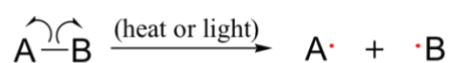
Electrophilic Addition mechanism between Ethene and Bromine

A nucleophilic addition reaction is an addition reaction where a chemical compound with an electron-deficient or electrophilic double or triple bond, a π bond, reacts with a nucleophile which is an electron-rich reactant with the disappearance of the double bond and creation of two new single, or σ , bonds



Radical chain reactions have three distinct phases: initiation, propagation, and termination

initiation



propagation



termination



Brief account on types of elimination reactions- (E1 and E2 only) with an example for each, explanation on E2 mechanism only taking an example.

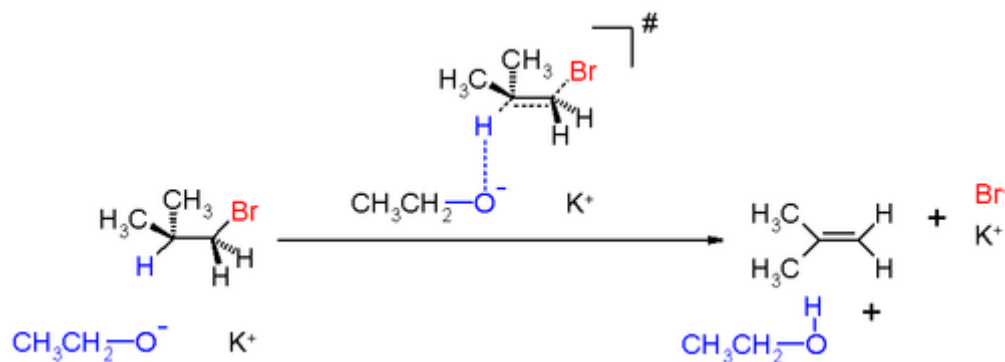
elimination reactions

E2 mechanism — bimolecular elimination

E1 mechanism — unimolecular elimination

E2 is a single step elimination, with a single transition state.

It is typically undergone by primary substituted alkyl halides, but is possible with some secondary alkyl halides and other compounds.

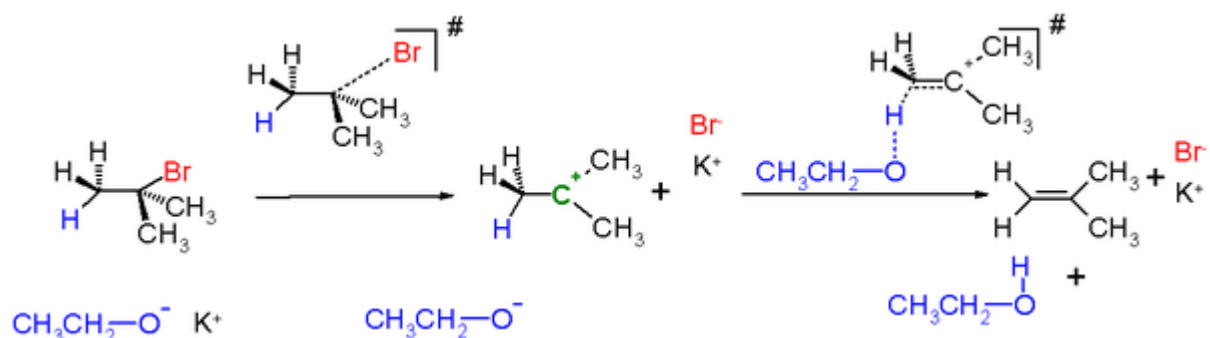


E1 is a model to explain a particular type of chemical elimination reaction. E1 stands for **unimolecular elimination** and has the following specifications

It is a two-step process of elimination: ionization and deprotonation.

Ionization: the carbon-halogen bond breaks to give a carbocation intermediate.

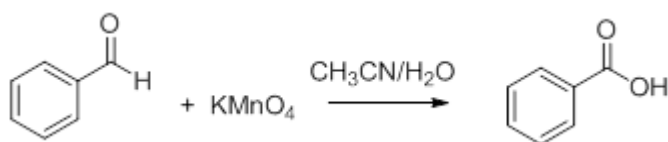
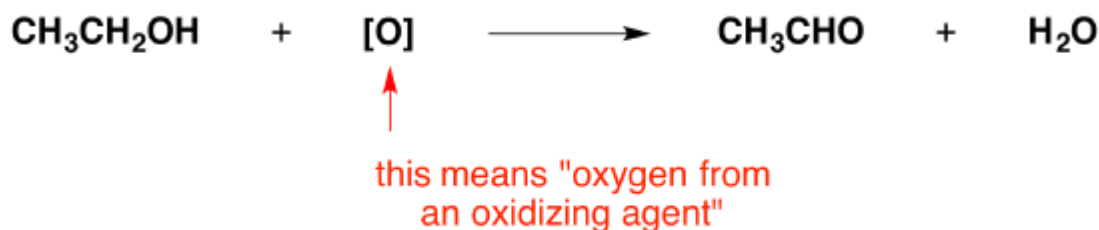
deprotonation of the carbocation



Explanation taking KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ as oxidizing agents only

KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ as oxidizing agents

The oxidizing agent used in these reactions is normally a solution of sodium or potassium dichromate(VI) acidified with dilute sulfuric acid. If oxidation occurs, then the orange solution containing the dichromate(VI) ions is reduced to a green solution containing chromium(III) ions. The electron-half-equation for this reaction is as follows

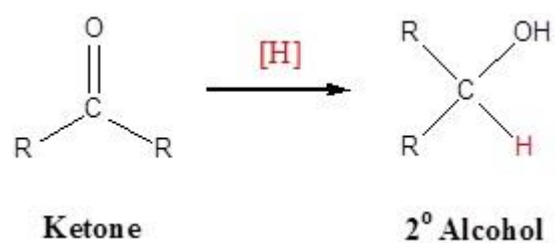
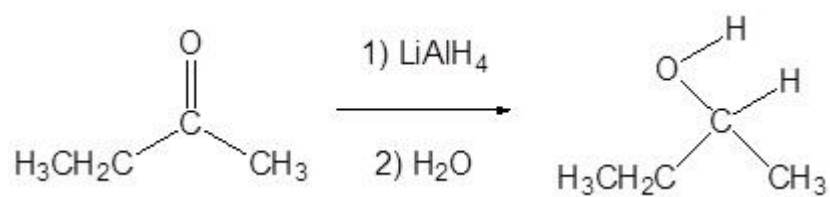
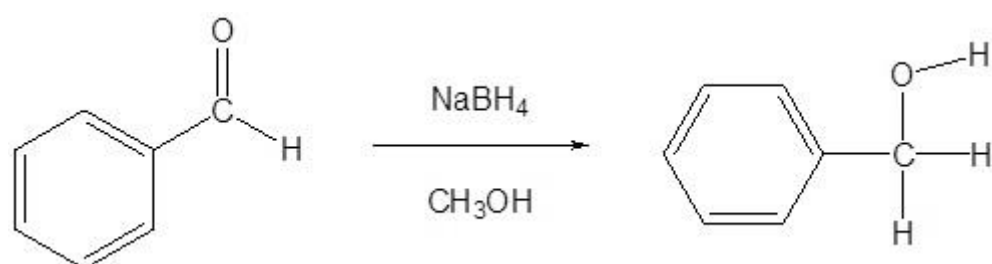


Explanation taking LiAlH_4 and NaBH_4 as reducing agents only

The most common sources of the hydride nucleophile are lithium aluminium hydride (LiAlH_4) and sodium borohydride (NaBH_4).

The hydride anion is not present during this reaction; rather, these reagents serve as a source of hydride due to the presence of a polar metal-hydrogen bond. Because aluminium is less electronegative than boron, the Al-H bond in LiAlH_4 is more polar, thereby, making LiAlH_4 a stronger reducing agent.

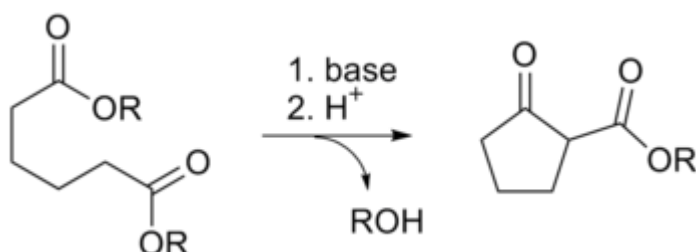
Addition of a hydride anion (H^-) to an aldehyde or ketone gives an alkoxide anion, which on protonation yields the corresponding alcohol. Aldehydes produce 1°-alcohols and ketones produce 2°-alcohols.



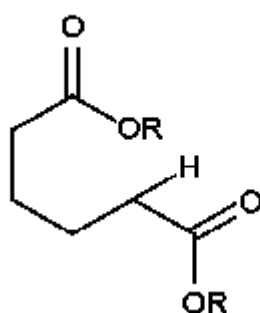
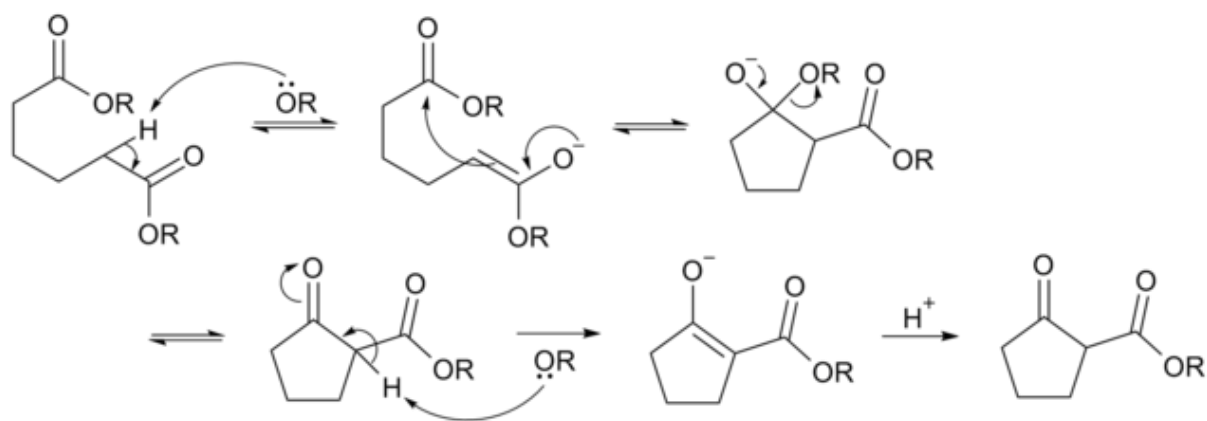
ELECTROPHILE	NUCLEOPHILE
Also called as Lewis acid	Also called as Lewis base
They are positively charged / neutral	They are negatively charged / neutral
They undergo electrophilic addition and electrophilic substitution reactions	They undergo nucleophilic addition and nucleophilic substitution reactions
Electron-deficient	Electron-rich
It accepts a pair of an electron to form a covalent bond	It donates a pair of an electron to form a covalent bond
All carbocations	All carbanions
Example: Hydronium Ion	Example: Chloride Ion

Dieckmann Condensation

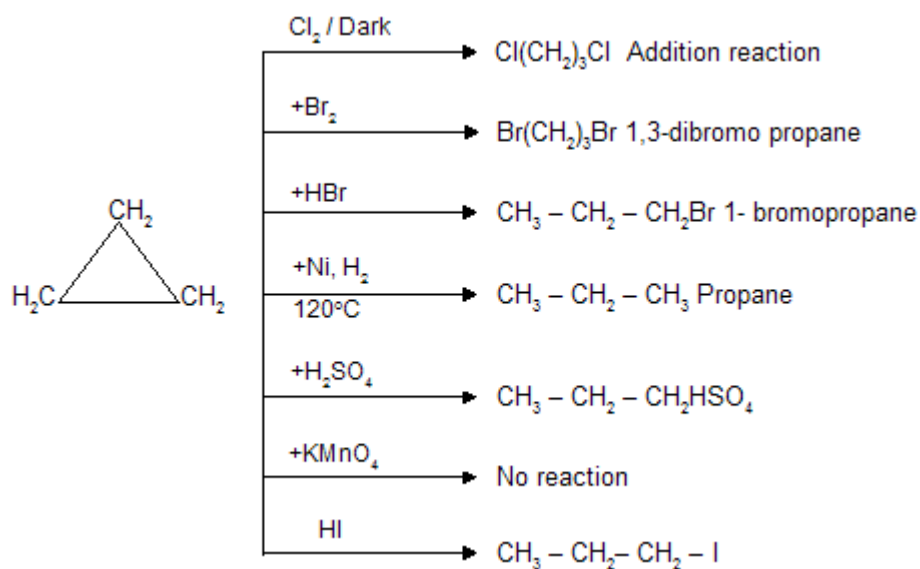
The **Dieckmann condensation** is the intramolecular chemical reaction of diesters with base to give β -ketoesters



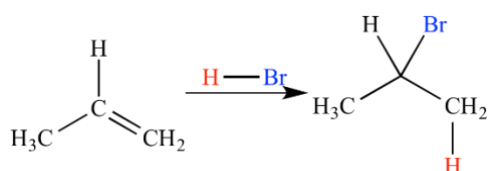
deprotonation of an ester at the α -position generates an enolate ion which then undergoes a 5-exo-trig nucleophilic attack to give a cyclic enol. Protonation with a Bronsted-Lowry acid (H_3O^+ for example) re-forms the β -keto ester



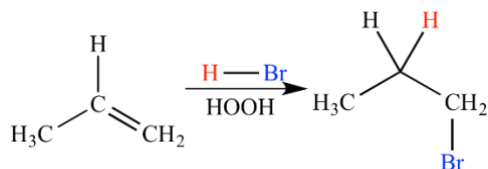
Addition of $\text{Cl}_2/\text{Br}_2/\text{HI}/\text{H}_2\text{SO}_4/\text{H}_2$ to cyclopropane



Markovnikov's rule (Markovnikov addition): In an addition reaction of a protic acid HX (hydrogen chloride, hydrogen bromide, or hydrogen iodide) to an alkene or alkyne, the hydrogen atom of HX becomes bonded to the carbon atom that had the greatest number of hydrogen atoms in the starting alkene or alkyne

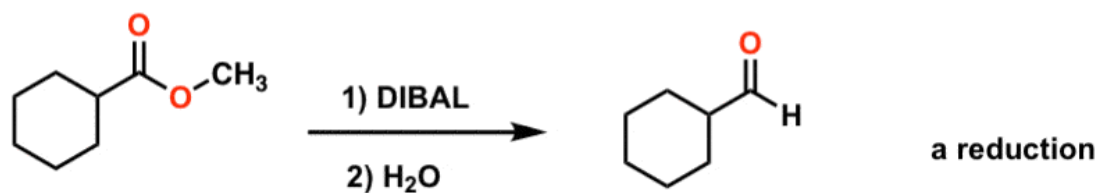
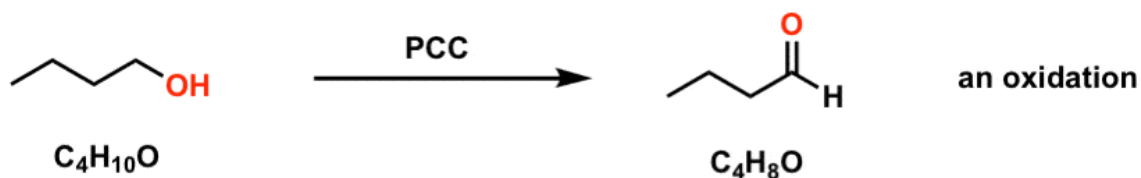


Addition of hydrogen bromide to propene follows Markovnikov's rule



Anti-Markovnikov addition of hydrogen bromide to propene, illustrating the peroxide effect

Oxidations and reductions



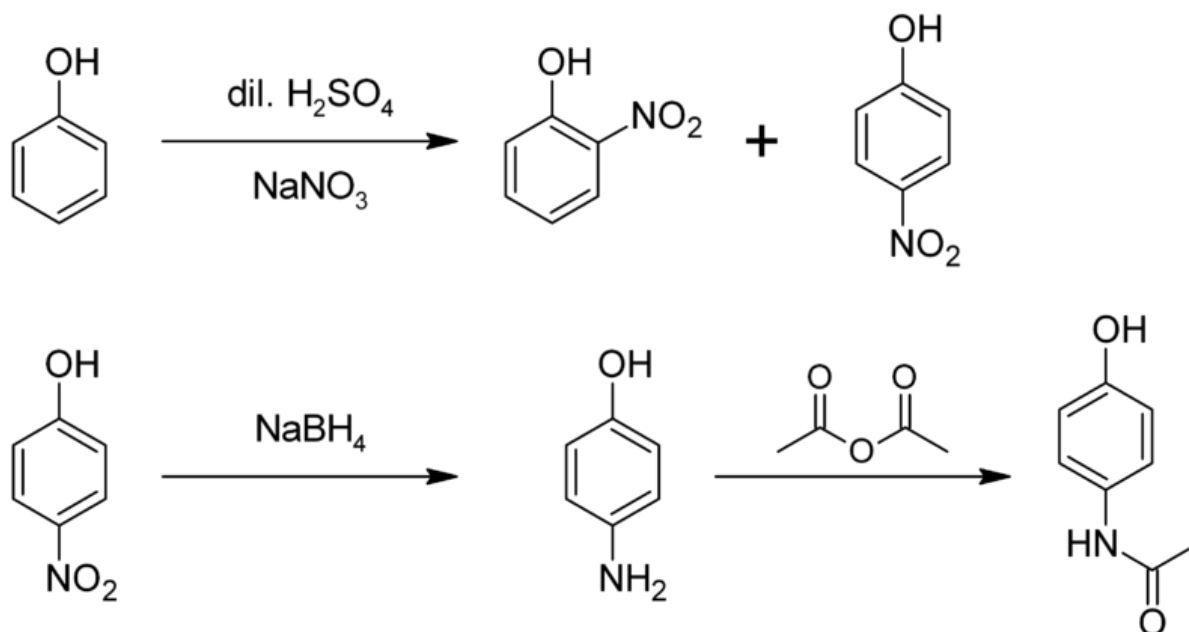
Drug molecules Explanation

A drug is a chemical that interacts with proteins in the body to affect a physiological function

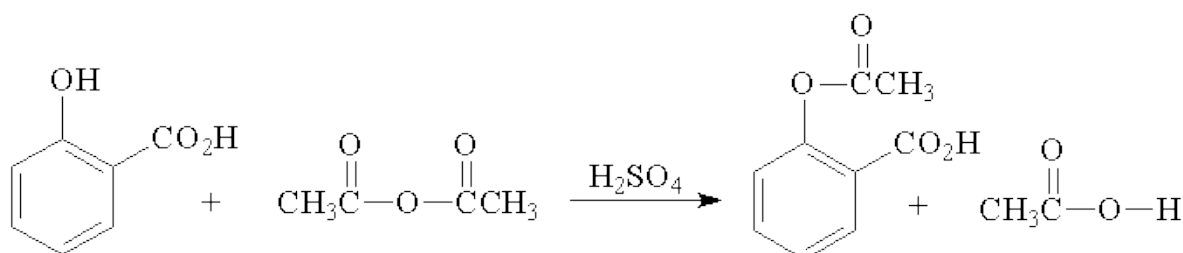
For example, anticancer drugs bind to proteins on the surface of cancer cells this stimulates the cells to die. In this case cell death is the physiological action of the drug

Paracetamol is a common painkiller used to treat aches and pain. It can also be used to reduce a high temperature.

It's available combined with other painkillers and anti-sickness medicines. It's also an ingredient in a wide range of cold and flu remedies.



Synthesis of Aspirin and its uses



It works by stopping the production of certain natural substances that cause fever, pain, swelling, and blood clots. Aspirin is also available in combination with other medications such as antacids, pain relievers, and cough and cold medications

medicinal drugs and its uses

Antipyretics: reducing fever (pyrexia/pyresis)

Analgesics: reducing pain (painkillers)

Antimalarial drugs: treating malaria.

Antibiotics: inhibiting germ growth.

Antiseptics: prevention of germ growth near burns, cuts and wounds.

UNIT-4

Introduction to concept of macromolecules

A macromolecule is a very large molecule important to biophysical processes, such as a protein or nucleic acid. It is composed of thousands of covalently bonded atoms. Many macromolecules are polymers of smaller molecules called monomers.

The most common macromolecules in biochemistry are biopolymers (nucleic acids, proteins, and carbohydrates) and large non-polymeric molecules such as lipids, nanogels and macrocycles. Synthetic fibers and experimental materials such as carbon nanotubes are also examples of macromolecules.

Macromolecules are composed of much larger numbers of atoms than ordinary molecules. For example, a molecule of polyethylene, a plastic material, may consist of as many as 2,500 methylene groups, each composed of two hydrogen atoms and one carbon atom. The corresponding molecular weight of such a molecule is on the order of 35,000. Insulin, a protein hormone present in the pancreas and responsible for regulation of blood-sugar levels, has a molecular unit derived from 51 amino acids (by themselves molecules containing carbon, hydrogen, oxygen, nitrogen, and sometimes sulfur).

There are three main types of biological macromolecules, according to mammalian systems:

Carbohydrates

Nucleic acids

Proteins

Lipids

Macromolecules are basically polymers, long chains of molecular sub-units called monomers. Carbohydrates, proteins and nucleic acids are found as long polymers. Due to their polymeric nature and large size, they are known as macromolecules.

There are three major groups of macromolecules that are essential in the industry, apart from biological macromolecules. These include plastics, fibres, and elastomers.

Elastomers are macromolecules that are flexible and stretchy. The elastic property lets these materials to be used in products like hair bands and elastic waistbands. These objects could be stretched, and they return to their original structure once released.

We wear fibre macromolecules. Nylon, Polyester, and acrylic fibres are used in everything from blouses, belts to shirts and shoes. Natural fibres include wool, cotton, and silk.

Hence, there are many objects that we use today are made up of macromolecules. Many types of plastics are made through a process known as polymerization, which is the joining of monomer units from plastic products

Tacticity

Tacticity (from Greek: τακτικός, romanized: taktikos, "relating to arrangement or order") is the relative stereochemistry of adjacent chiral centers within a macromolecule. The practical significance of tacticity rests on the effects on the physical properties of the polymer.

Tacticity refers to the manner in which the pendant groups are arranged along the hydrocarbon chain. In reality, hydrocarbon chains are not long, flat chains lying across a surface, but are instead three-dimensional chains with some atoms projecting out of the plane.

An isotactic polymer is one in which all of the pendant groups are located on the same side of the hydrocarbon backbone chain. A popular form of polypropylene that is commonly marketed is an example of an isotactic polymer.

A syndiotactic polymer is one in which the pendant groups have a regular, alternating pattern along the hydrocarbon backbone chain. Gutta-percha, which is a type of permanent dental filling that is used in root canals because of its biological inertness, is an example of a syndiotactic polymer.

An atactic polymer is one in which the pendant groups are randomly arranged along the hydrocarbon backbone. Polystyrene is an example of an atactic polymer.

The mechanical, physical, and chemical properties of polymers depend upon their tacticity. In general, syndiotactic polymers form the most rigid, crystalline structures of the three tacticities. Isotactic polymers are semi-crystalline, and atactic polymers are amorphous in form, with no crystalline structure. If you picture in your mind a hydrocarbon backbone with pendant groups jutting out in any and every direction, you can imagine why it would be difficult to pack such molecules together into an organized crystal. That's why polymers with a more regular structure, like the isotactic and syndiotactic types, can have a crystalline structure.

Classification of Polymers

- Natural Polymers: ...
- Semi-synthetic Polymers: ...
- Synthetic Polymers: ...
- Linear Polymers. ...
- Branched-chain Polymers. ...
- Cross-linked Polymers. ...
- Classification Based on Polymerization. ...
- Classification Based on Monomers.

There are 3 principal classes of polymers – thermoplastics, thermosets, and elastomers. Differentiation between these classes is best defined by their behaviour under applied heat.

Thermoplastic polymers can be either amorphous or crystalline.

Thermoplastics are a class of polymers that can be softened and melted by the application of heat, and can be processed either in the heat-softened state (e.g. by thermoforming) or in the liquid state (e.g. by extrusion and injection molding).

Properties: Hard, brittle, opaque, good electrical and heat resistance, resistant to deformation under load, low cost, resistant to most acids.

Example: acrylic, polyester, polypropylene, polystyrene, nylon and Teflon

Thermosetting Polymers are the type of polymers where the macromolecular chains tend to bond with one another forming the cross-linked 3D network. These polymers are also known as Thermosetting plastics or Thermosets. The definition of the word Thermosetting translates to a term which means setting permanently upon heating. Thus the Thermosetting Polymers get the hard texture after they are exposed to heating to their pre-Thermoset form.

Properties: Rigid, clear, very tough, chemical resistant, good adhesion properties, low curing, low shrinkage.

Example: Bakelite, Epoxy Resin, Melamine Resin, Duroplast, and Urea-Formaldehyde

An elastomer is a polymer with viscoelasticity (i.e. both viscosity and elasticity) and with weak intermolecular forces, generally low Young's modulus and high failure strain compared with other materials

Properties

Temperature: The specific working temperature of elastomers vary depending on the factors like media compatibility, seal design, and dynamic and static operation.

Low-temperature flexibility: The rate of recovery of elastomeric material can be studied by subjecting the material to low-temperature retraction.

Hardness: The measurement of the material's resistance towards the deforming force for a defined length of time is done by measuring the hardness. It differs from material to material. The soft compounds deform easily and have high friction, while the harder compounds have high resistance and low friction.

Ageing: This property helps to understand the behaviour of a material when exposed to heat. If the elastomers are pushed beyond their ageing resistance, they will suffer from hardening, cracking, and splitting.

Colour: Colouring is used mainly to differentiate between the compound grades based on their usage.

Elongation at break: This property is used for testing the moment of rupture when the material is under tensile stress.

Examples: Natural rubber: These are used in the automotive industry and in the manufacture of medical tubes, balloons, adhesives.

Polyurethanes: These are used in the textile industry for manufacturing elastic clothing like lycra.

Polybutadiene: These are used for providing wear resistance in wheels of vehicles.

Silicone: These are used in the manufacture of medical prostheses and lubricants as they have excellent chemical and thermal resistance.

Neoprene: These are used in the manufacture of wet-suits and in industrial belts.

Types of Polymerization

Linear polymers: Consists of a long and straight-chain of monomers. PVC is a linear polymer.

Branched polymers: They are linear polymers containing some branches. ...

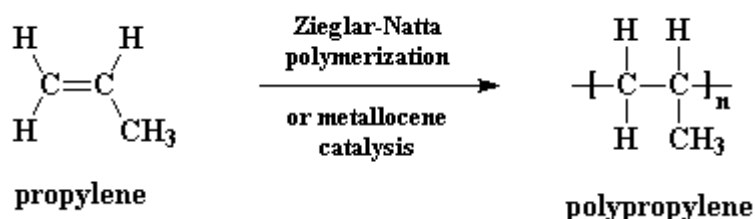
Network or cross-linked polymer: Polymers having cross-linked bonds with each other is called cross-linked or network polymer.

In addition polymerization (sometimes called chain-growth polymerization), a chain reaction adds new monomer units to the growing polymer molecule one at a time through double or triple bonds in the monomer. Example: polyethylene, polyvinyl chloride (PVC), acrylics, polystyrene, polytetrafluoroethylene, and polyoxymethylene (acetal).

Condensation polymerization is a process that involves repeated condensation reactions between two different bi-functional or tri-functional monomers. Example: nylon 6,6 polyester, bakelite

Addition Polymerization

Poly Propylene



Properties

Semi-rigid.

Translucent.

Good chemical resistance.

Tough.

Good fatigue resistance.

Integral hinge property.

Good heat resistance.

Applications

polypropylene uses are not limited to not only useful for tote bags but also encompass a much wider range of other products, including ropes, twine, tape, carpets, upholstery, clothing and camping equipment. Its waterproof properties make it especially effective for the marine sector.

Properties of Polystyrene

Polystyrene exists in an amorphous state because of the presence of bulky phenyl groups, packing of polystyrene chains is not efficient.

Polystyrene is non-polar in nature.

The polystyrene melting point is 240 degrees Celsius.

Polystyrene density is 1.05 g/cm³

The polystyrene boiling point is 430 degrees Celsius.

Polystyrene thermal conductivity is 0.003 W/m.K.

Polystyrene-specific gravity is 1.054.

Polystyrene has a good optical property like it is a transparent polymer allowing high transmission of all wavelengths. Moreover, its high refractive index gives it a particularly high brilliance.

Due to the chain stiffening effect of the benzene ring, polystyrene is hard but brittle. It emits a characteristic metallic sound when dropped.

Being a non-polar amorphous polymer, its softening temperature is low. It cannot withstand the temperature of boiling water.

Polystyrene has a low tendency for moisture absorption. Moreover, it has good electrical insulation characteristics. Therefore, it is used in making polystyrene insulation products.

Polystyrene has reasonable chemical resistance but mediocre oil resistance.

Use of Polystyrene

It is used for making polystyrene products like polystyrene sheets, polystyrene foam, brush handles, and combs.

It is used for making talcum powder.

It is used for making polystyrene plastic like small jars, bottle caps, polystyrene cups, and storage containers.

It is used for making audio cassettes.

The demand for styrene in liquid form is estimated to be more than 15 million metric tonnes, and the need for its many applications mainly determines it. Western and Eastern Europe and North America have the highest yearly capacity for styrene manufacturing.



Properties of PVC

By nature, PVC is a lightweight, sturdy and abrasion-resistant material.

This versatile thermoplastic polymer is resistant to the action of all inorganic chemicals.

PVC is an excellent material for insulation due to its high dielectric strength and vapour barrier capacity.

It can withstand extreme climatic conditions, shock and is free from corrosion. Hence, it is the preferred method for several outdoor applications.

Since the durability is more, long-life is assured.

PVC products are self-extinguishing due to high chlorine content.

PVC can be made more flexible and softer by adding plasticizers such as phthalate and can be bent as per requirement.

PVC is an intrinsic flame retardant.

It offers good tensile strength and is rigid by nature.

It is economical and is an affordable solution.

It demands less maintenance and offers resistance to grease and oil.

Applications

Plasticized PVC is used in flooring or (PVC-U) unplasticized PVC is used in making window frames.

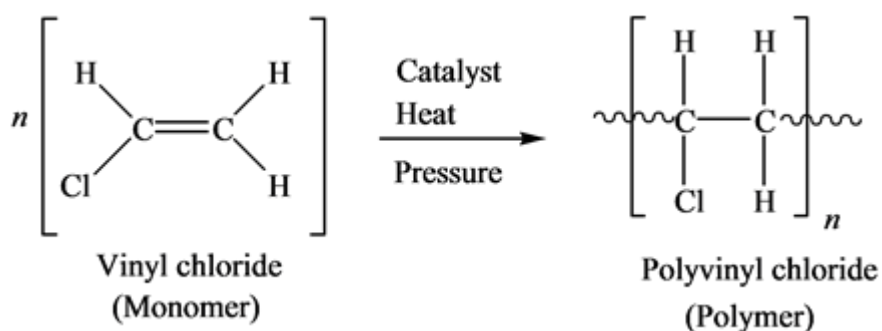
It is used in making sewage pipes and other pipe applications where cost or vulnerability to corrosion limit the use of metal.

Used in construction fields for insulation on electrical wires or in flooring for hospitals, schools, homes, and other areas where a sterile environment is a priority.

It is used in various industries like building, electronics, electrical, automotive, medical and packaging.

PVC fabric is used in the manufacture of aprons shower curtains, raincoats, jackets and sports bags.

It is used in the garden hose and imitation leather upholstery.



Properties of Teflon

It is a white solid compound at room temperature.

Its density is about 2200 kg/m³ 2.2 g/cm³

Its melting point is 600 K.

It is a chemical resistance compound, the only chemicals that can affect these compounds are alkali metals.

It shows good resistance towards heat and low temperature.

It has a low water absorption capacity.

It has an anti-adhesion ability due to which it is used as non-stick kitchen utensils.

Uses of Teflon

It is used in making waterproof fabric.

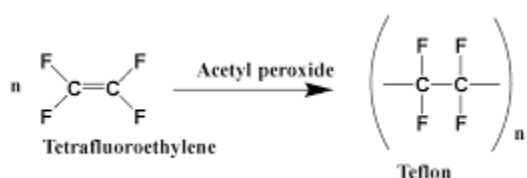
It is used in making non-stick cookware.

It is used in making an anti-friction device.

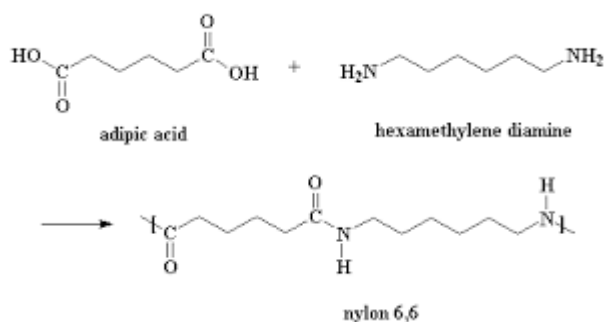
It is used for coating medical appliances (surgical devices).

Due to its high resistance to corrosion, it is used for coating the lining of laboratory appliances.

Preparation of Polytetrafluoroethylene (PTFE) or Teflon



Nylon



Properties of Nylon

There are many properties of the nylon fabric, which include the following:

They have a dense molecular structure

These are extremely elastic

They are very resilient and durable

Nylon is an abrasion-resistant fabric

The fabric is water-resistant in nature

Nylon fabric has resistance to stains, heat, UV rays, and chemicals

There is resistance to mould and mildew

The fabric is one that dries quickly

Uses of Nylon

Nylon is a fabric that has many applications in our daily lives. Some of them are:

The fabric is used for car components that are close to the engine

It is used for making toys and many other plastic utilities

The fabric is used for making swimwear as it is known for its waterproof nature

The resins of the Nylon fabric are used for perfect food packaging

This fabric is used for tents, ropes, tires and various other military supplies

Properties of Polyester Fibre

There are a few properties of the Polyester Fibre that one must know of:

The fibre is strong, resilient, and durable

It is very resistant to stretching and shrinking

The fibre has resistance to many chemicals

The fibre dries very quickly

One can expect it to be wrinkle-resistant

There is a good resistance to moulds, abrasions, and mildew from this fibre

The fibre is able to retain heat-set pleats

The fibre is recyclable

PROPERTIES

Good Abrasion Resistance

Good Impact Resistance

Good Toughness

Low Viscosity

High Elongation

Good Flexibility

Good tear Strength

Low Shrinkage

Hydrolytically Stable

Resilient

Thermal properties of polyurethanes are influenced mainly by molecular weight between the cross links , degree of segments in stiff sequence.

Mechanical properties such as elongation break, tear strength, tensile strength are largely influenced by the presence of aromatic groups, long alkyl chain , branching and cross linking and also degree of secondary bonding forces.

Chemical properties of Polyurethane are greatly influenced by the types of isocyanates and polyols used to make it.

USE OF POLYURETHANES

Polyurethanes are used in

The manufacture of flexible, high-resilience foam seating

Rigid foam insulation panels

Microcellular foam seals and gaskets

Durable elastomeric wheels and tires(such as roller coaster wheels)

Automotive suspension bushings

Electrical potting compounds

High performance adhesives

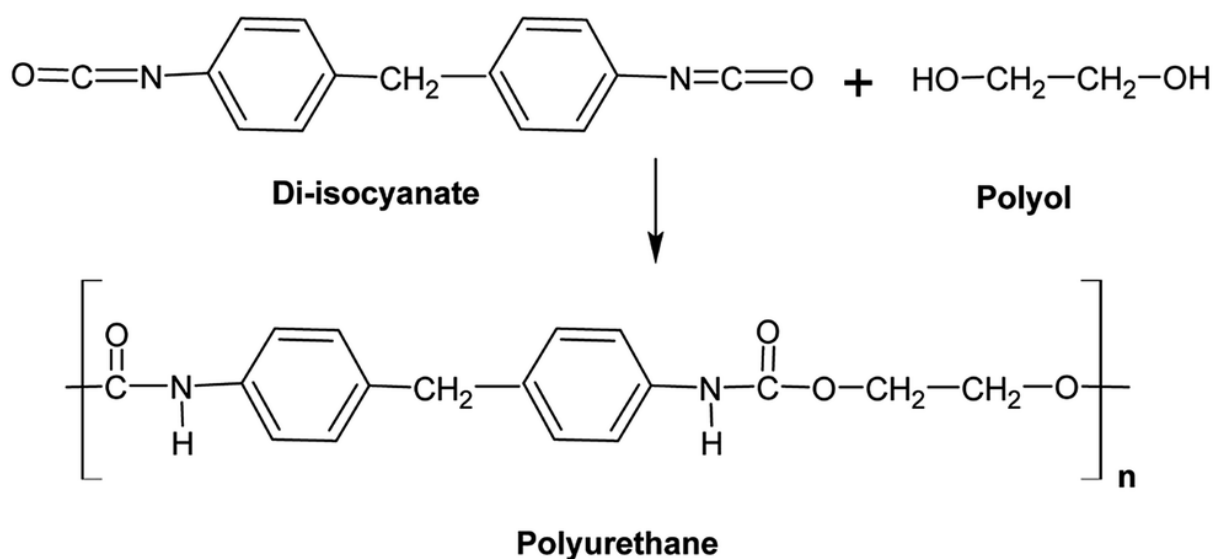
Surface coating and surface sealants

Synthetic fibres

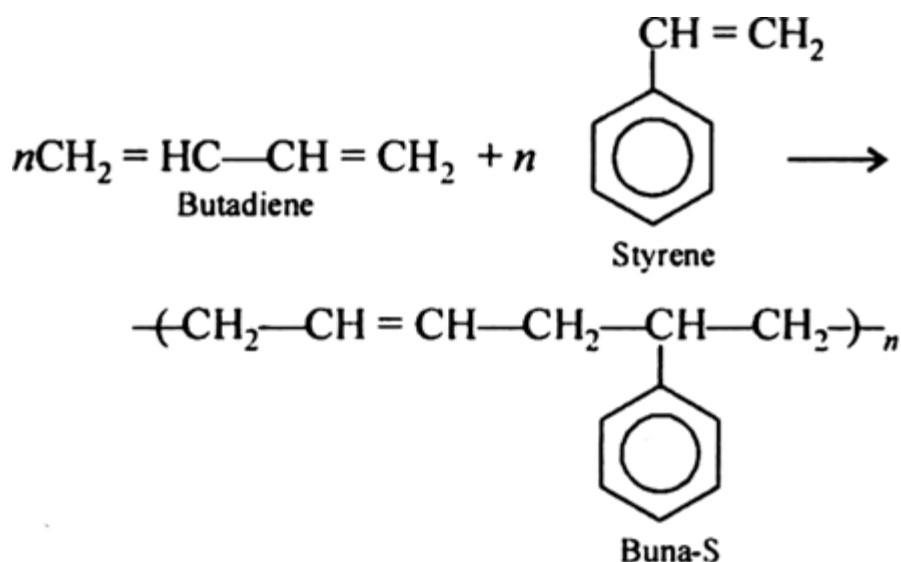
Carpet underlay

Hard plastic parts(e.g, for electronic instrument)

Hoses and skateboard wheels



A synthetic rubber is any artificial elastomer. They are polymers synthesized from petroleum byproducts.



Uses of Synthetic Rubber

Let us look at the uses of synthetic rubber as listed below:

Synthetic rubber can be preferred over natural rubber for a few uses if the price differential is not greater.

The transport industry is one of the largest users of rubber for tire production.

Rubber can also be used by the construction industry in hoses, tubes, elevator belts, seismic bearings, and more.

Industries that produce consumer goods make use of rubber in making erasers, good footwear, sports items, and more.

Polyisoprene synthesis is given as the artificial rubber that has the same properties as those of the natural rubber in the chemical composition of ingredients which is used in its manufacture.

Properties

In general, synthetic rubber exhibits greater durability and longevity than natural rubber. These qualities largely stem from the material's resistance to damage and degradation from chemicals, high and low temperature, ozone, sunlight, and weathering.

PET

High strength.

High rigidity and hardness.

Very low moisture absorption.

Good creep resistance.

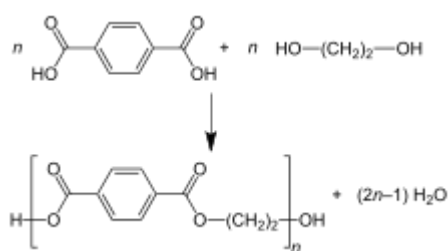
Low sliding friction and sliding wear.

Resistant to hydrolysis (up to +70 °C)

Not suitable for contact with media containing >50% alcohol.

Good chemical resistance against acids.

PET is a clear, strong, and lightweight plastic that is widely used for packaging foods and beverages, especially convenience-sized soft drinks, juices and water.



Conducting polymers-Introduction

Conducting polymers consist of both localized and delocalized states, and the delocalization of π bonds depends heavily upon disorder, and this delocalization plays an essential role in the generation of charge carriers like polarons, bipolarons, solitons, etc.

Conducting polymers contain functional groups that have pseudocapacitance characteristics and thus exhibit conductivity as the material itself.

Conducting polymers are extensively studied due to their outstanding properties, including tunable electrical property, optical and high mechanical properties, easy synthesis and effortless fabrication and high environmental stability over conventional inorganic materials.

The main chain contains	No heteroatom	<u>Heteroatoms</u> present	
		<u>Nitrogen-containing</u>	<u>Sulfur-containing</u>
Aromatic cycles	<ul style="list-style-type: none"> Poly(fluorene)s polyphenylenes polypyrenes polyazulenes polynaphthalenes 	<p>The N is in the aromatic cycle:</p> <ul style="list-style-type: none"> poly(pyrrole)s (PPY) polycarbazoles polyindoles polyazepines <p>The N is outside the aromatic cycle:</p> <ul style="list-style-type: none"> polyanilines (PANI) 	<p>The S is in the aromatic cycle:</p> <ul style="list-style-type: none"> poly(thiophene)s (PT) poly(3,4-ethylenedioxythiophene) (PEDOT) <p>The S is outside the aromatic cycle:</p> <ul style="list-style-type: none"> poly(p-phenylene sulfide) (PPS)
Double bonds	<ul style="list-style-type: none"> Poly(acetylene)s (PAC) 	<ul style="list-style-type: none"> 	
Aromatic cycles and double bonds	<ul style="list-style-type: none"> Poly(p-phenylene vinylene) (PPV) 	<ul style="list-style-type: none"> 	

In p-type doping, the molecular dopant acts as the electron acceptor, and the EA of dopant is equal to or higher than the IE of the organic matrix. In n-type doping, the molecular dopant acts as the electron donor, and the EA of the organic matrix is equal to or higher than the IE of dopant.

The term electrochemical p-doping (n-doping), in connection with conducting polymers, is generally understood as a process that involves both oxidation (reduction) of the polymer backbone and the concomitant changes in the electronic structure.

Properties of Conducting Polymers

Conductivity polymers have high melting and softening points because the mobility of the repeat units is highly restricted due to the presence of a fully aromatic ring structure and the absence of free rotating groups.

Conductivity polymers show excellent chemical, thermal and oxidative stability due to low hydrogen content and aromatic structure.

They can be processed into a highly ordered crystalline thin film that is electrically conducting upon doping.

They are insoluble in many common solvents.

Applications of Conducting Polymers

They are used in the manufacturing of chemical sensors, electro-magnetic shielding, antistatic coatings, corrosion inhibitors, etc.

They are also used in compact electronic devices such as polymer-based transistors, light-emitted diode (LEDs), and lasers.

They are used for microwave-absorbent coating particularly radar-absorptive coatings on stealth aircraft.

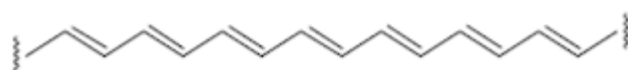
They are used in the manufacturing of printed circuit board because it protects the copper from corrosion and prevents its solderability.

Following are some common examples of conducting polymers:

Polyacetylene or Polyethyne having a repeating unit $(C_2H_2)_n$, is a rigid, rod-like polymer that consists of long carbon chains with alternating single and double bonds between the carbon atoms.

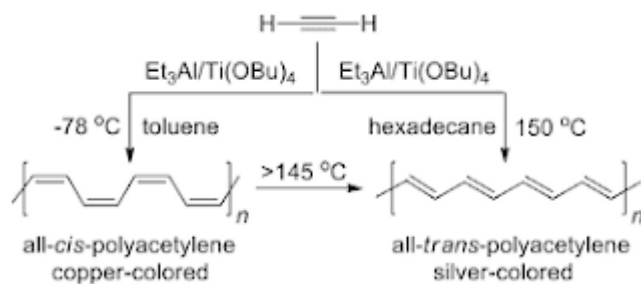


all-cis-polyacetylene
(copper coloured)



all-trans-polyacetylene
(silver coloured)

Structure of Polyacetylene



Properties of Polyacetylene

Films of *cis*-polyacetylene are flexible and can be readily stretched while *trans*-polyacetylene is much more brittle.

Both *cis* and *trans*-polyacetylene show high thermal stability.

They are insoluble in common solvents.

Applications of Polyacetylene

Doped polyacetylene offers a particularly high electrical conductivity therefore it can be used in electric wiring or electrode material in lightweight rechargeable batteries.

Tri-iodide oxidized polyacetylene can be used as a sensor to measure glucose concentration.



Poly(3-hexylthiophene) (P3HT) is an important conducting polymer because of its excellent electrical conductivity, electroluminescence, and nonlinear optical properties. However, its physical, thermal, and mechanical properties are not very good and finds difficulties in many applications.

Regioregular poly(3-hexylthiophene) (P3HT) is used as a model polymer for research in organic solar cells. It is popular despite its dissimilarity in many respects to the high-performing class of polymers based on the donor-acceptor (DA) motif

Mechanical properties of solids elaborates the characteristics such as the resistance to deformation and their strength. Strength is the ability of an object to withstand the applied stress, to what extent can it bear the stress. Resistance to deformation is how resistant any object is to the change of shape. If the resistance to deformation is less, the object can easily change its shape and vice versa.

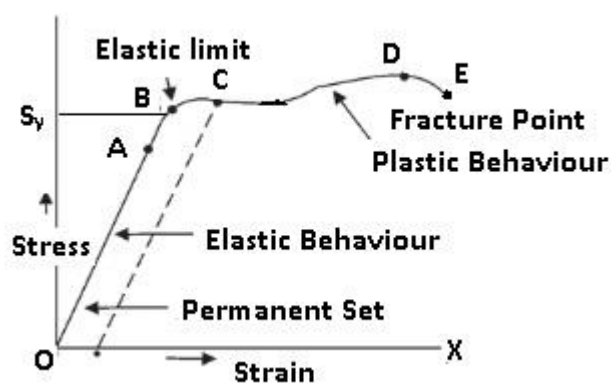
mechanical properties of solids include:

Elasticity: When we stretch an object, it changes its shape and when we leave, it regains its shape. Or we can say it is the property to regain the original shape once the external force is removed. Example: Spring

Plasticity: When an object changes its shape and never comes back to its original shape even when external force is removed. It is the property of permanent deformation. Example: Plastic materials.

Ductility: When an object can be pulled in thin sheets, wires or plates, it has the ductile properties. It is the property of being drawn into thin wires/sheets/plates. Example: Gold or Silver

Strength: The ability to withstand applied stress without failure. Many categories of objects have higher strength than others.



It is a curve between stress and strain.

A graph is plotted between the stress (which is equal in magnitude to the applied force per unit area) and the strain produced.

The graph helps us to understand how a given material deforms with increasing loads.

The curve between O and A, is a straight line. This means stress is directly \propto to strain. In this region Hooke's Law is applicable.

In this region the material behaves like an elastic body.

In the region from A to B, stress and strain are not directly \propto . But still the material returns to its original dimension after the force is removed. They exhibit elastic properties.

The point B in the curve is known as yield point (also known as elastic limit) which means till this point the material will be elastic in behaviour and the stress corresponding to point B is known as yield strength (S_y) of the material.

The region between O and B is called as Elastic region.

From point B to point D we can see that strain increases rapidly even for small change in stress.

Even if we remove the force the material does not come back to its original position. At this point stress is zero but strain is not zero as body has changed its shape.

The material has undergone plastic deformation.

The material is said to be permanent set.

The point D on the graph is known as ultimate tensile strength (S_u) of the material.

From D to E we can see that stress decreases even if strain increases.

Finally at point E fracture occurs. This means the body breaks.

Conclusion:-

An object is brittle if D and E are very close. This means fracture point is near to tensile strength.

For example:-Glass which is brittle.

Composite materials

composite material, also called composite, a solid material that results when two or more different substances, each with its own characteristics, are combined to create a new substance whose properties are superior to those of the original components in a specific application.

Types of composites

polymer matrix composites (PMCs), metal matrix composites (MMCs), ceramic matrix composites (CMCs), and carbon matrix composites (CAMCs).

Some common composite materials include concrete, fiberglass, mud bricks, and natural composites such as rock and wood.

Types of Composites. Composite materials are usually classified by the type of reinforcement they use. ...

Mud Building Bricks. ...

Concrete and Reinforced Concrete. ...

Fiberglass. ...

Natural Composites.

Composites are now being used in vehicle and equipment applications, including, panels, frames, interior components and other parts. Some composite infrastructure applications include buildings, roads, bridges and pilings.

Key among them are strength, light weight, corrosion resistance, design flexibility and durability.

Strong. Per pound, composites are stronger than other materials such as steel. ...

Resistant. Composites resist damage from weather and harsh chemicals that can eat away at other materials. ...

Durable. Simply put, composites last

Young's Modulus or Elastic Modulus or Tensile Modulus, is the measurement of mechanical properties of linear elastic solids like rods, wires, etc. There are some other numbers exists which provide us a measure of elastic properties of a material. Some of these are Bulk modulus and Shear modulus etc. But the value of Young's Modulus is mostly used. This is due to the reason that it gives information about the tensile elasticity of a material.

Young's modulus equation is $E = \text{tensile stress} / \text{tensile strain} = (FL) / (A * \text{change in } L)$, where F is the applied force, L is the initial length, A is the square area, and E is Young's modulus in Pascals (Pa). Using a graph, you can determine whether a material shows elasticity

Fibre Reinforced Composites

A fiber-reinforced composite (FRC) is a composite building material that consists of three components

Example: fiberglass and wood

the fibers as the discontinuous or dispersed phase,

the matrix as the continuous phase, and

the fine interphase region, also known as the interface.

This is a type of advanced composite group, which makes use of rice husk, rice hull, rice shell, and plastic as ingredients. This technology involves a method of refining, blending, and compounding natural fibers from cellulosic waste streams to form a high-strength fiber composite material in a polymer matrix. The designated waste or base raw materials used in this instance are those of waste thermoplastics and various categories of cellulosic waste including rice husk and saw dust.

metal matrix composites (MMCs), ceramic matrix composites (CMCs), carbon/carbon composites (C/C), and polymer matrix composites (PMCs) or polymeric composites

Polymer composites

Polymer composites are a combination of polymers (i.e., thermosets or thermoplastics) with various continuous and noncontinuous reinforcements/fillers, principally added to polymers to improve the material performance. Polymer composites are increasingly being used in various engineering fields.

Example: MRI scanners, C scanners, X-ray couches, mammography plates, tables, surgical target tools, wheelchairs, and prosthetics.

Glass Fiber Reinforced Plastic (GFRP) Composites:

Carbon Fiber Reinforced Polymer (CFRP) Composites:

Aramid-Fiber Reinforced Polymer Composites:

Metal Matrix Composites:

Ceramics Matrix Composite:

Carbon-Carbon Composites (CCC):

Hybrid Composites:

Structure Composites:

particle reinforced

Particulate composites consist of a matrix reinforced with a dispersed phase in the form of particles. The type, shape and spatial arrangement of the reinforcing phase are the key parameters in determining the mechanical behavior of the composite.

1. Large Particle Composites 2. Cermet (Cer + met \approx Ceramics + Metal) 3. Concrete

4. Reinforced Concrete

structural composites

A structural composite is a multi-layered and normally low-density composite used in applications requiring structural integrity, ordinarily high tensile, compressive, and torsional strengths and stiffnesses. The properties of these composites depend not.

Fibre reinforced composites. Particulate reinforced composites.

Carbon Fiber.

Resin.

Graphene.

Aircraft.

Nanotubes.

Fiber-Reinforced Composite.

Polymer Composite.

Textile Fiber.

Matrix materials

There are three main types of composites based on the type of matrix they employ – **polymer matrix composites (PMC)**, **ceramic matrix composites (CMC)**, and **metal matrix composites (MMC)**.

The matrix **binds the fiber reinforcement, transfers loads between fibers, gives the composite component its net shape and determines its surface quality**. A composite matrix may be a polymer, ceramic, metal or carbon.

Kevlar is the trade name (registered by DuPont Co.) of aramid (poly-para-phenylene terephthalamide) fibers. Kevlar fibers were originally developed as a replacement of steel in automotive tires. Distinctive features of Kevlar are high impact resistance and low density

Polyamides

Polyamides (nylons) are made from **either the condensation of diamines and dibasic acids or the condensation of amino acids containing both amine and acid functional groups in single molecules**. Major polyamides for packaging materials are polyamide 6 and polyamide 66.

PA material or polyamide is **a material more commonly known as nylon**, which is also typically numbered to identify the nylon plastic type (such as 6, 66, 11 and 12). These numbers relate to the molecular structure of the nylon polymer and each structure type will have different properties.

Polyamide is a polymer held together with amide bonds. Fabrics such as **wool, silk and nylon** are all examples of polyamides — wool and silk are natural polyamides, whereas nylon is synthetic. Synthetic polyamide thermoplastics are important in engineering because they offer high performance at a reasonable cost.

Metal Matrix Composites

In materials science, a metal matrix composite (MMC) is **a composite material with fibers or particles dispersed in a metallic matrix, such as copper, aluminum, or steel**. The secondary phase is typically a ceramic (such as alumina or silicon carbide) or another metal (such as steel).

Applications

Applications

- Pushrods for racing engines.
- Carbide drills.
- Tank armors.
- Automotive industry - disc brakes, driveshaft, engines.
- Aircraft components - structural component of the jet's landing gear.
- Bicycle frames.
- Space systems.
- High density multi-chip modules in electronics.

The advantages of MMCs over polymer matrix composites are:

- Higher temperature capability.
- Fire resistance.
- Higher transverse stiffness and strength.
- No moisture absorption.
- Higher electrical and thermal conductivities.
- Better radiation resistance.
- No outgassing.

MMC manufacturing can be broken into three types—solid, liquid, and vapor.

Solid state methods

Powder blending and consolidation (powder metallurgy): Powdered metal and discontinuous reinforcement are mixed and then bonded through a process of compaction, degassing, and thermo-mechanical treatment (possibly via hot isostatic pressing (HIP) or extrusion)

Foil diffusion bonding: Layers of metal foil are sandwiched with long fibers, and then pressed through to form a matrix

Liquid state methods

Electroplating and electroforming: A solution containing metal ions loaded with reinforcing particles is co-deposited forming a composite material

Stir casting: Discontinuous reinforcement is stirred into molten metal, which is allowed to solidify

Pressure infiltration: Molten metal is infiltrated into the reinforcement through use a kind of pressure such as gas pressure

Squeeze casting: Molten metal is injected into a form with fibers pre-placed inside it

Spray deposition: Molten metal is sprayed onto a continuous fiber substrate

Reactive processing: A chemical reaction occurs, with one of the reactants forming the matrix and the other the reinforcement

Semi-solid state methods

Semi-solid powder processing: Powder mixture is heated up to semi-solid state and pressure is applied to form the composites.

Vapor deposition

Physical vapor deposition: The fiber is passed through a thick cloud of vaporized metal, coating it.

In-situ fabrication technique

Controlled unidirectional solidification of a eutectic alloy can result in a two-phase microstructure with one of the phases, present in lamellar or fiber form, distributed in the matrix

Applications of metal matrix composites

- Pushrods for racing engines.
- Carbide drills.
- Tank armors.
- Automotive industry - disc brakes, driveshaft, engines.
- Aircraft components - structural component of the jet's landing gear.
- Bicycle frames.
- Space systems.
- High density multi-chip modules in electronics.

Examples – Carbon fibres in Aluminium

Matrix

Some examples of most commonly used metallic matrix configurations are: **Aluminum-based composites**; aluminum as matrix can be either cast alloy or wrought alloy (i.e., AlMgSi, AlMg, AlCuSiMn, AlZnMgCu, AlCu, AlSiCuMg) Magnesium-based composites.

In materials science, ceramic matrix composites (CMCs) are a subgroup of composite materials and a subgroup of ceramics. They consist of ceramic fibers embedded in a ceramic matrix. The fibers and the matrix both can consist of any ceramic material, whereby carbon and carbon fibers can also be regarded as a ceramic material.

The manufacturing processes usually consist of the following three steps:

Lay-up and fixation of the fibers, shaped like the desired component

Infiltration of the matrix material

Final machining and, if required, further treatments like coating or impregnation of the intrinsic porosity.

The first and the last step are almost the same for all CMCs: In step one, the fibers, often named rovings, are arranged and fixed using techniques used in fiber-reinforced plastic materials, such as lay-up of fabrics, filament winding, braiding and knotting. The result of this procedure is called fiber-preform or simply preform.

For the second step, five different procedures are used to fill the ceramic matrix in between the fibers of the preform:

Deposition out of a gas mixture

Pyrolysis of a pre-ceramic polymer

Chemical reaction of elements

Sintering at a relatively low temperature in the range 1,000–1,200 °C (1,830–2,190 °F)

Electrophoretic deposition of a ceramic powder

Procedures one, two and three find applications with non-oxide CMCs, whereas the fourth one is used for oxide CMCs; combinations of these procedures are also practiced. The fifth procedure is not yet established in industrial processes. All procedures have sub-variations, which differ in technical details. All procedures yield a porous material.

The third and final step of machining – grinding, drilling, lapping or milling – has to be done with diamond tools. CMCs can also be processed with a water jet, laser, or ultrasonic machining.

Ceramic matrix composites (CMCs) are widely used in **aerospace sector (gas turbines, structural re-entry thermal protection) and energy sector (heat exchangers, fusion reactor walls)**. These applications require a joint either permanent or temporary between CMC components with surrounding materials.

The desirable characteristics of ceramic matrix composites include high-temperature stability, high thermal shock resistance, high hardness, high corrosion resistance, light weight, non-magnetic and non-conductive properties, and versatility in providing unique engineering solutions.

Carbon fiber (CF) **reinforced carbon-silicon carbide** (C/C-SiC) composites are one of the most promising lightweight materials for re-entry thermal protection, rocket nozzles and brake discs applications.

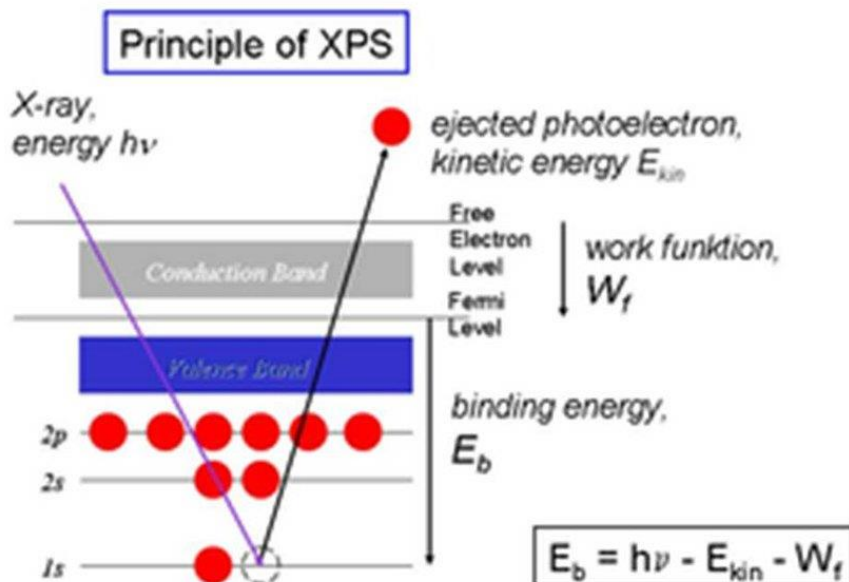
SiC is also used for products such as bulletproof vests, ceramic plates, thin filament pyrometry, foundry crucibles, and car clutches.

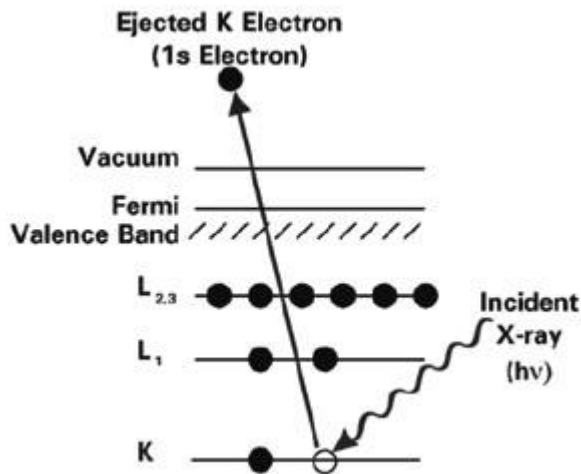
Examples

C/SiC and C/C-SiC applications lie in fields where conventional materials, due to their insufficient mechanical properties at high temperatures or limited damage tolerance behaviour can no longer be considered and includes in principal all areas of lightweight construction. Some examples are given for high temperature ($T > 1,000\text{ }^{\circ}\text{C}$), medium temperature and low temperature ($T < 450\text{ }^{\circ}\text{C}$) regimes.

XPS

X-ray photoelectron spectroscopy (or XPS) belongs to the group of surface analysis methods wherein the sample under investigation is bombarded with photons/electrons/ion/etc. for exciting the emission of photons/electrons/ion/etc





The photoemission process involved for XPS surface analysis. The discs represent electrons and the bars represent energy levels within the material being analyzed. The equation governing the process is:

$$KE = h\nu - BE$$

Surface analysis by XPS involved irradiation of the sample by low-energy (and mono-energetic) x-rays

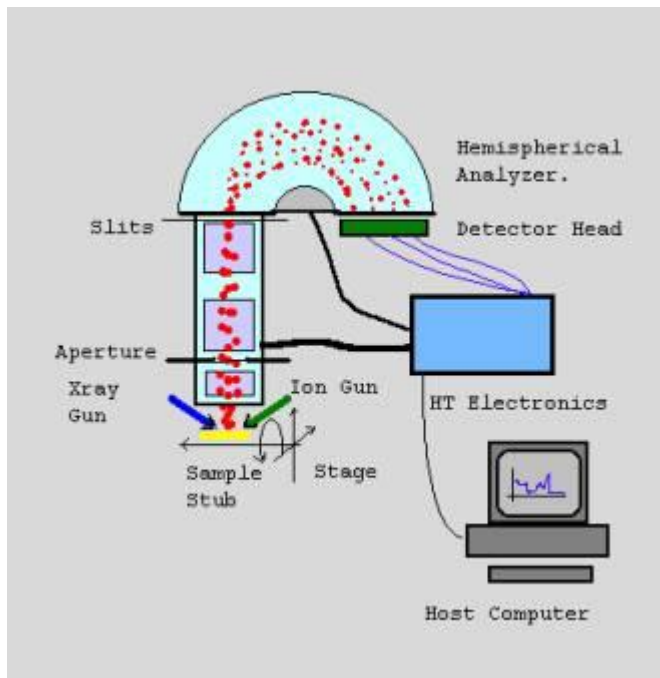
and the subsequent analysis of the energy of emitted electrons. Typically used x-rays are K α lines of Mg

(1.2536 keV) and Al (1.4866 keV). The penetration depth of these photons in solids is limited to a few

microns. Thus, interactions take place between the incident photons are the surface atoms leading to the

photoelectric emission of electrons. The kinetic energy (K.E.) of the emitted electrons is expressed as

$$K.E. = h\nu - B.E. - \phi_s$$



X-Ray diffraction and crystal structure- Bragg's law

In physics, Bragg's law, or Wulff–Bragg's condition, a special case of Laue diffraction, gives the angles for coherent and incoherent scattering from a crystal lattice. When X-rays are incident on an atom, they make the electronic cloud move, as does any electromagnetic wave. The movement of these charges re-radiates waves with the same frequency, blurred slightly due to a variety of effects; this phenomenon is known as Rayleigh scattering (or elastic scattering). The scattered waves can themselves be scattered but this secondary scattering is assumed to be negligible.

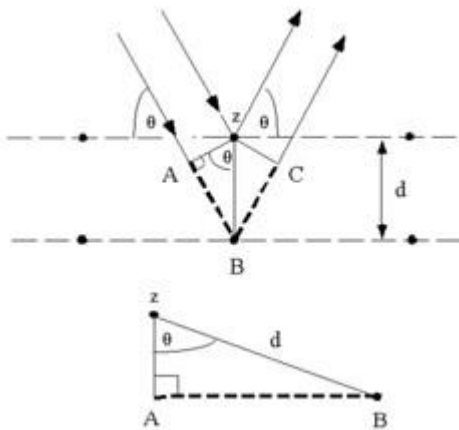
$$n\lambda = 2d \cdot \sin\theta$$

- n is an integer determined by the order given,
- λ is the wavelength of x-rays, and moving electrons, protons and neutrons,
- d is the spacing between the planes in the atomic lattice, and
- θ is the angle between the incident ray and the scattering planes.

A similar process occurs upon scattering neutron waves from the nuclei or by a coherent spin interaction with an unpaired electron. These re-emitted wave fields interfere with each other either constructively or destructively (overlapping waves either add up together to produce stronger peaks or are subtracted from each other to some degree), producing a diffraction pattern on a detector or film. The resulting wave interference pattern is the basis of diffraction analysis. This analysis is called Bragg diffraction.

Bragg diffraction occurs when electromagnetic radiation or subatomic particle waves with wavelength comparable to atomic spacings, are incident upon a crystalline sample, scattered

by the atoms in the system and undergo constructive interference in accordance to Bragg's law.



Consider conditions necessary to make the phases of the beams coincide when the incident angle equals and reflecting angle. The rays of the incident beam are always in phase and parallel up to the point at which the top beam strikes the top layer at atom z . The second beam continues to the next layer where it is scattered by atom B . The second beam must travel the extra distance $AB + BC$ if the two beams are to continue traveling adjacent and parallel.

$$n\lambda = AB + BC$$

$$AB = d \sin \theta$$

$$AB = BC$$

$$n\lambda = 2AB$$

$$n\lambda = 2d \cdot \sin \theta$$

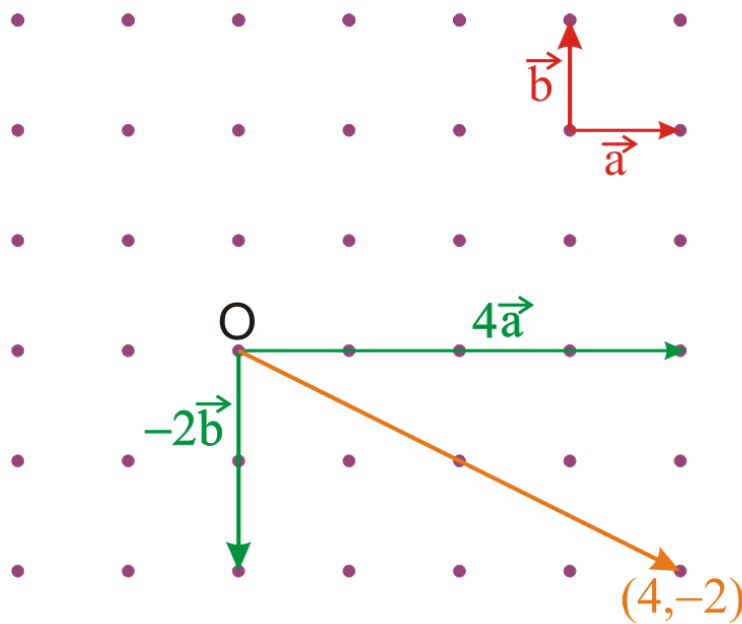
- ☐ Miller indices are used to specify directions and planes.
- ☐ These directions and planes could be in [lattices](#) or in [crystals](#).
- ☐ *(It should be mentioned at the outset that special care should be given to see if the indices are in a lattice or a crystal).*
- ☐ The number of indices will match with the dimension of the lattice or the crystal: in 1D there will be 1 index, in 2D there will be two indices, in 3D there will be 3 indices, etc.
- ☐ Sometimes, like in the case of Miller-Bravais indices for hexagonal lattices and crystals, additional indices are used to highlight the symmetry of the structure. In the case of the Miller-Bravais indices for hexagonal structures, a third redundant index is added ($h\ k\ i\ l$) \rightarrow 4 indices are used in 3D space. The use of such redundant indices bring out the *equivalence* of the members of a 'family'.

- ❑ Some aspects of Miller indices, especially those for planes, are not intuitively understood and hence some time has to be spent to familiarize oneself with the notation.

STEPS in the determination of Miller indices for directions

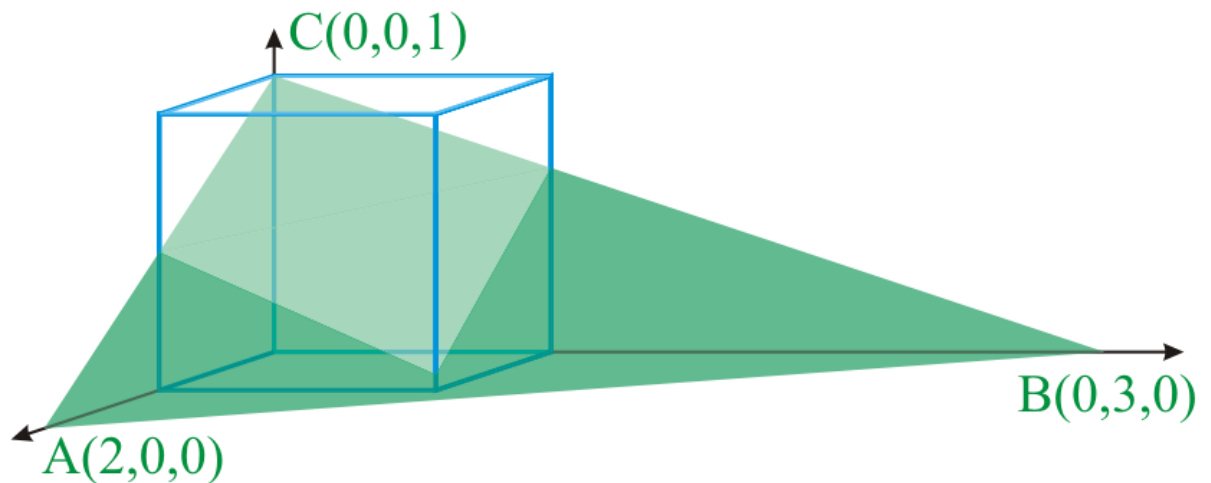
- Position the vector, such that start (S: (x_1, y_1)) and end points (E: (x_2, y_2)) are lattice points and note the value of the coordinates. Subtract to obtain: $((x_2 - x_1), (y_2 - y_1))$.
- Write these number in square brackets, without the 'comma': $[* *]$.

'Remove' the common factors.



Normally, we 'take out' the common factor

Miller Indices with magnitude $\rightarrow 2[2\bar{1}]$



- ❑ Find intercepts along axes $\rightarrow 2 \ 3 \ 1$
- ❑ Take reciprocal $\rightarrow 1/2 \ 1/3 \ 1^*$
- ❑ Convert to smallest integers in the same ratio $\rightarrow 3 \ 2 \ 6$
- ❑ Enclose in parenthesis $\rightarrow (326)$ *Note the type of brackets*
- Note: (326) does NOT represent one plane but *an infinite set of parallel planes* passing through lattice points.

Set of planes should not be confused with a family of planes

Applications. X-ray powder diffraction is most widely used for the **identification of unknown crystalline materials** (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology.

XPS can be used **to analyze the surface chemistry of a material after an applied treatment such as fracturing, cutting or scraping**. From non-stick cookware coatings to thin-film electronics and bio-active surfaces, XPS is the standard tool for surface material characterization.