Crystal Field Theory

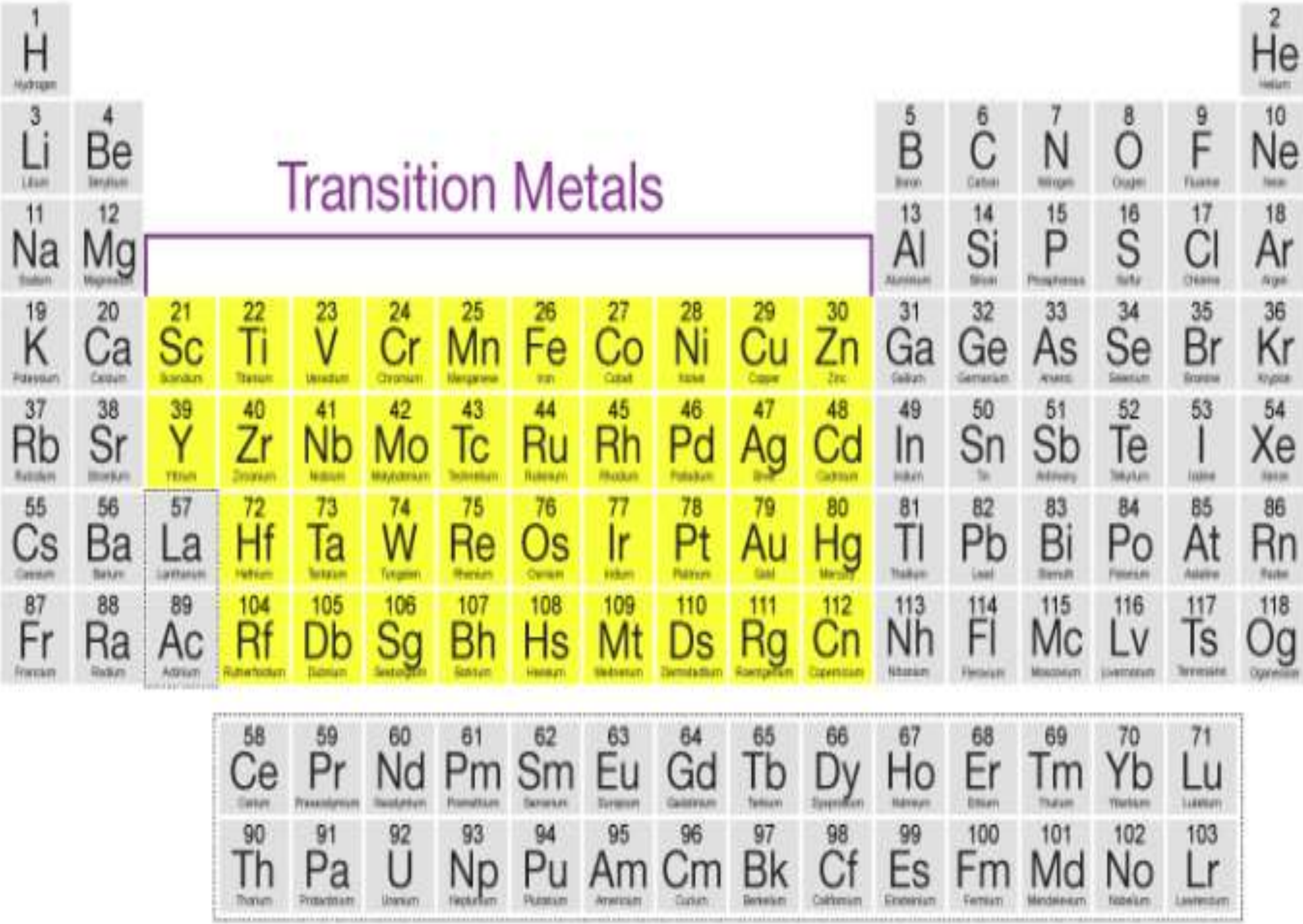
- Crystal field theory (CFT) describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands.
- It describes the effect of the attraction between the positive charge of the metal cation and negative charge or the non-bonding electrons of the ligand.
- CFT qualitatively describes the strength of the metal-ligand bonds. Based on the strength of the metal-ligand bonds, the energy of the system is altered. This may lead to a change in magnetic properties as well as color, but it does not attempt to describe bonding.
- This theory was developed by Hans Bethe and John Hasbrouck van Vleck.

Terms used in the CFT

- Transition metal
- Ligand
- Cordination complex
- Coordination number
- Degeneracy

What is Transitional metal

- Elements which in their ground state or in any of their oxidation state have partially filled d-orbital are called transition elements.
- The name transition given to the elements of d-block is only because of their position between s-block and p-block elements.
- Some of the most common examples include iron, chromium, manganese, vanadium, titanium, copper, cobalt, nickel, tungsten, gold, and platinum.

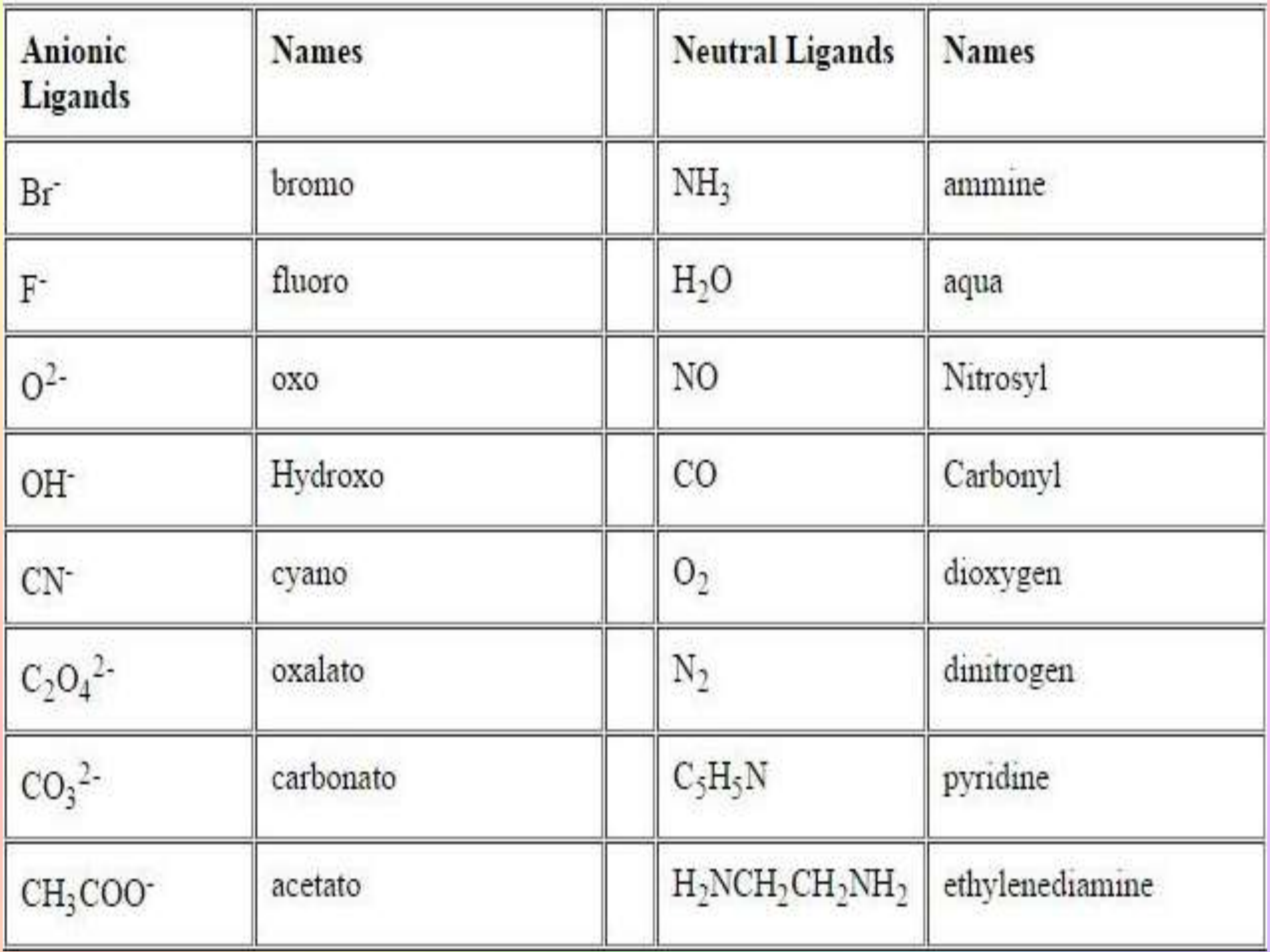


Transition Metals

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
			90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Ligand

- A ligand is an ion or molecule (functional group) that binds to a central metal atom to form a coordination complex
- The term ligand come from the latin word *ligare* (which meaning to bind)
- Ligands can be anions, cations, or neutral molecules.

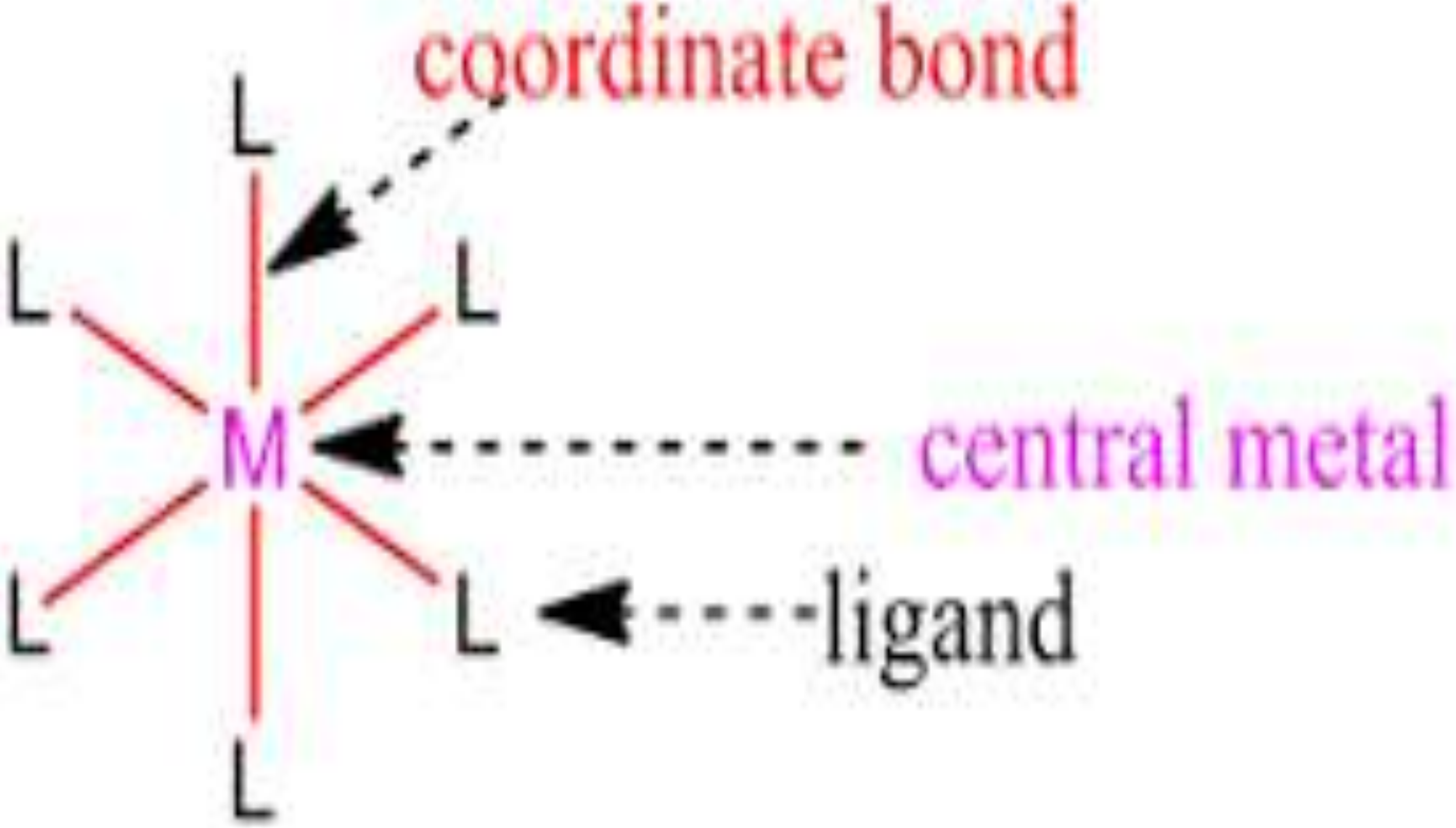


Anionic Ligands	Names		Neutral Ligands	Names
Br^-	bromo		NH_3	ammine
F^-	fluoro		H_2O	aqua
O^{2-}	oxo		NO	Nitrosyl
OH^-	Hydroxo		CO	Carbonyl
CN^-	cyano		O_2	dioxygen
$C_2O_4^{2-}$	oxalato		N_2	dinitrogen
CO_3^{2-}	carbonato		C_5H_5N	pyridine
CH_3COO^-	acetato		$H_2NCH_2CH_2NH_2$	ethylenediamine

Coordination complex

- Coordination compounds are chemical compounds that consist of an array of anions or neutral molecules that are bound to a central atom via coordinate covalent bonds. Coordination compounds are also referred to as coordination complexes.
- A coordination complex consists of a central atom or ion, which is usually metallic and is called the *coordination centre*,
- These molecules or ions that are bound to the central atom are referred to as ligands (also known as complexing agents).

metal complex



coordinate bond

central metal

ligand

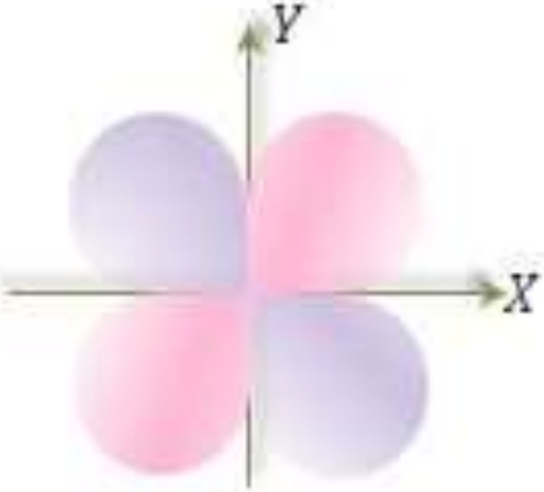
Coordination number

- The coordination number is the number of ligands attached to the central metal atom or ion.
- For example, in the complex ions, $[PtCl_6]^{2-}$ and $[Fe(H_2O)_6]^{2+}$, the coordination number of Pt and Fe are 6 and 6, respectively. Here Pt and Fe have connected to six ligands Cl^- and H_2O, respectively.
- Another example, tetra carbonylnickel Ni(CO)4 has a coordination number of 4 as 4 CO ligands are attached to Ni atom.

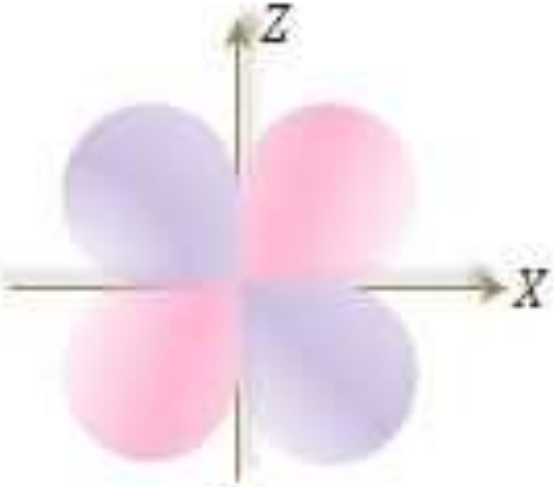
Description of *d*-Orbitals

To understand CFT, one must understand the description of the lobes:

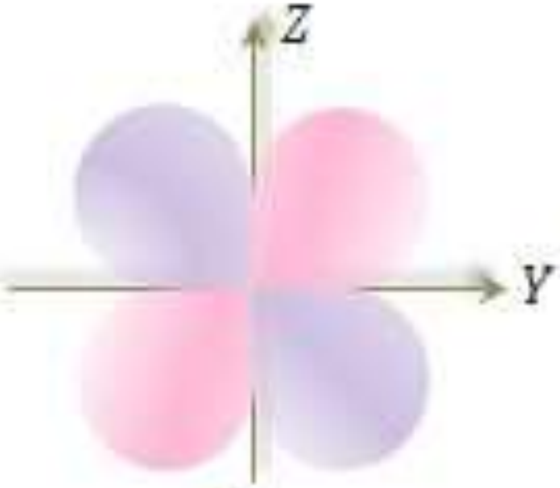
- d_{xy}: lobes lie in-between the x and the y axes.
- d_{xz}: lobes lie in-between the x and the z axes.
- d_{yz}: lobes lie in-between the y and the z axes.
- $d_{x^2-y^2}$: lobes lie on the x and y axes.
- d_{z2}: there are two lobes on the z axes and there is a donut shape ring that lies on the xy plane around the other two lobes.



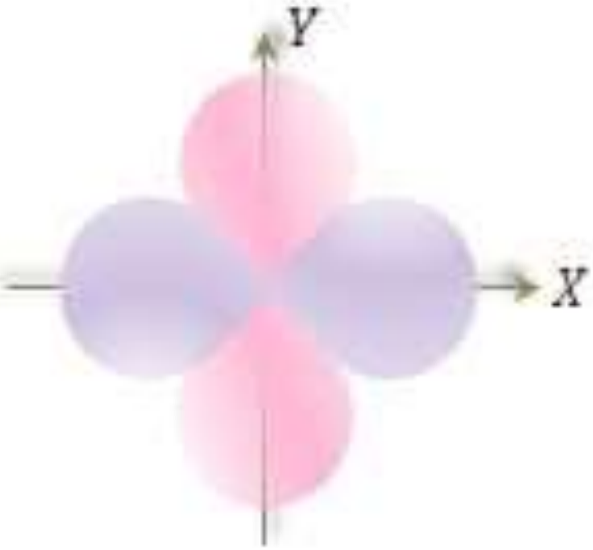
d_{xy}



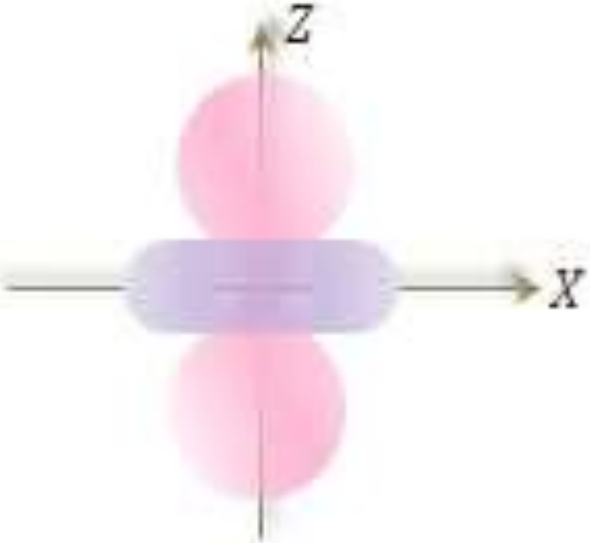
d_{xz}



d_{yz}

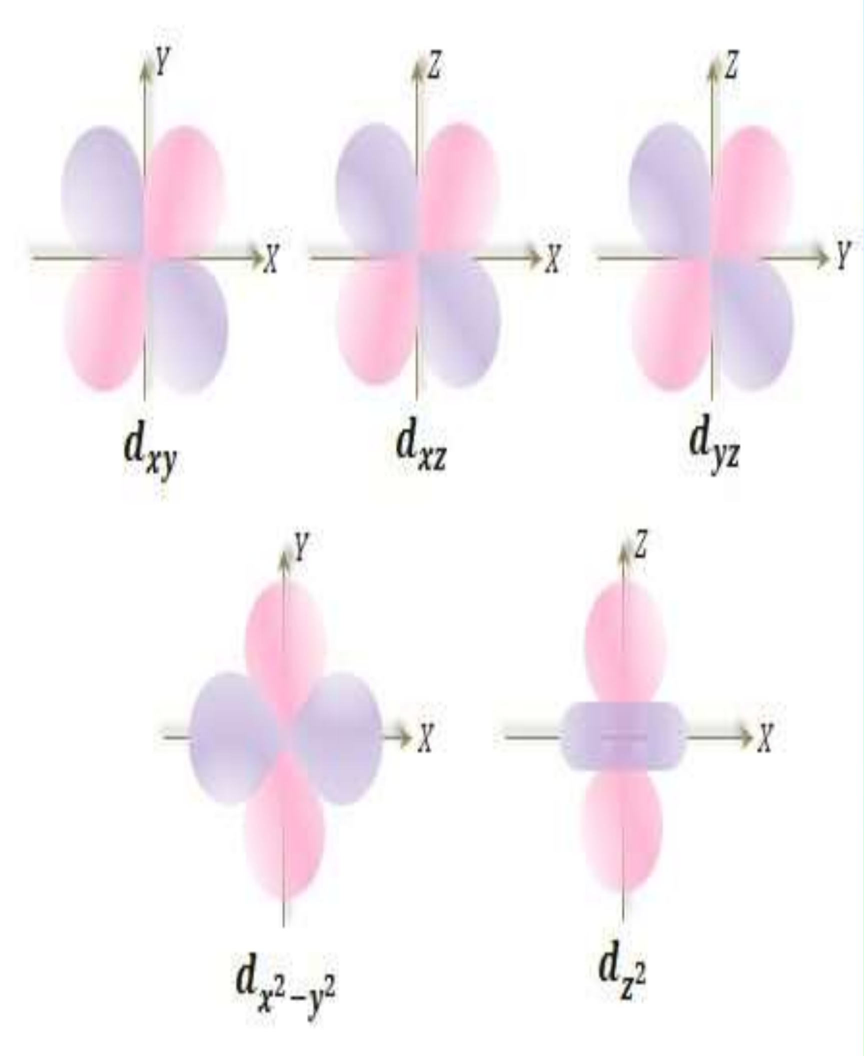


$d_{x^2-y^2}$

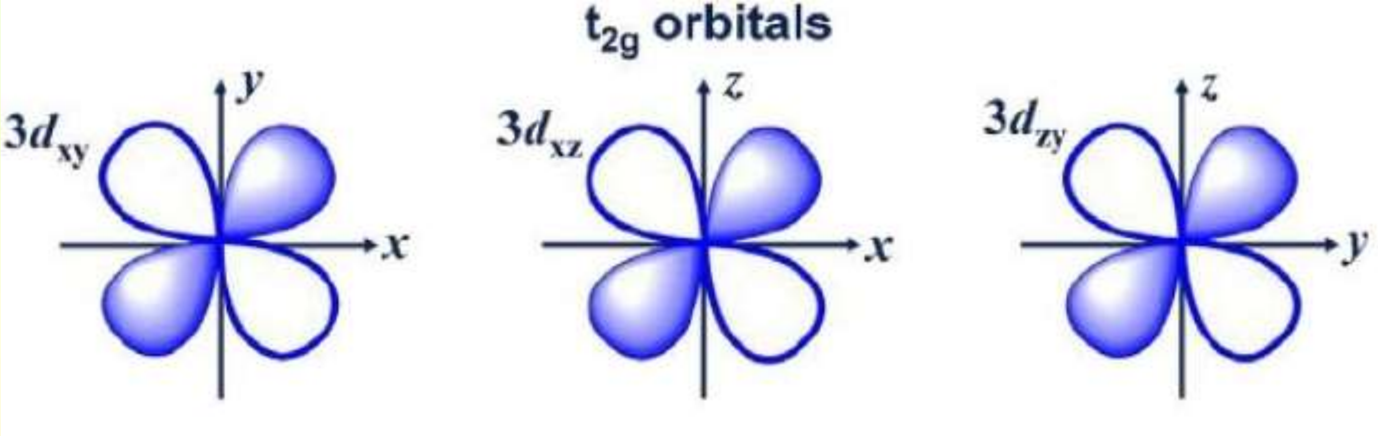


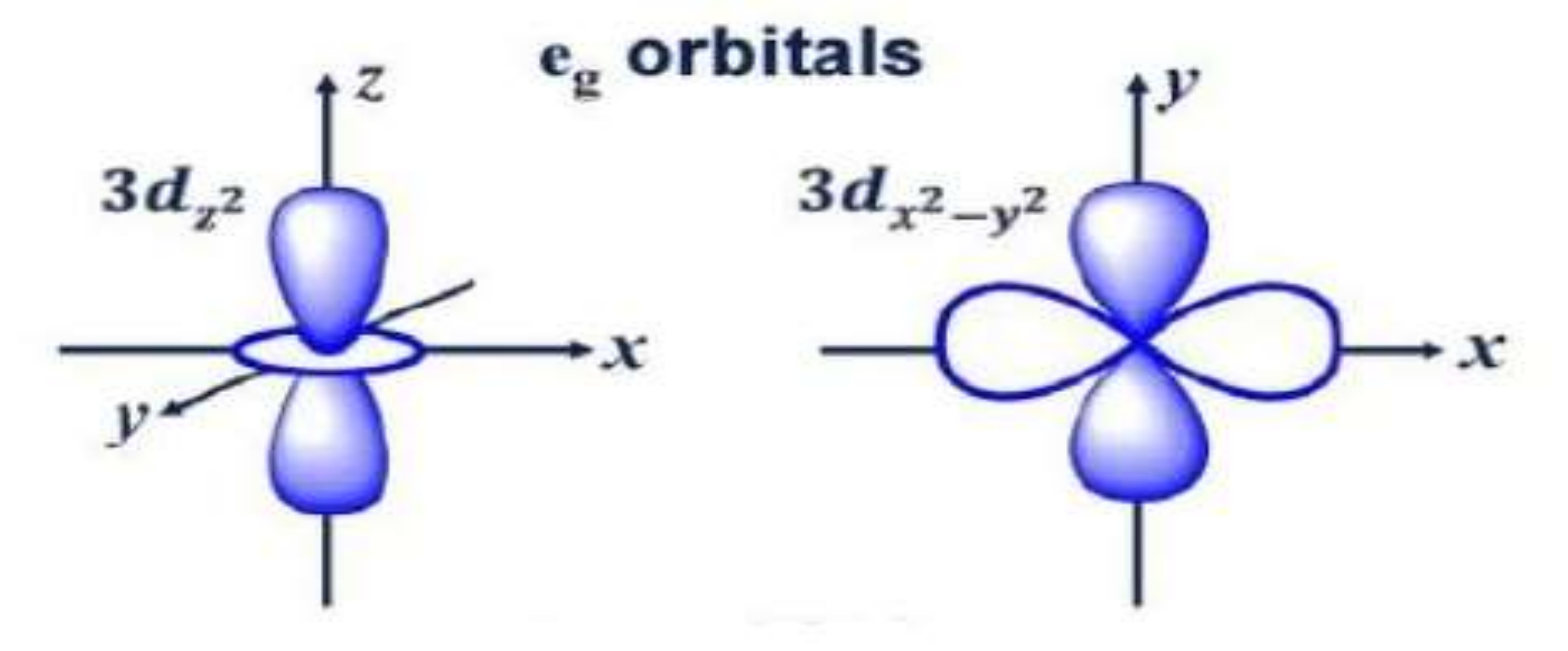
d_{z^2}

Degenerate orbitals



- ➢ Electron orbitals having the same energy levels are called degenerate orbitals.
- ➢ The degree degeneracy of d orbitals is 5


t_{2g} orbitals
$3d_{xy}$
y
x
$3d_{xz}$
z
x
$3d_{zy}$
z
y

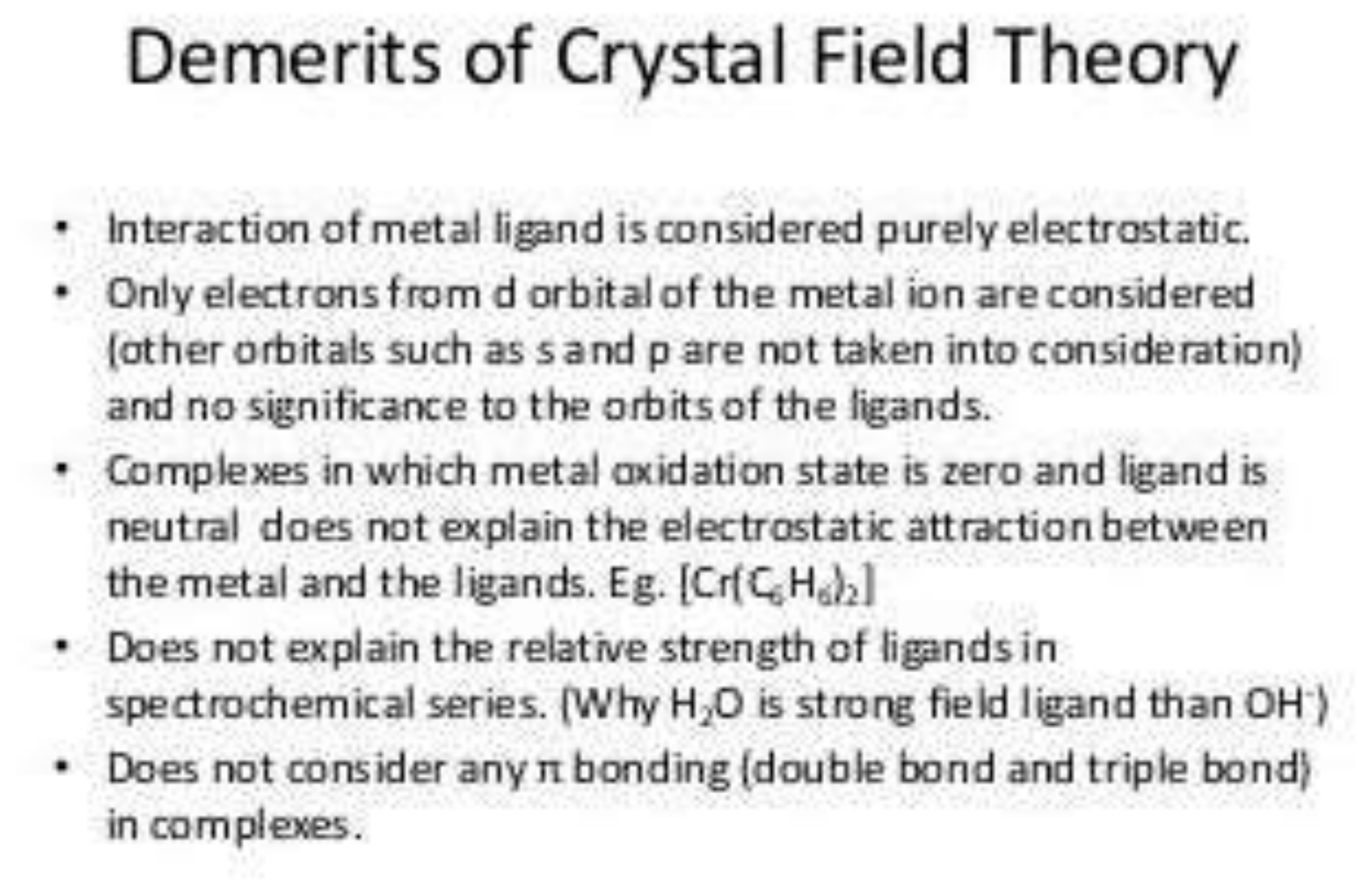

e_g orbitals
$3d_{z^2}$
z
x
y
$3d_{x^2-y^2}$
y
x

Postulates of CFT

- **The central metal atom is surrounded by ligands, which contain one or more lone pair of electrons.**
- **Ligands are treated as point charges.**
- **The negative ligands are considered as negative point charges, while neutral ligands are considered as dipoles.**
- **The bonding between the metal atoms and ligands are purely electrostatic or coulombic attractions.**
- **All the d-orbitals in the central metal has same energy i.e., Degenerate in the free atom, however when a complex is formed the degeneracy is destroyed. The orbitals now has different energies.**

Merits of Crystal Field Theory

- Explains the split degeneracy of d-orbitals in a complex.
- Theory does explain the colour and spectra of complexes.
- Accounts for magnetic property of the complexes.
- Explains the stability of particular oxidation state in aqueous solutions.

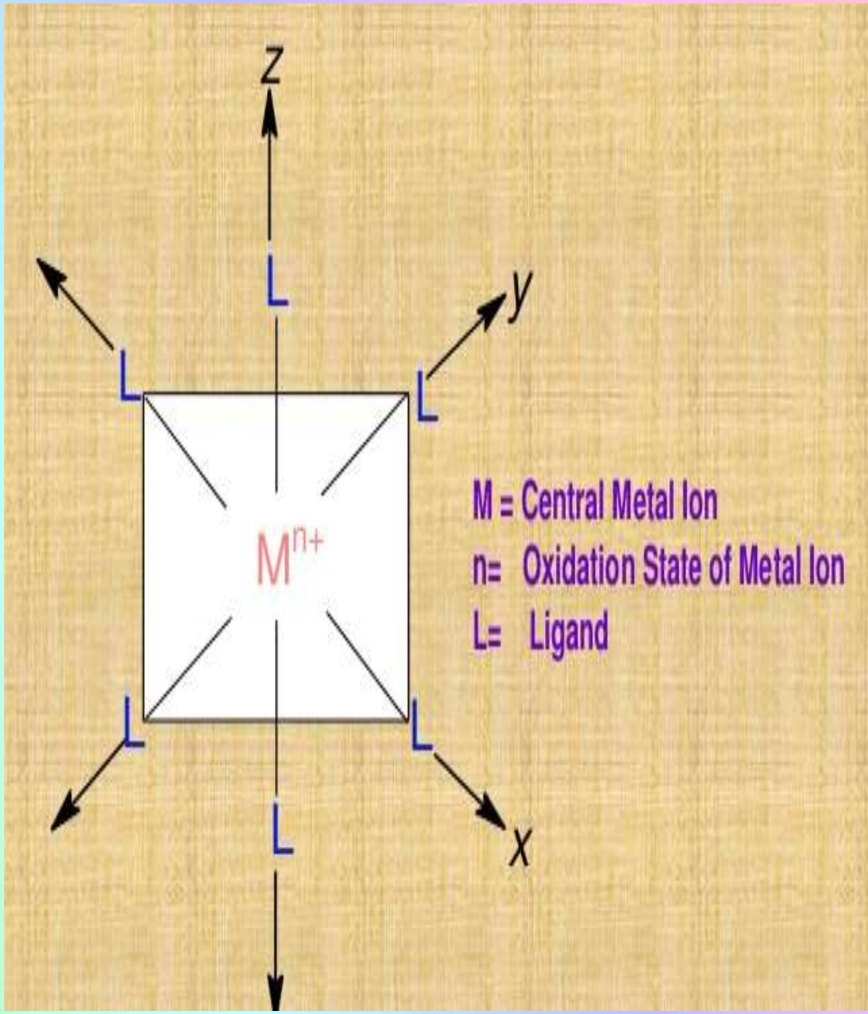


Demerits of Crystal Field Theory

- Interaction of metal ligand is considered purely electrostatic.
- Only electrons from d orbital of the metal ion are considered (other orbitals such as s and p are not taken into consideration) and no significance to the orbits of the ligands.
- Complexes in which metal oxidation state is zero and ligand is neutral does not explain the electrostatic attraction between the metal and the ligands. Eg. $[Cr(C_6H_6)_2]$
- Does not explain the relative strength of ligands in spectrochemical series. (Why H_2O is strong field ligand than OH^-)
- Does not consider any π bonding (double bond and triple bond) in complexes.

Crystal field splitting in octahedral complex

- In octahedral complex central metal atom is surrounded by 6 ligands
- In an octahedral complex ligands approaches along the x,y & z axes.
- The electrons residing in the $d_{x^2-y^2}$ & d_{z2} orbitals experience a greater repulsion. So the energy of these orbitals are increased.
- The lobes of d_{xy}, d_{xz}, d_{yz} orbitals point in between the axis will experience a lower repulsion. So, the energy of these orbitals is decreased.
- Thus, the 5 d-orbitals(which are degenerate) split into 2 sets. t2g & eg sets of orbitals.
- The difference in energy between the dz^2 and dx^2-y^2 orbitals and the dxz, dxy, and dyz orbitals that is known as crystal field splitting.

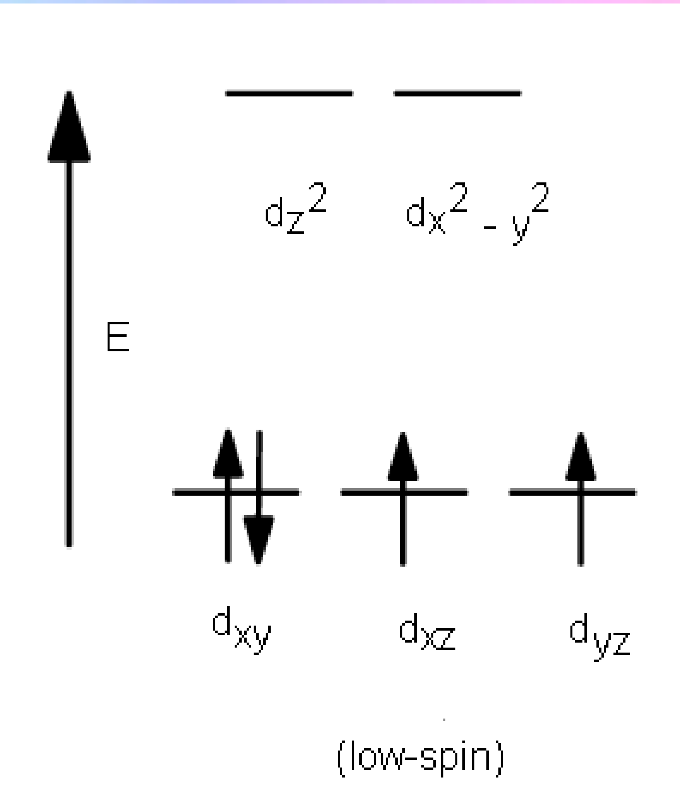


Electrons in d-orbitals

- Electrons are filled in the orbitlas according to aufbau principle and Hund’s rule.
- According to aufbau principle electrons are filled from lower to higher energy orbitals that is electrons enter the most stable t2g orbitals of lower energy.
- Following Hund's rule, electrons are filled in order to have the highest number of unpaired electrons.
- For example, if a metal has more than 3 electrons it has two options to follow
- Either it has the ability to fill a higher energy orbital (d_{z^2} or $d_{x^2-y^2}$) or pair with an electron residing in the d_{xy}, d_{xz}, or d_{yz} orbitals. This pairing of the electrons requires energy (spin pairing energy).
- Spin pairing energy: The energy required for pairing of electrons in a single oribital.

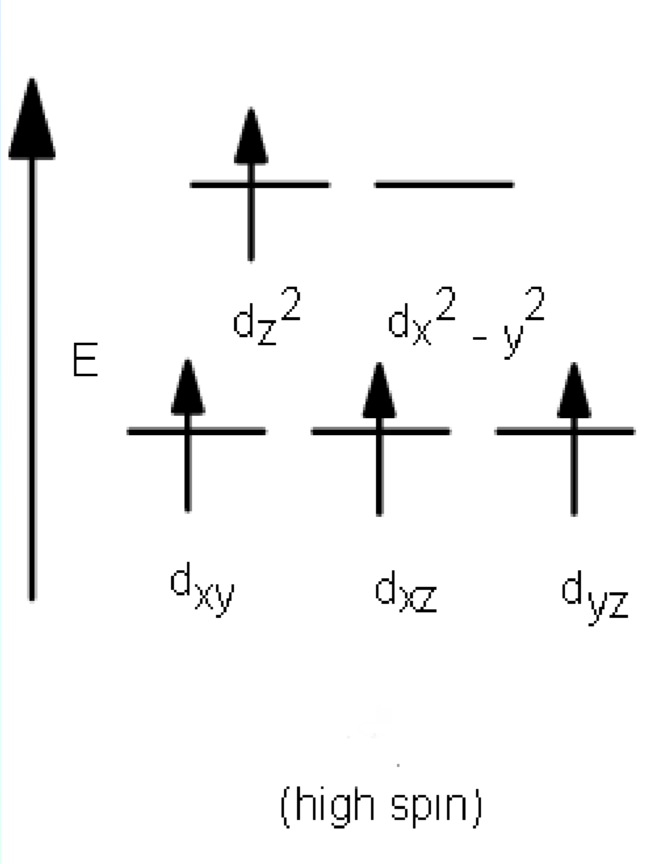
Electrons in d-orbitals

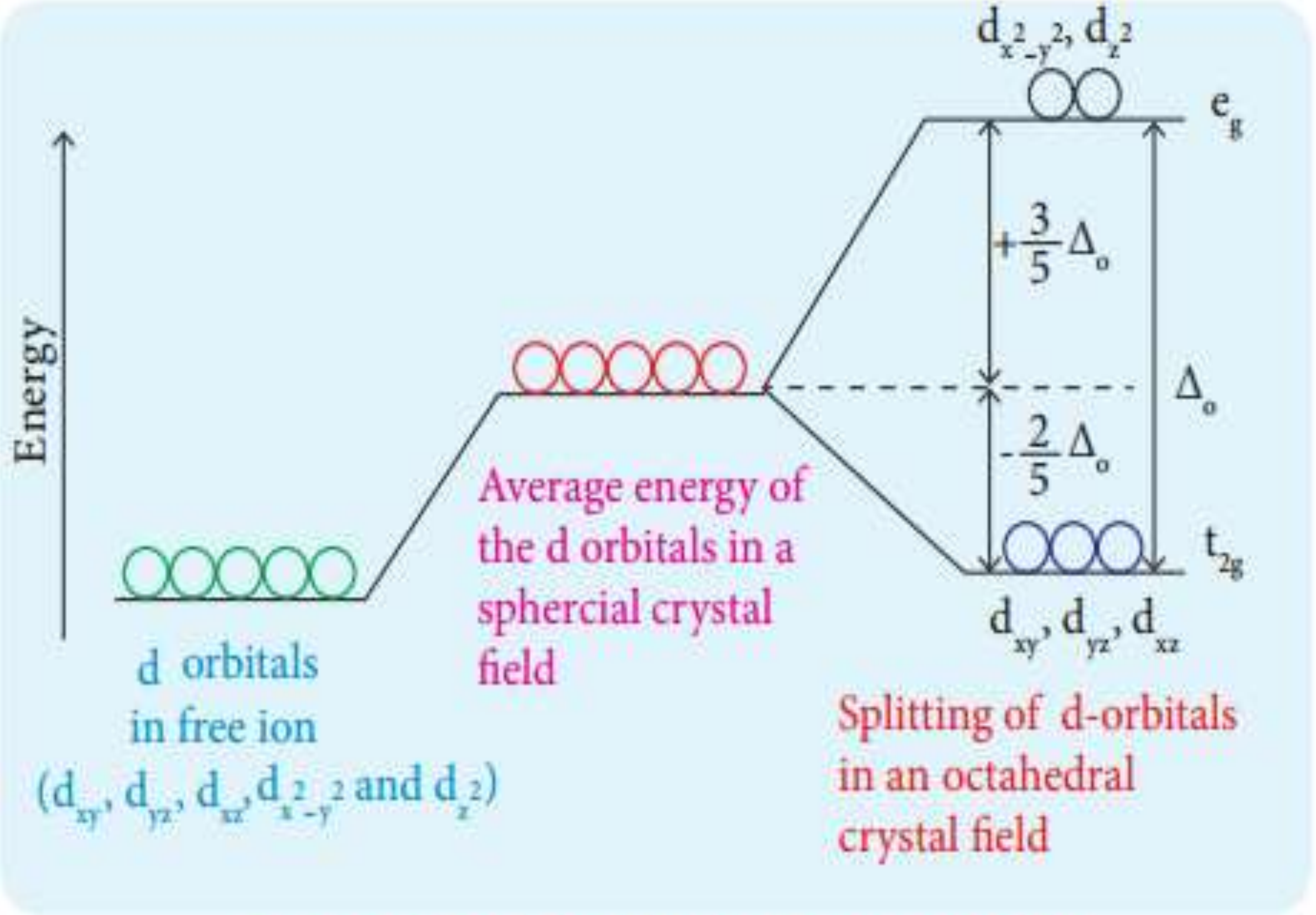
- If the pairing energy is less than the crystal field splitting energy, Δ_o, then the next electron will go into the d_{xy}, d_{xz}, or d_{yz} orbitals due to stability. This situation allows for the least amount of unpaired electrons, and is known as low spin.



Electrons in d-orbitals

- If the pairing energy is greater than Δ_o, then the next electron will go into the $d_z{}^2$ or $d_x{}^2$-$_y{}^2$ orbitals as an unpaired electron. This situation allows for the most number of unpaired electrons, and is known as high spin

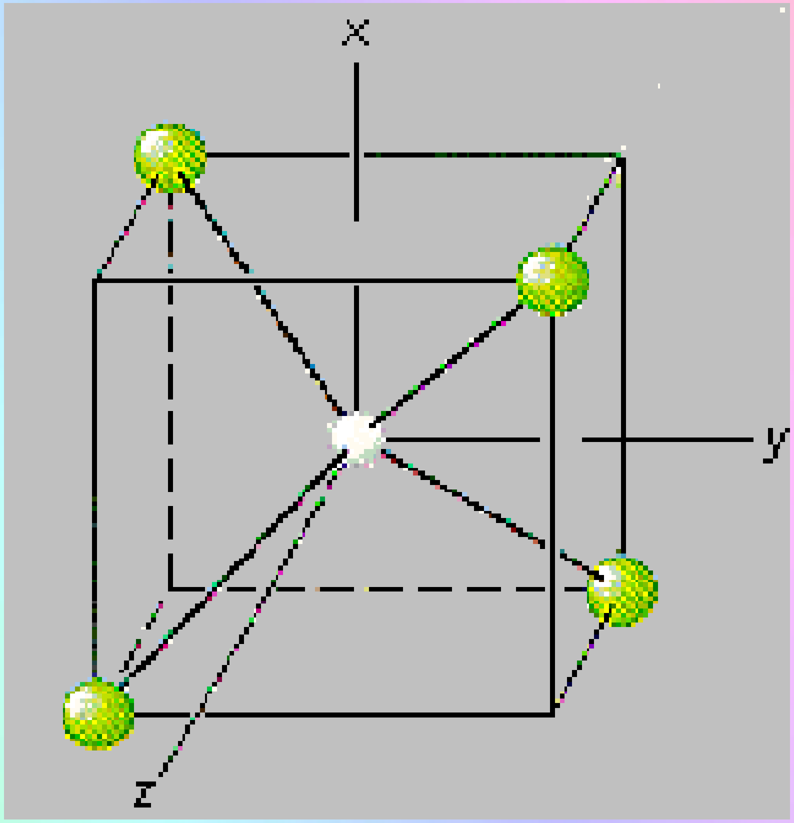


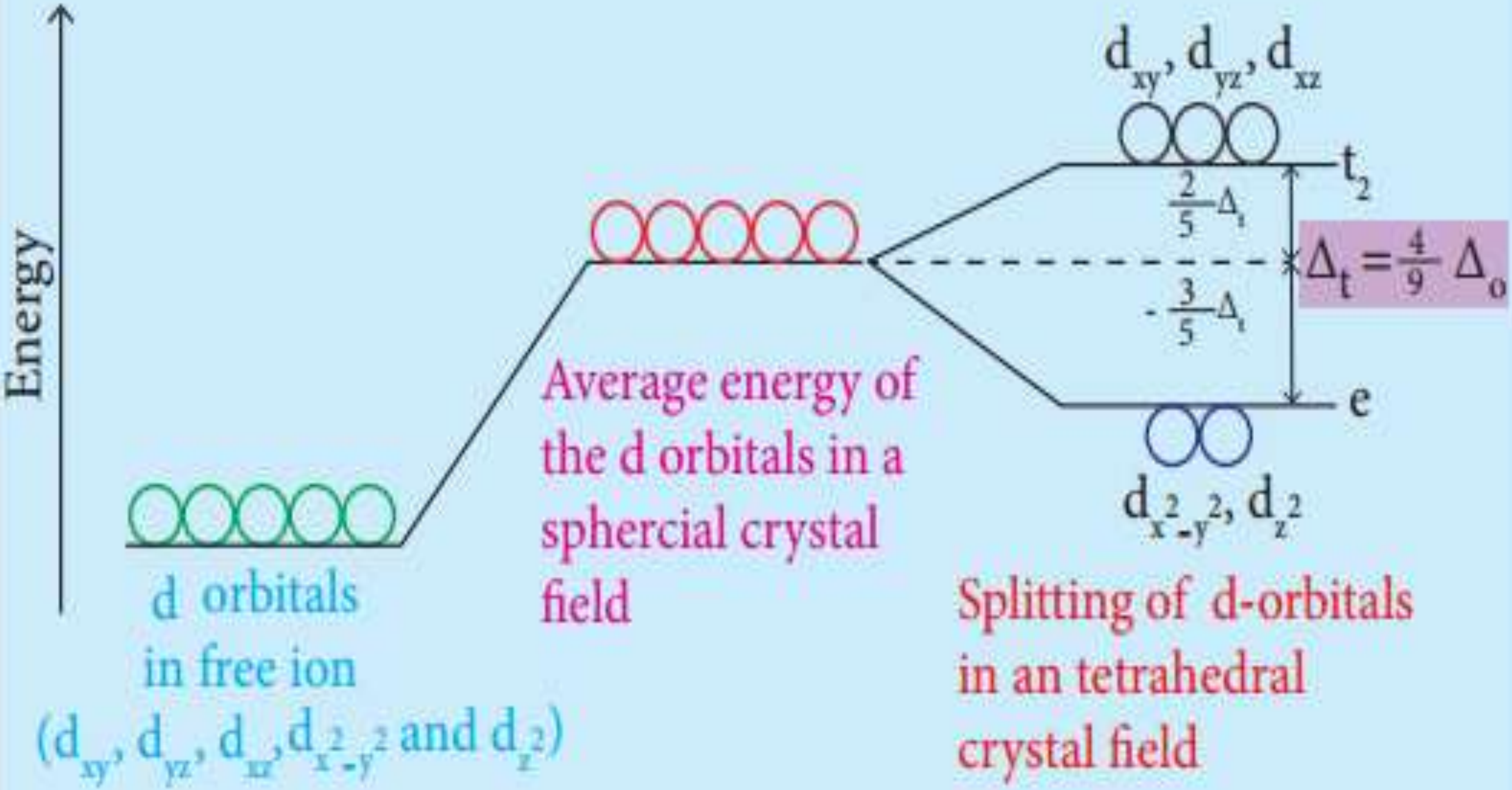


Crystal field splitting in octahedral field

Crystal Field Splitting in Tetrahedral Complex

- In tetrahedral complex central metal atom is surrounded by 4 ligands
- In a tetrahedral complex ligands approaches inbetween the x,y & z axes.
- The electrons residing in the
- $d_{x^2-y^2}$ & d_{z2} orbitals experience a less repulsion. So the energy of these orbitals are decreased.
- The lobes of d_{xy}, d_{xz}, d_{yz} orbitals point in between the axis will experience a greater repulsion. So, the energy of these orbitals is increased.
- Thus, the 5 d-orbitals(which are degenerate) split into 2 sets. t_{2g} & e_g sets of orbitals.
- This is known as crystal field splitting in tetrahedral complexes.





d orbitals in free ion (d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2})

Average energy of the d orbitals in a sphercial crystal field

Splitting of d-orbitals in an tetrahedral crystal field

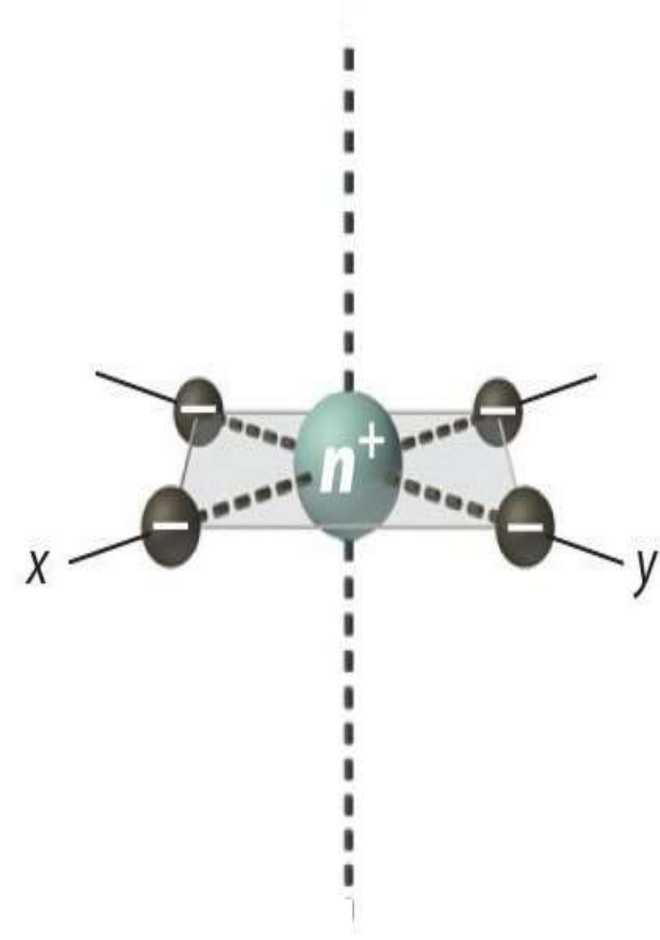
Crystal field splitting in tetrahedral field

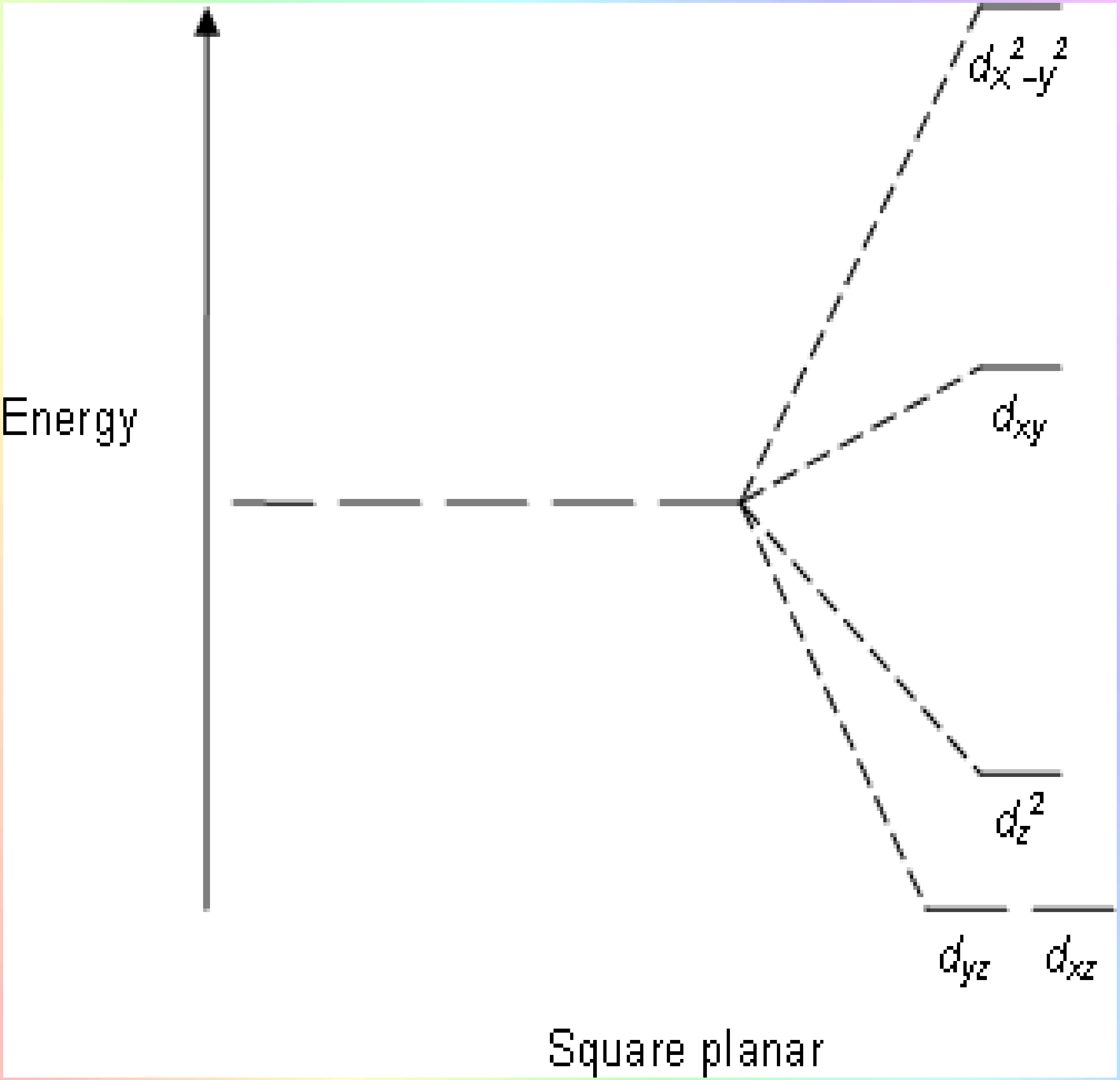
Crystal Field Splitting in Square planar Complexes

- Square planar coordination can be imagined to result when two ligands on the z-axis of an octahedron are removed from the complex, leaving only the ligands in the x-y plane
- In a square planar complexes four ligands are attached to the central metal atom and four ligands approach along X and y axes.
- In a square planar complex four ligands are approaching along X and Y axes. Therefore four ligands in a square planar arrangement would have greatest influence on $d_{x^2-y^2}$ orbital, so the energy of the orbital is raised most.
- The d_{xy} orbital lying in the same plane but between the ligands will also have greater energy, though the effect
- will be lesser than orbital.
- The d_{xz} , d_{yz} will always be affected equally and will remain degenerate.
- There are four different energy levels for the square planar

  (from the highest energy level to the lowest energy level):

  dx2-y2, dxy, dz2, and both dxz and dyz.
- The splitting energy (from highest orbital to lowest orbital) in square planar complex is higher than octahedral complex




Energy
$d_{x^2-y^2}$
d_{xy}
d_{z^2}
d_{yz}
d_{xz}
Square planar

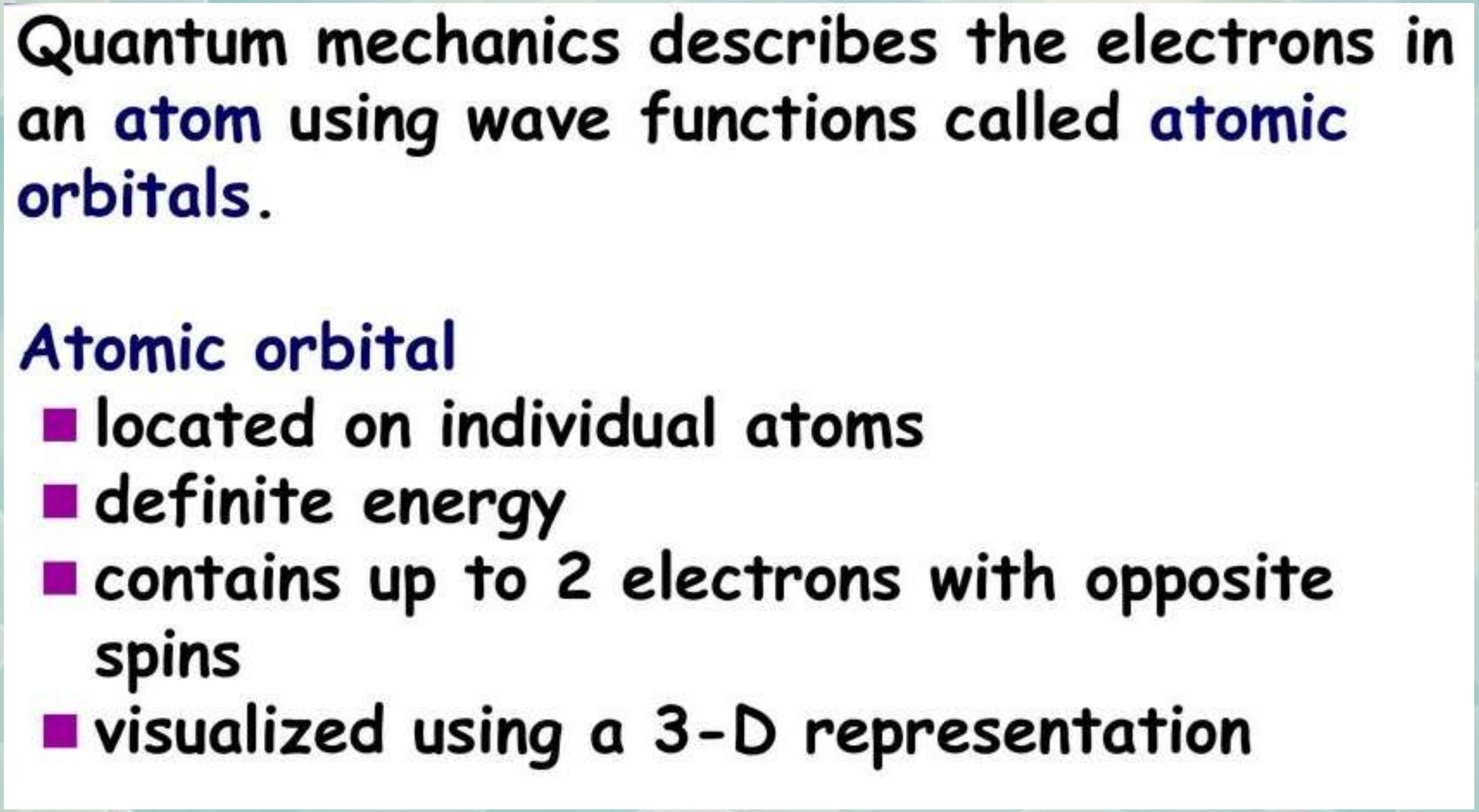
Molecular Orbital Theory

- The goal of the molecular orbital theory is to describe molecules in a similar way to how we describe atoms, that is, in terms of orbitals, orbital diagrams and electronic configurations.
- This theory was developed by Mulliken and Hund

Orbitals

- Electrons occupy different energy levels in atoms that are referred to as orbitals
- orbitals describe where an electron will likely be.
- Each orbital has its own
- specific energy and shape

Atomic orbital

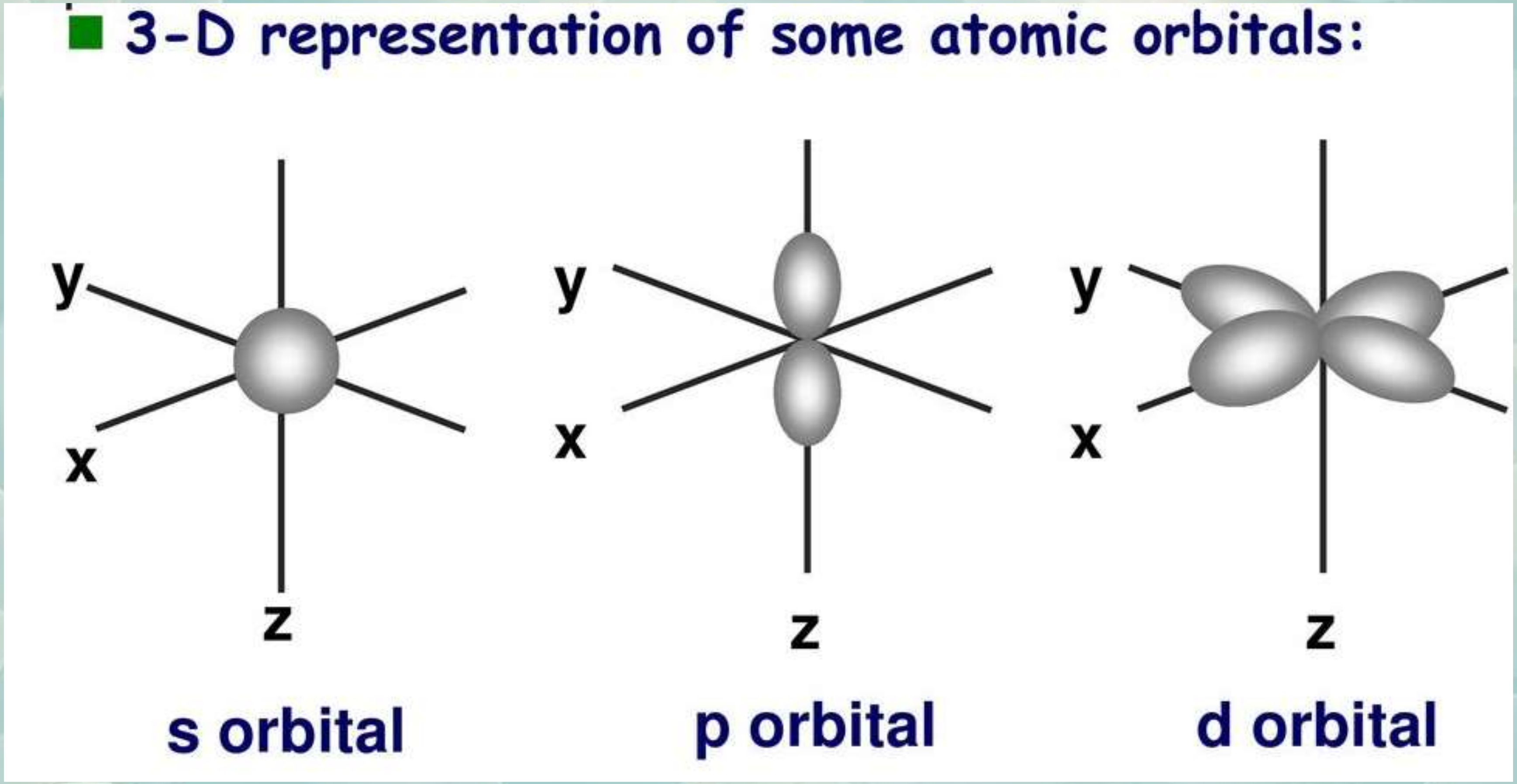


Quantum mechanics describes the electrons in an atom using wave functions called atomic orbitals.

Atomic orbital

- located on individual atoms
- definite energy
- contains up to 2 electrons with opposite spins
- visualized using a 3-D representation

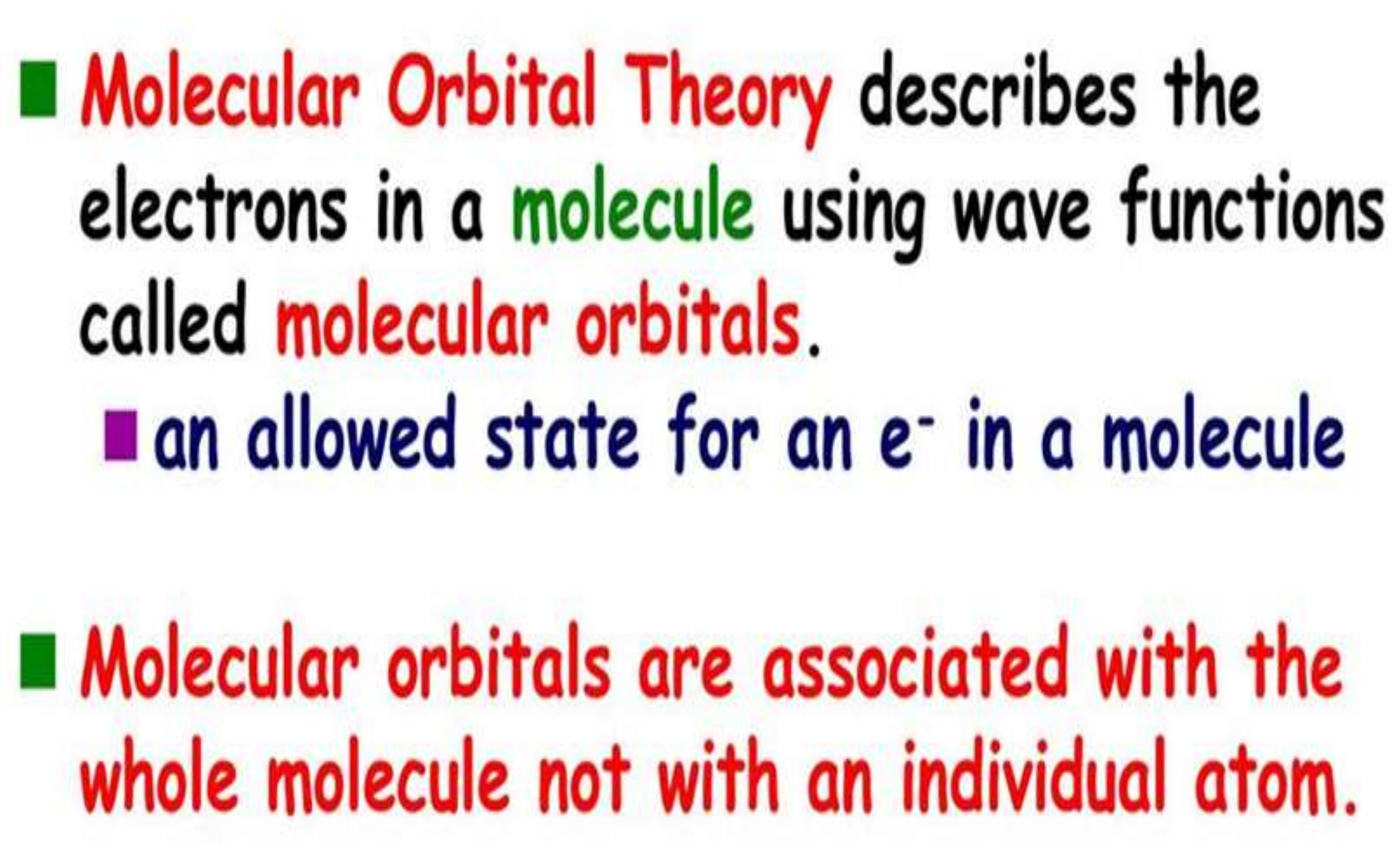
Atomic orbital



- 3-D representation of some atomic orbitals:

s orbital p orbital d orbital

Molecular orbital



- **Molecular Orbital Theory** describes the electrons in a **molecule** using wave functions called **molecular orbitals**.
  - an allowed state for an e^- in a molecule

- **Molecular orbitals are associated with the whole molecule not with an individual atom.**

Postulates of MO Theory

- The electrons in a molecule are present in various molecular orbitals.
- Atomic orbitals of comparable energies and proper symmetry combine to form MO
- A molecular orbital is poly centric i.e, in a molecule electron is influenced by two or more nuclei depending upon the no of atoms in a molecule
- The number of molecular orbitals are equal to the number of atomic orbitals.

Postulates of MO Theory

- When two atomic orbitals combine together to give two molecular orbitals. One is bonding molecular orbital(BMO).The other one is antibonding molecular orbital(ABMO)
- BMO has lower energy and greater stability than ABMO.
- MO like atomic orbitals are filled by the electrons according to Pauli's exclusion principle, Aufbau principle, Hund's rule.

Explanation of MOT

MOT can be explained using

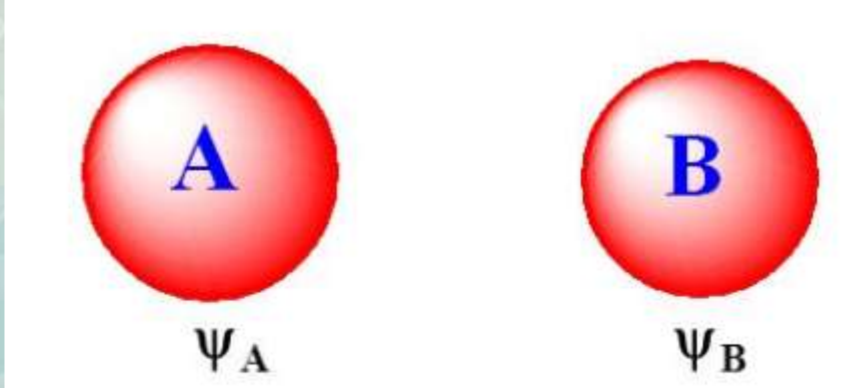
- Linear combination of atomic orbitals(LCAO)
- United atom method

- An MO can specify a molecule’s electron configuration, and most commonly, it is represented as a linear combination of atomic orbitals (the LCAO-MO method)
- These models provide a simple model of molecule bonding, understood through molecular orbital theory.

- A linear combination of atomic orbitals, or LCAO, is a quantum superposition of atomic orbitals and a technique for calculating molecular orbitals in quantum chemistry
- In quantum mechanics, electron configurations of atoms are described as wave functions.
- In a mathematical sense, these wave functions are the basic functions that describe the a given atom’s electrons.

- One of LCAO’s initial assumptions is that the number of molecular orbitals is equal to the number of atomic orbitals included in the linear expansion.
- Essentially, *n* atomic orbitals combine to form *n* molecular orbitals.

Consider to atoms A and B which has atomic orbitals described by wave functions



Formation of MO

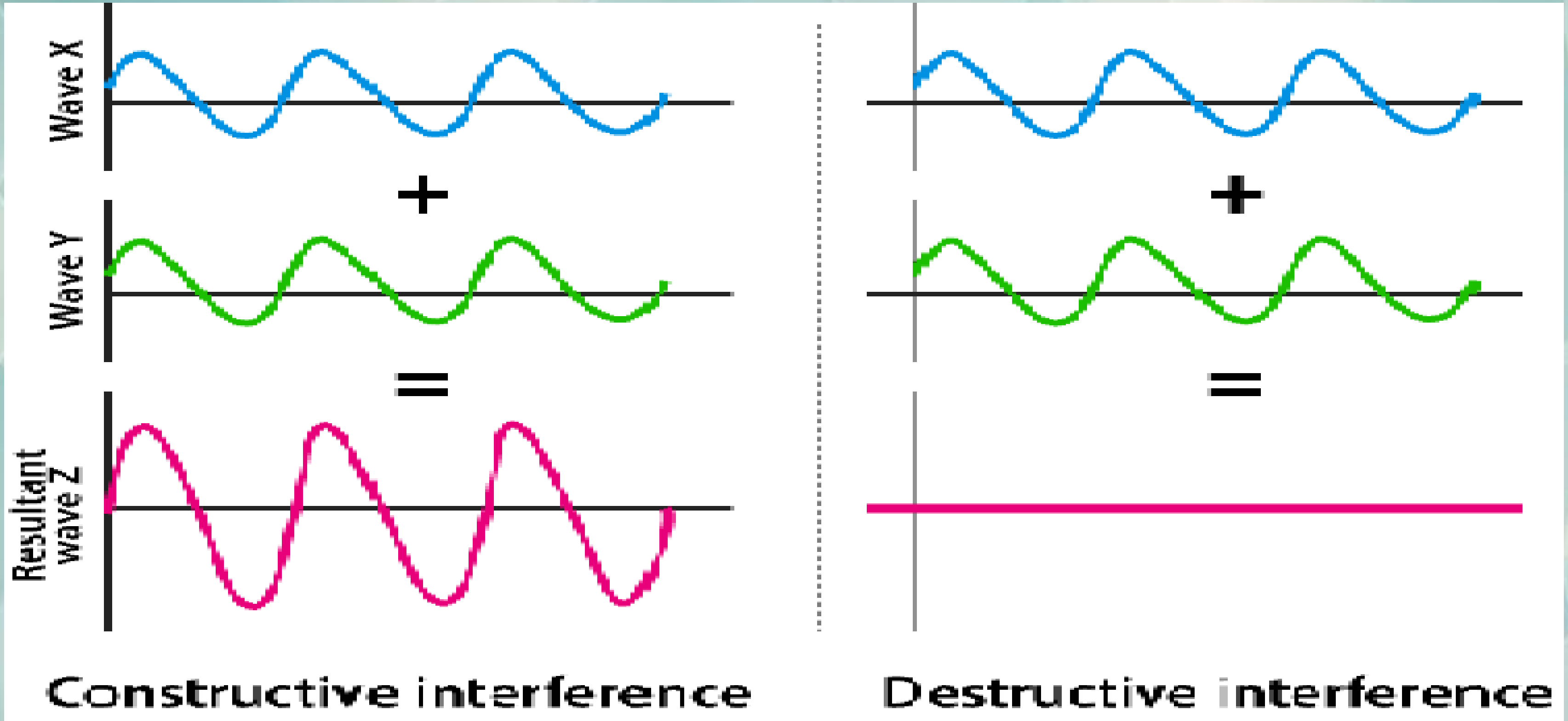
- The formation of MO can be understood in terms of constructive and destructive interference i.e, the waves can combine constructively or destructively.
- Constructive interference- $\psi_{MO} = \psi A + \psi B$
- Destructive Interference- $\psi_{MO} = \psi A - \psi B$

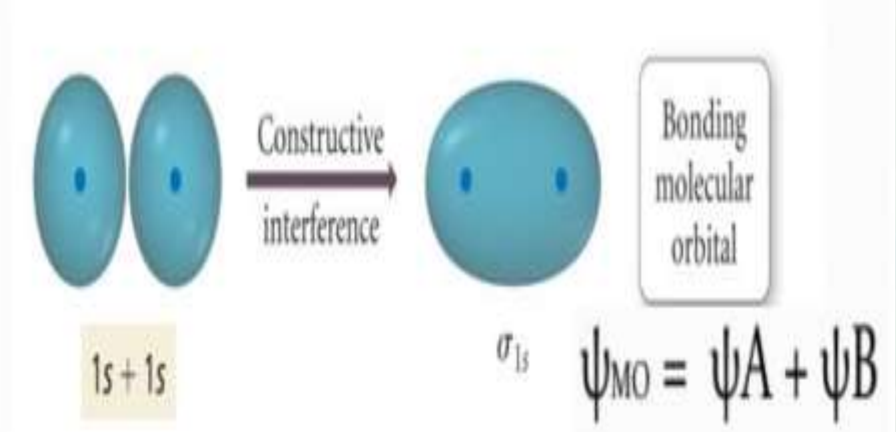
Constructive Interference/BMO

- Addition of atomic orbitals
- Leads to formation of Bonding MO (BMO)
- Decreases the Energy of MO
- Thereby, increases stability of MO

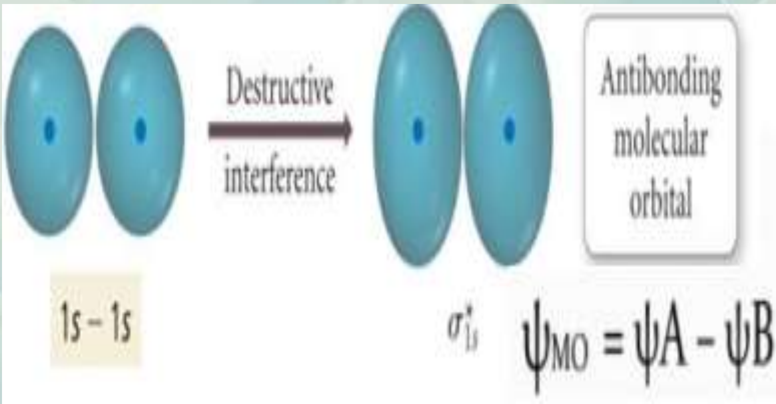
Destructive interference/ ABMO

- Subtraction of atomic orbitals
- Leads to formation of Anti-Bonding MO (ABMO)
- Increases the Energy of MO
- Thereby, decreases stability of MO



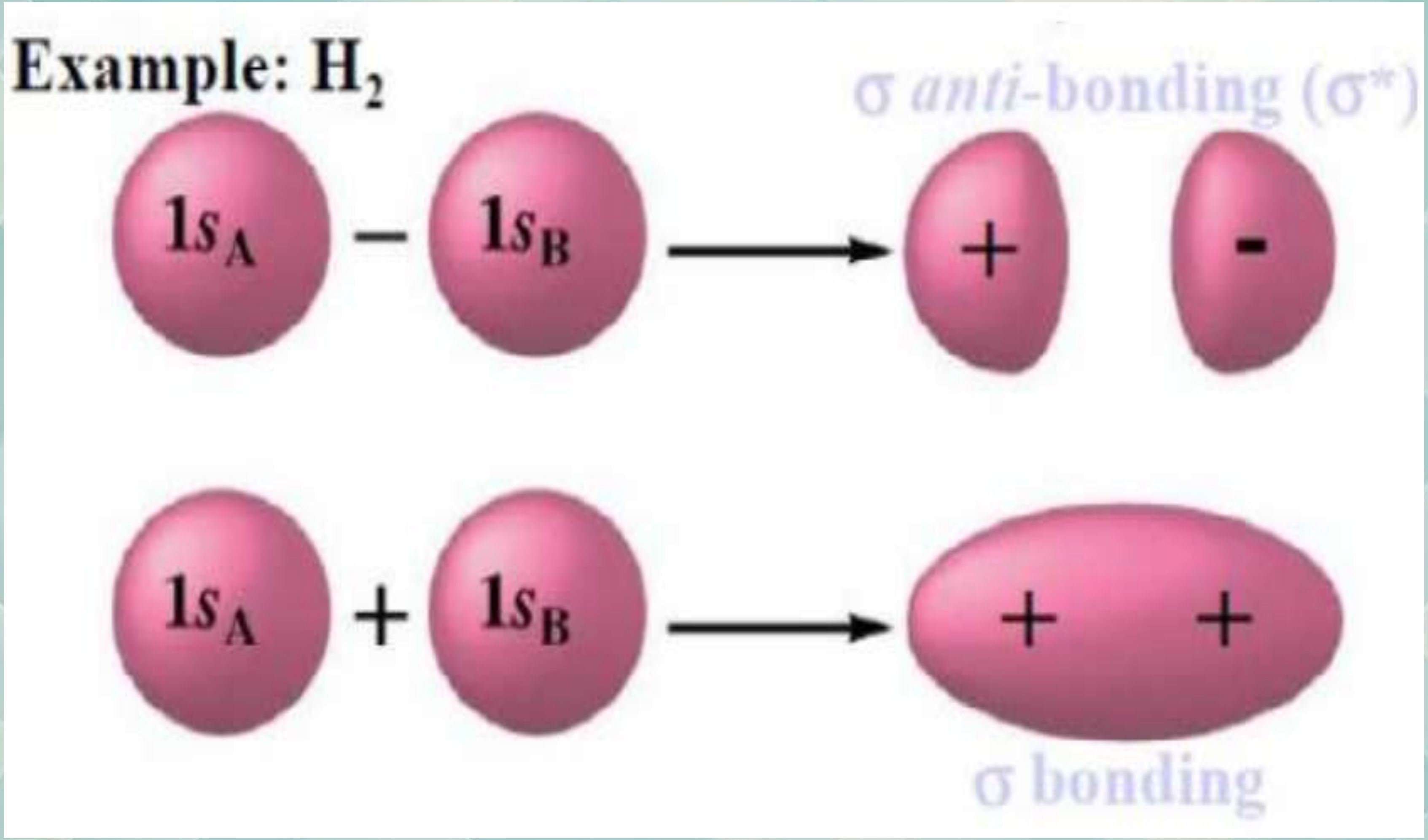


$$\psi_{MO} = \psi A + \psi B$$



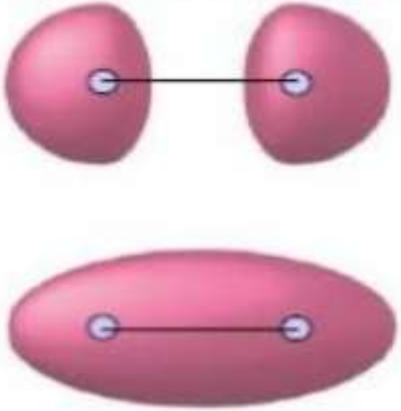
$$\psi_{MO} = \psi A - \psi B$$

Example: H_2



Bonding is driven by stabilization of electrons

- Electrons are negatively charged
- Nuclei are positively charged



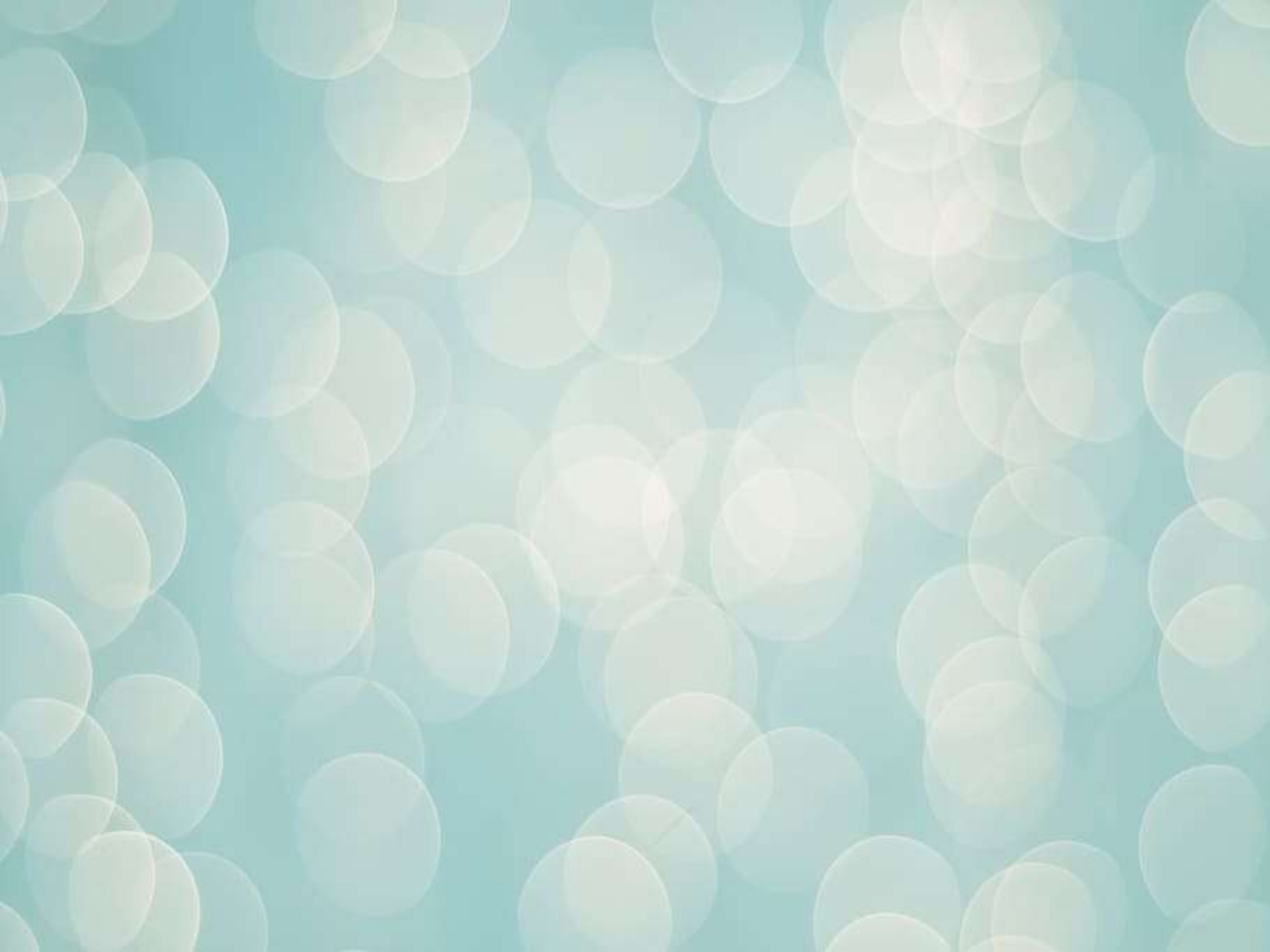
○ = ⊕ = nucleus

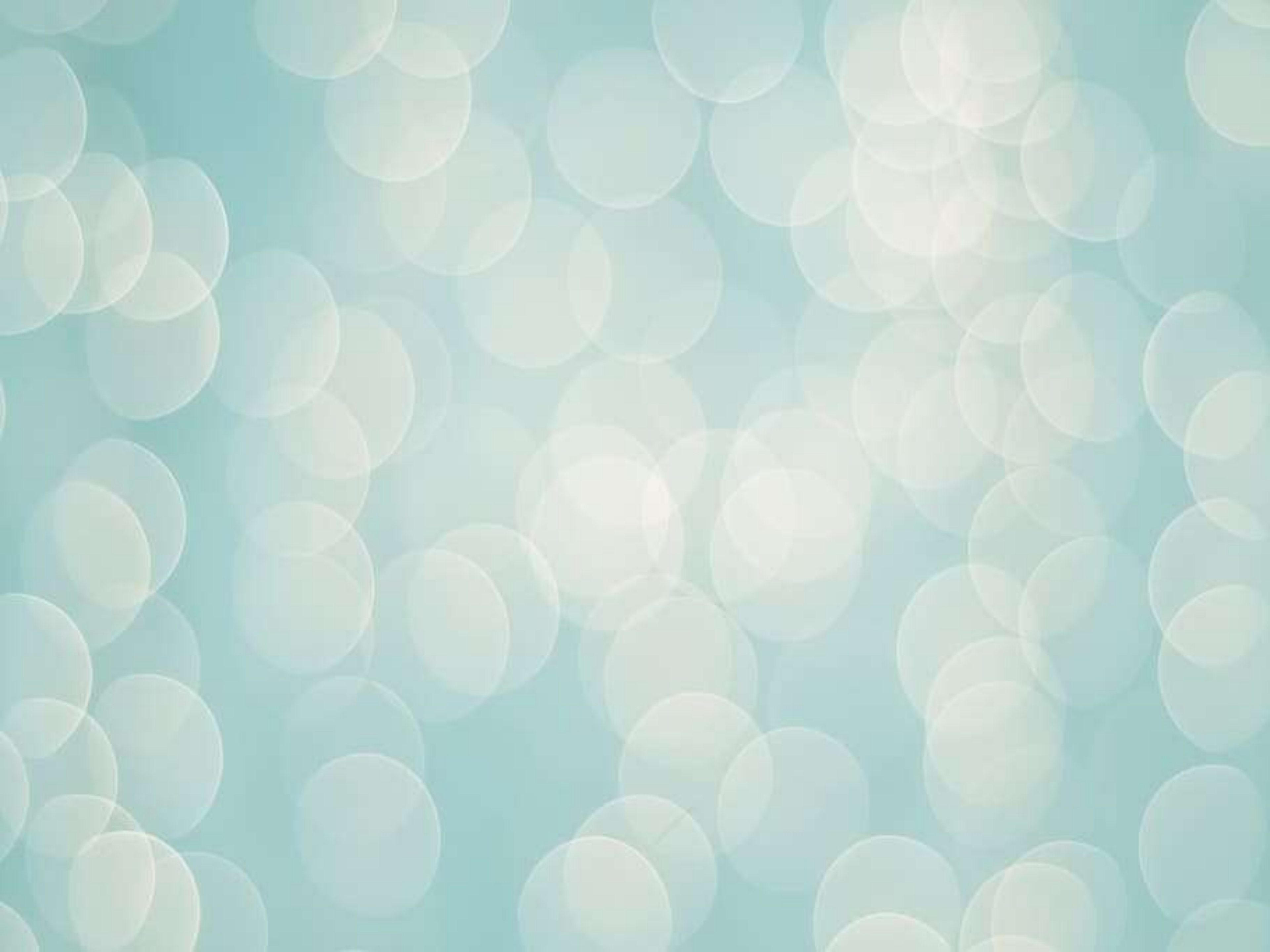
The bonding combination puts electron density between the two nuclei - stabilization

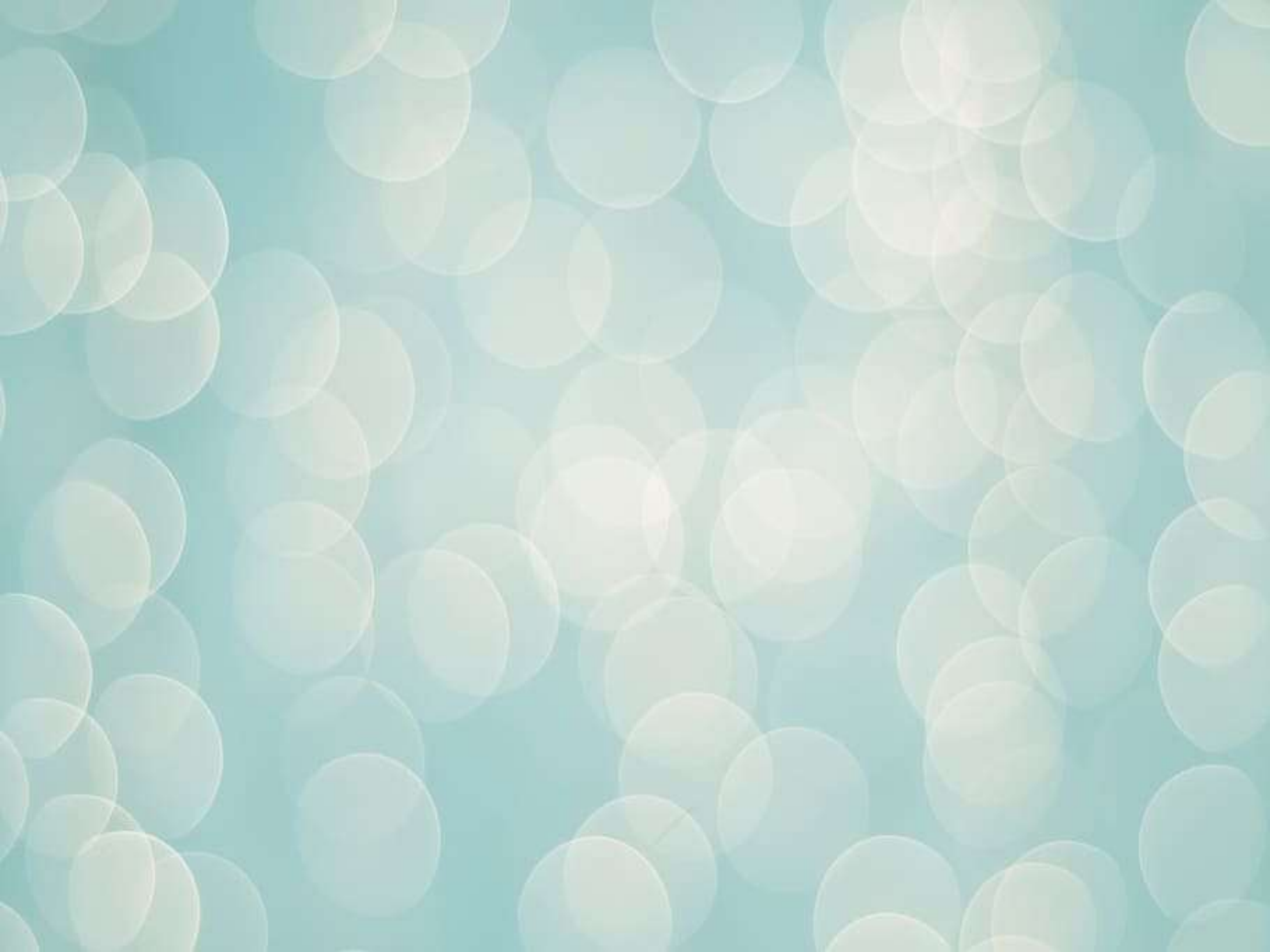
The antibonding combination moves electron density away from the nuclei - destabilization

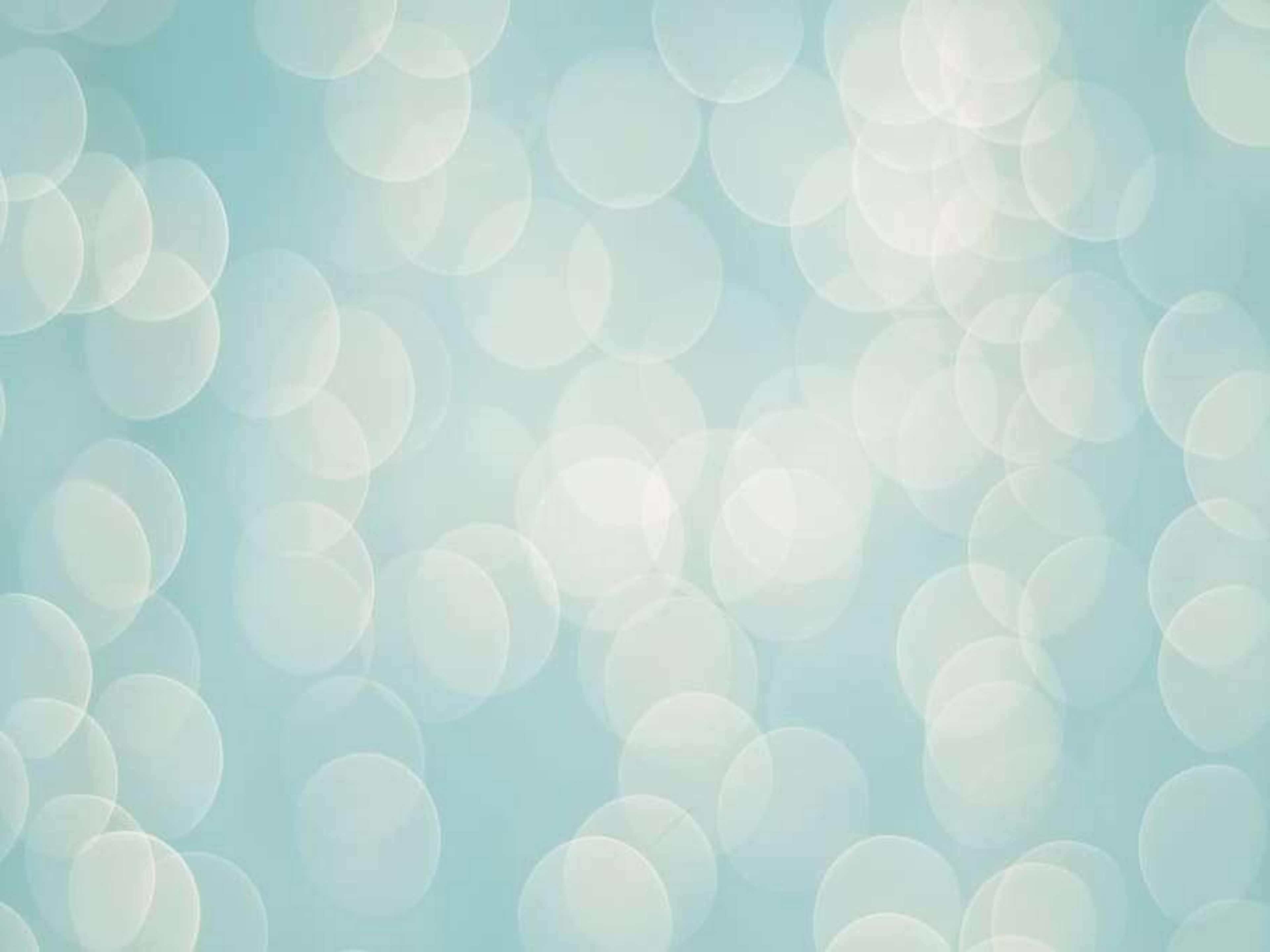
Conditions for the combination of atomic orbitals

- The combining orbitals must have the same or nearly same energy.
- The combining atomic orbitals must have the same symmetry about the molecular axis.
- The combining atomic orbitals must overlap to the maximum extent.



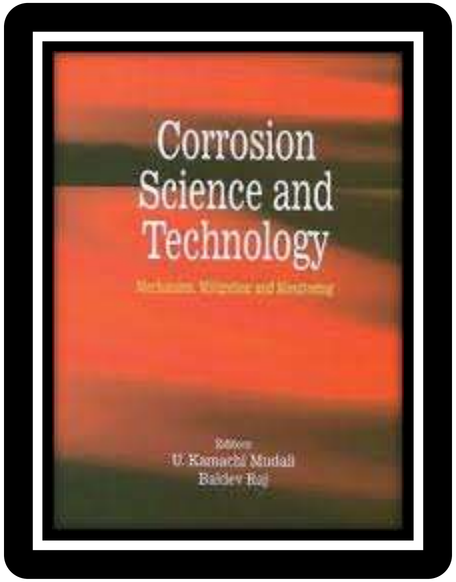






ENGINEERING CHEMISTRY

Corrosion and its control



Corrosion Science and Technology

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CORROSION AND ITS CONTROL

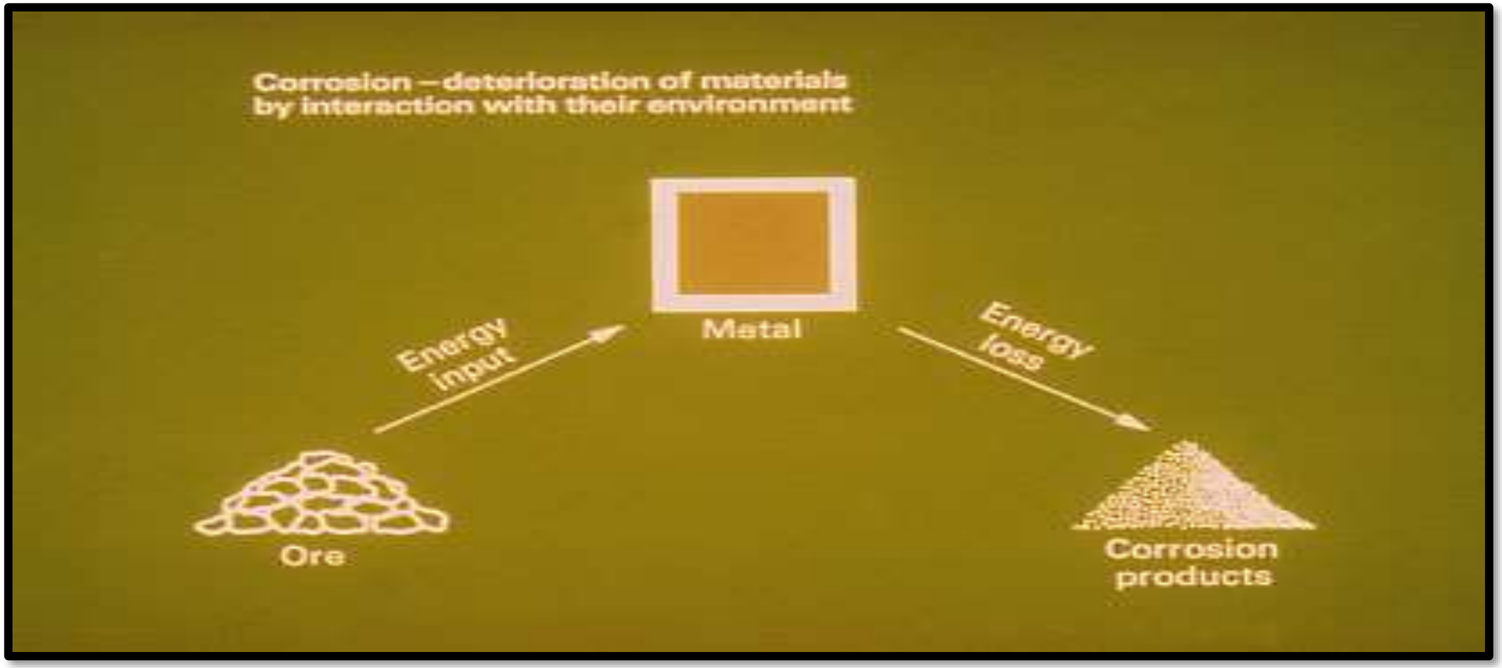
- INTRODUCTION
- CAUSES OF CORROSION
- THEORIES OF CORROSION
- CORROSION REACTIONS

- FACTORS EFFECTING THE CORROSION
- TYPES OF CORROSION
- CORROSION CONTROL METHODS

INTRODUCTION

- Destruction of a metal by chemical or electrochemical reaction with its environment.
- Physical or mechanical wearing away of a metal is not called corrosion but is called erosion
- If corrosion and erosion take place together the destruction of the metal takes place very much faster
- Corrosion is an unintentional attack on a material by reaction with a surrounding medium
- The corrosion problem should be very seriously considered in all those cases where the structure or the equipment is meant to last many years say 20 years…

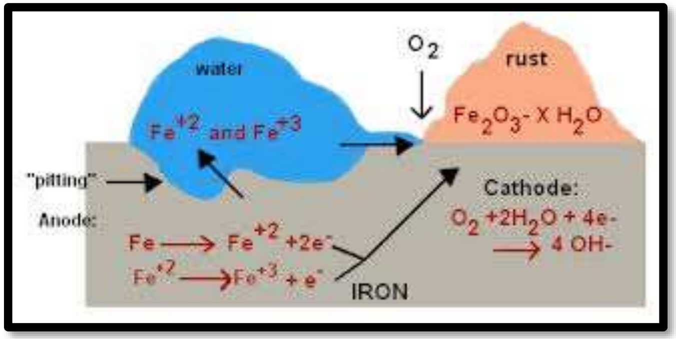
Definition of Corrosion



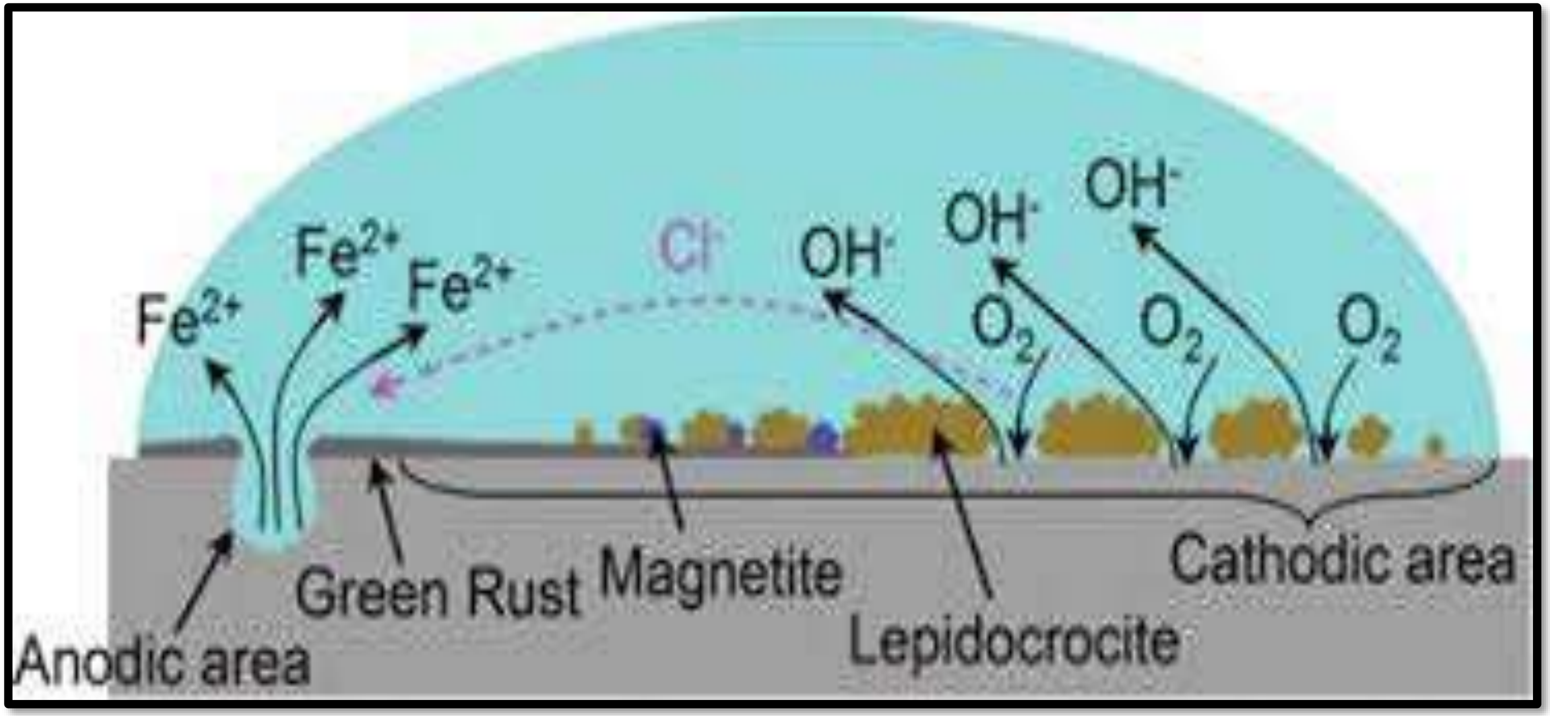
Corrosion – deterioration of materials by interaction with their environment

Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals.

Rusting of iron



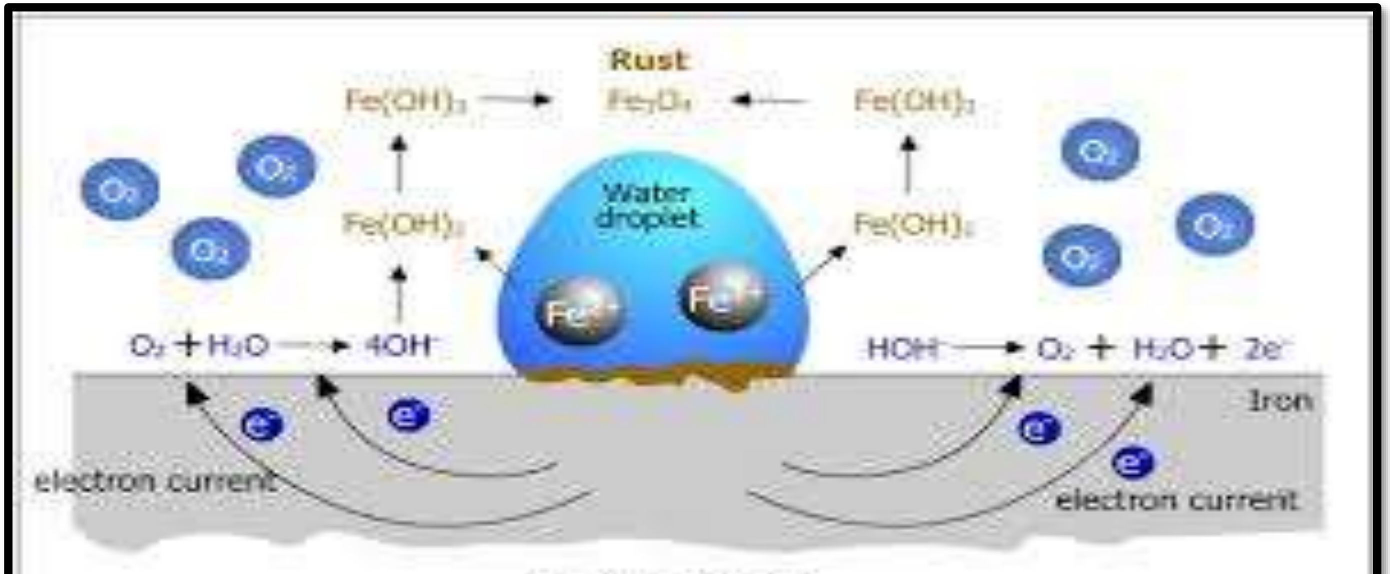
Formation of green rust



CAUSES OF CORROSION

- The chemical combined state of the metal is known as **“ore”**
- The ore has low energy in its thermodynamical state.
- The extracted metal has high energy ,thermodynamically unstable .
- Metal converts itself into stable state by reacting with the environment and undergoes corrosion.
- The corroded metal is thermodynamically stable.

Formation of rust



Formation of Rust.

Effects or disadvantages of corrosion

- The valuable metallic properties like conductivity,malleability, ductility etc are lost due to corrosion.
- Life span of the metallic parts of the machineries is reduced.
- The process of corrosion is very harmful and is responsible for the enormous wastage of metal in the form of its compound.
- The failure of the machinery takes place due to lose of useful properties of metals.
- The approximate estimate of loss of metal due to corrosion is 2 to 2.5 billion dollars per annum all over the world.


1 mm

TYPES OF CORROSION

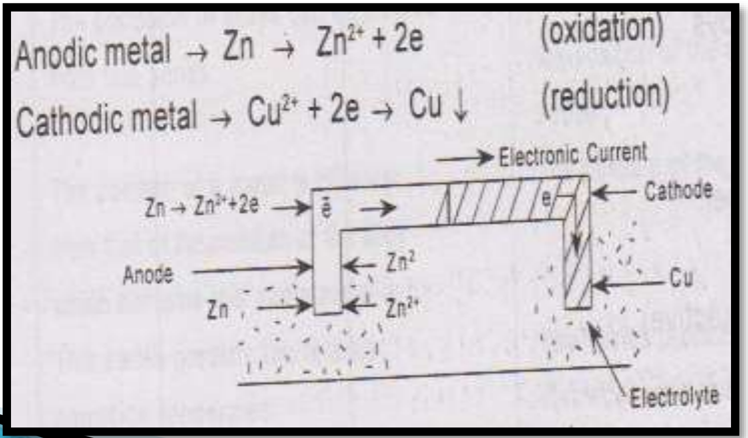
Different types of electrochemical corrosions are

- Galvanic corrosion
- Pitting corrosion
- Intergrannular corrosion
- Water line corrosion

Galvanic corrosion

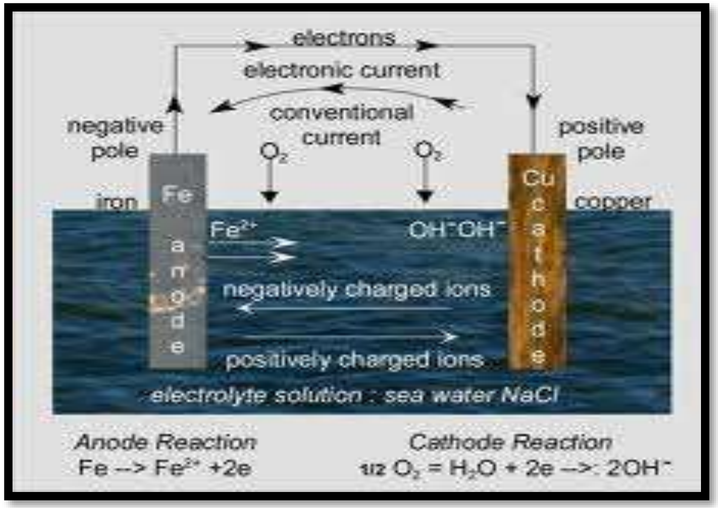
- This corrosion occurs when different metals are in contact and exposed to corrosive atmosphere.

- The metal which has higher electrode potential value will form anode and undergoes corrosion. Example: Zn-Cu galvanic cell zinc behaves as anode and corrosion occurs, copper behaves as cathode and protected.



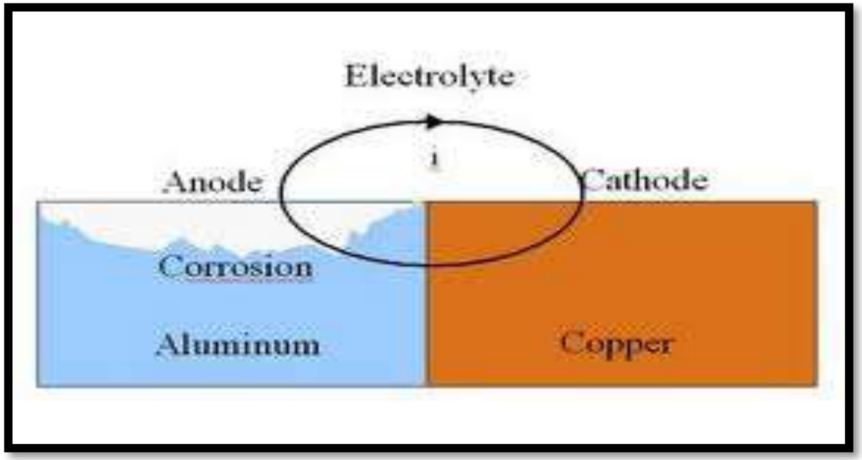
Anodic metal → Zn → $Zn^{2+} + 2e$ (oxidation)

Cathodic metal → $Cu^{2+} + 2e \rightarrow Cu\downarrow$ (reduction)



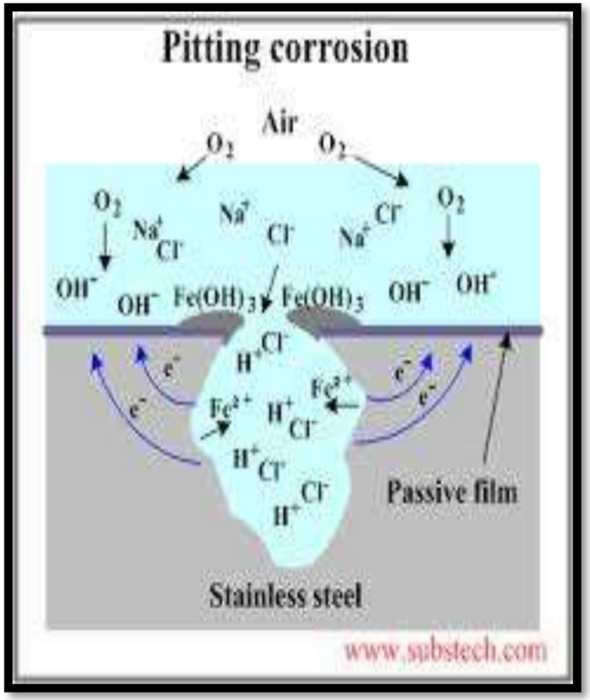
Anode Reaction
$Fe \rightarrow Fe^{2+} + 2e$

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


Electrolyte
i
Anode
Cathode
Corrosion
Aluminum
Copper

Pitting corrosion

- When corrosion starts on a metal surface at certain spots they become less open to oxygen with the result that corrosion proceeds faster at those very spots making deeper and deeper cavities.
- Pitting corrosion can be explained on the basis of differential aeration.
- The pit created becomes deeper, its bottom becomes less open to oxygen which makes it more anodic.
- The part which has higher oxygen concentration is cathodic.



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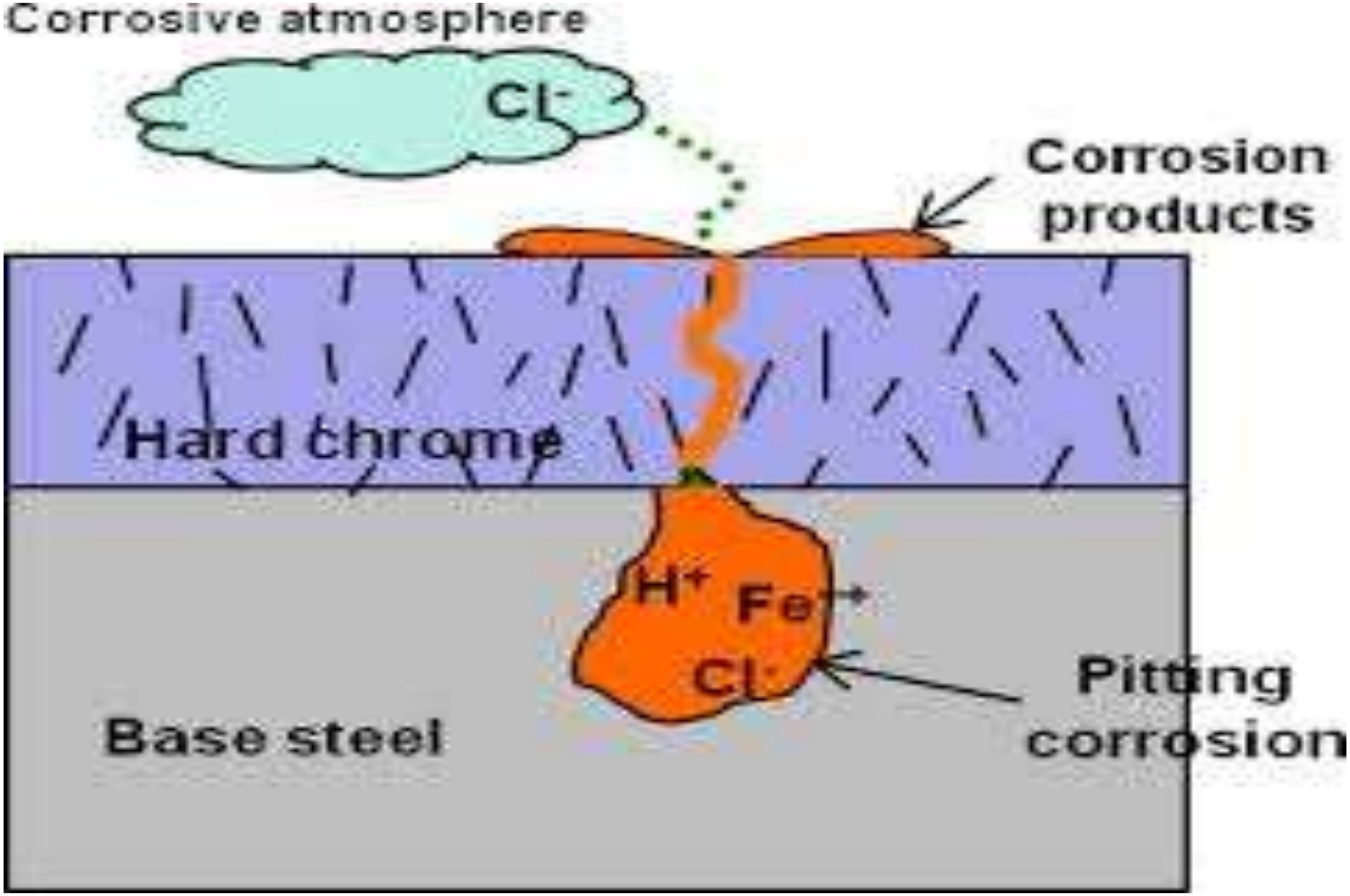

Corrosive atmosphere
Cl-
Corrosion products
Hard chrome
H+
Fe++
Cl-
Pitting corrosion
Base steel

Water line corrosion

- The concentration of oxygen dissolved in water is greater at the surface than deeper down. This causes formation of a concentration cell.

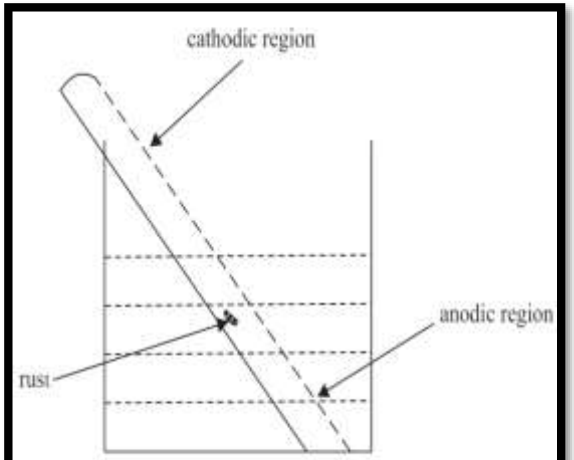


Fig. 13.3 Water line corrosion

- Anode is the lower portion .
- Cathode is at the water level.
- Due to the poor conductivity of water the ions just below the water level are available for reaction, the metal corrodes just below the water level.

Theories of corrosion

THEORIES OF CORROSION

- In atmospheric corrosion the metals tend to revert to the states in which they occur in nature.

- Several theories of corrosion have been proposed from time to time..

- The three theories are
  - i) ACID THEORY
  - ii) CHEMICAL CORROSION (**DRY CORROSION**)
  - iii) ELECTROCHEMICAL CORROSION (**WET CORROSION**)

ACID THEORY

Acid theory of corrosion considers acid to be the main cause.

Rusting takes place faster in acid solutions than in neutral or basic solutions.

Oxygen and water are necessary for rusting of iron.

This is not true for all the metals like Zn etc..

Rate of corrosion in absence of Carbon di oxide is also seen.

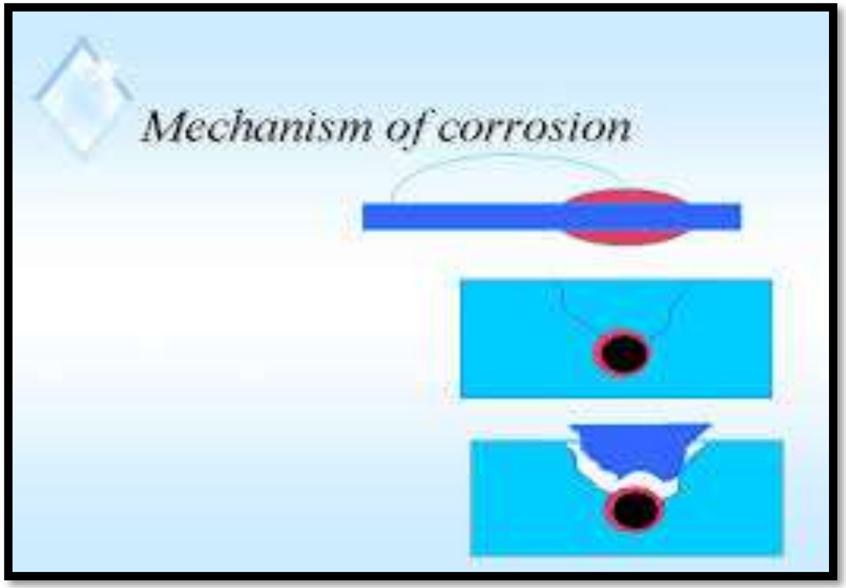
Dry corrosion or chemical corrosion

- The direct chemical reaction of environment/atmospheric gases or inorganic liquids with metal surfaces .
- There are three types of chemical corrosion

i) Oxidation corrosion

ii) Corrosion by other gases

iii) Liquid metal corrosion



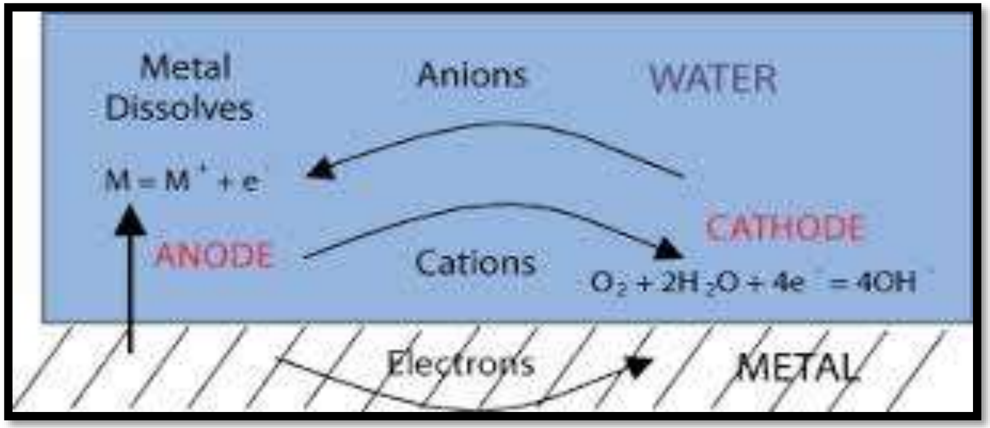
(1.) Oxidation Corrosion: This is carried out by the direct action of oxygen low or high temperatures on metals in absence of moisture.

Alkali metals and Alkaline earth metals are rapidly oxidized at low temperatures. At high temperature all metals are oxidized (except Ag, Au, Pt).

$M \rightarrow M_2^+ + 2e^-$ (Oxidation)

$O_2 + 2e^- \rightarrow 2O_2^-$ (Reduction)

$M + O_2 \rightarrow M_2^+ + 2O^{2-}$ (Metal oxide)



Mechanism:-

1. When temp increases the metal undergoes oxidation and losses e$^-$

$$2M \rightarrow 2M^{+n} + 2ne^-$$

Metal Ion

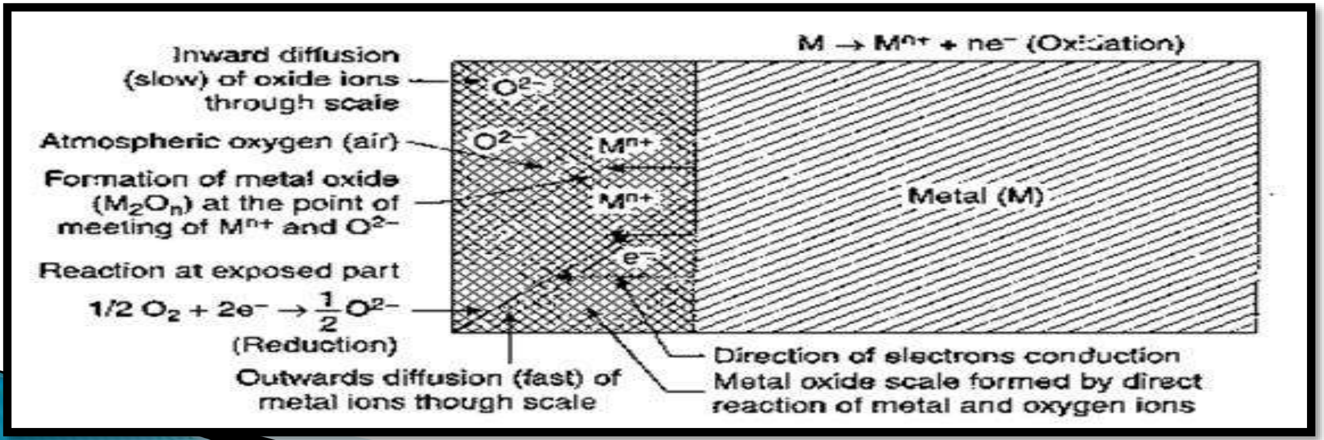
2. Electron are gained by the oxygen molecules forms oxide ions

$$nO_2 + 4ne^- \rightarrow 2n\,O^{2-}$$

Oxide Ion

3. Scale of metal oxide formed $2M + nO_2 \rightarrow 2M + 2n\,O^2$

Metal Oxide



2.) **Corrosion due to other gases:** This type of corrosion is due to gases like SO_2, CO_2, Cl_2, H_2S, F_2 etc. In this corrosion, the extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved. The degree of attack depends on the formation of protective or non protective films on the metal surface which is explained on the basis of Pilling Bedworth rule.

(i) If the volume of the corrosion film formed is more than the underlying metal, it is strongly adherent, non-porous does not allow the penetration of corrosive gases.

$Ag + Cl_2 \rightarrow 2AgCl$ (protective film)

(ii) If the volume of the corrosion film formed is less than the underlying metal, it forms pores/cracks and allow the penetration of corrosive gases leading to corrosion of the underlying metal.

Ex. In petroleum industry, H_2S gas at high temperature reacts with steel forming a FeS scale. Fe (steel) + H_2S FeS (porous)

3.) **Liquid metal corrosion:** This corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. The corrosion reaction involves either dissolution of a solid metal by a liquid metal or internal penetration of the liquid metal into the solid metal.

Eg. Coolant (sodium metal) leads to corrosion of cadmium in nuclear reactors.

Wet or Electrochemical corrosion

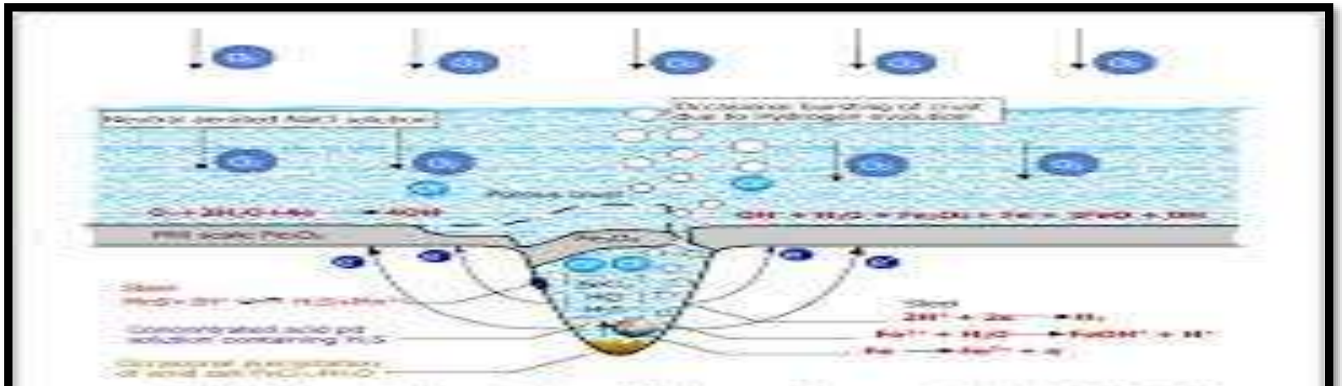
- The electrochemical corrosion occurs when

  i) a conducting liquid is in contact with a metal.

  ii) when two dissimilar metals or alloys are immersed partially in the solution.

- Corrosion occurs due to the presence of anodic and cathodic areas.

- At anode oxidation reactions takes place
- At cathode reduction reactions takes place



Electrochemical reactions that occur when a pit is initiated at sulphide inclusion in a carbon steel.

- Occurs when aqueous solution or liquid electrolytes are present

- Wet corrosion takes place in environments where the relative humidity exceeds 60 %.

- Wet corrosion is most efficient in waters containing salts, such as NaCl (e.g. marine conditions), due to the high conductivity of the solution.

Mechanism Of Electrochemical Corrosion

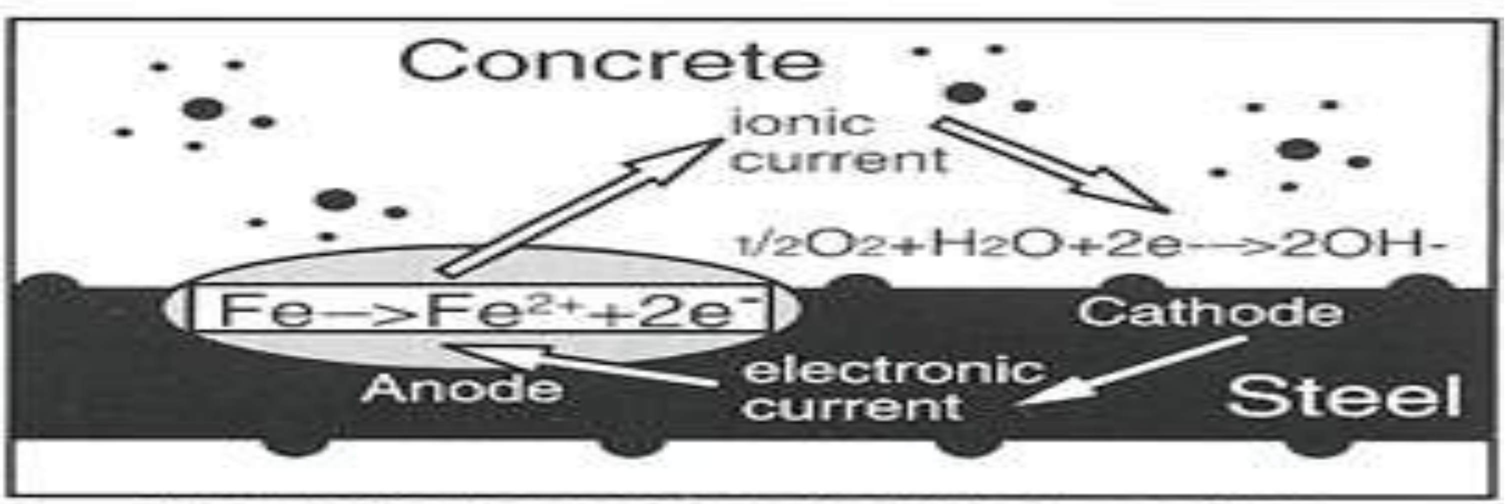


Figure 1: The anodic and cathodic reactions

Mechanism Of Electrochemical Corrosion

Anodic Reaction:

Dissolution of metal takes place.

As result metal ions are formed with the liberation of free electrons.

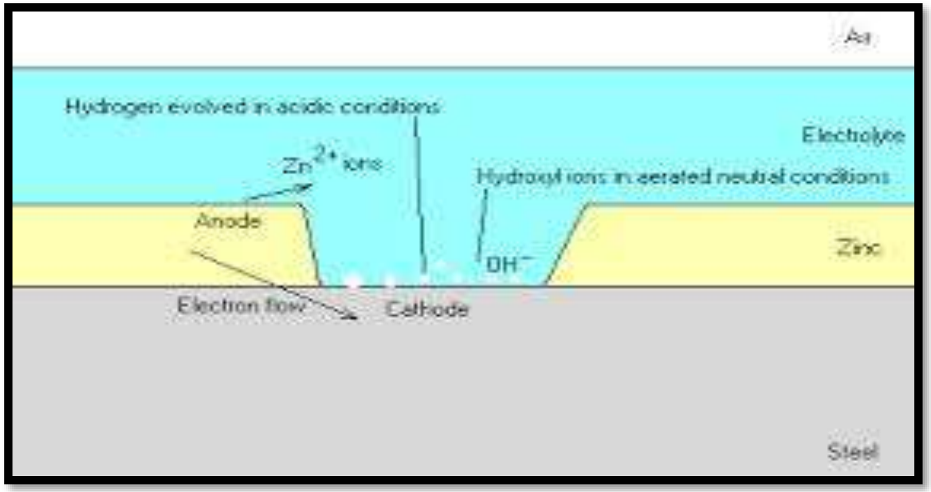
$$M \leftrightarrow M^{+n} + e^-$$

Metal Ion

Cathodic Reaction

(i) Hydrogen Evolution :- Occurs usually in acidic medium

$$2H^+ + 2e^- \leftrightarrow H_2 (g)$$



(ii) Oxygen Absorption :- occurs when solution is aerated sufficiently.

$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$ (In acidic medium)

$O_2 + 4H^+ + 4e^- \leftrightarrow 4OH^-$ (In basic medium)

Wet corrosion takes by the following ways.

- Hydrogen gas evolution

- Oxygen gas absorption

This type of corrosion occurs in acidic medium.

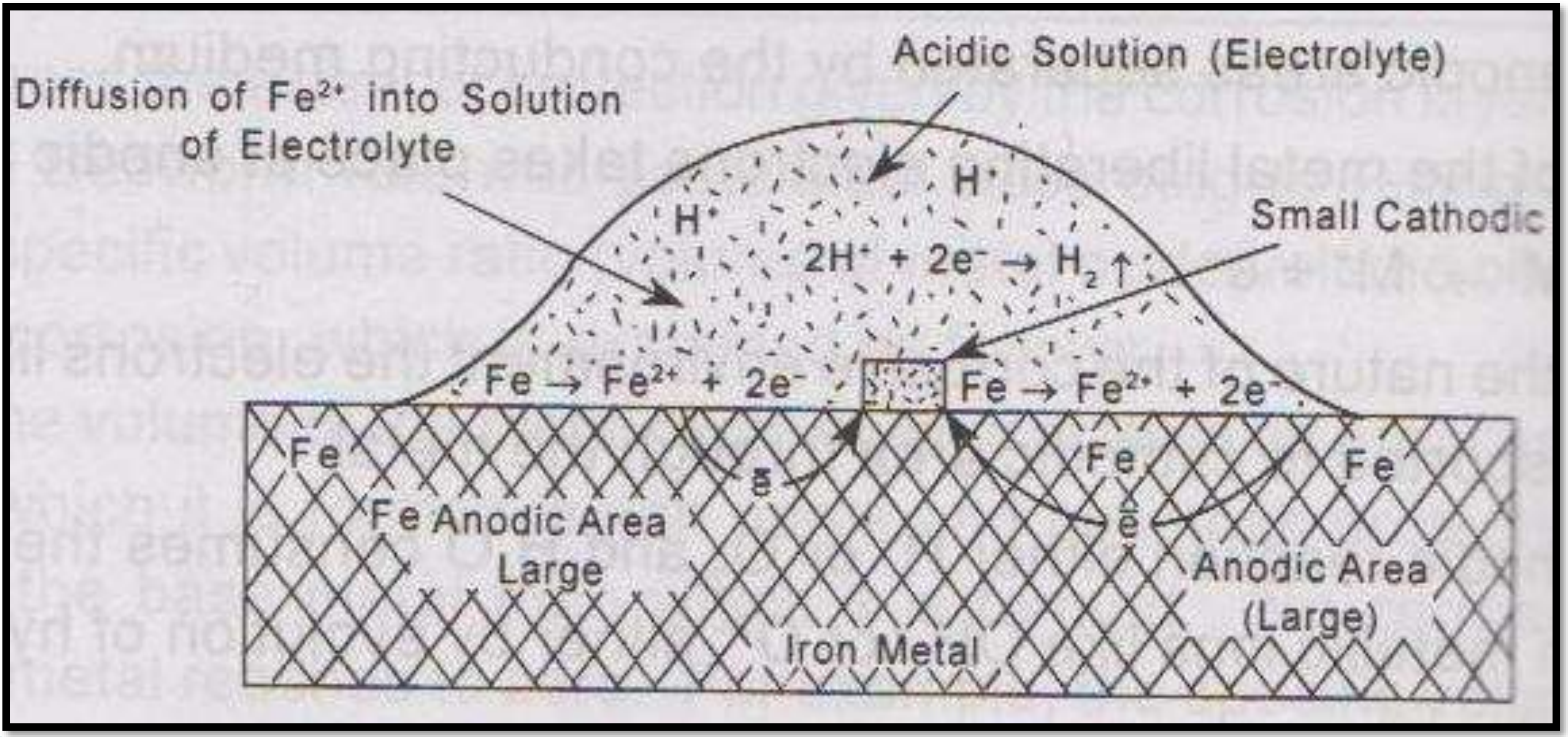
E.g. Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons. Anode: $Fe ---- \rightarrow Fe_2^{+} + 2e^{-}$ (Oxidation)

- The electrons released flow through the metal from anode to cathode, whereas H+ ions of acidic solution are eliminated as hydrogen gas.

  Cathode: $2H^{+} + 2e^{-} ---- \rightarrow H_2$ (Reduction)
- The overall reaction is: $Fe + 2H^{+} ----- \rightarrow Fe_2^{+} + H_2$

- All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H_2 gas.

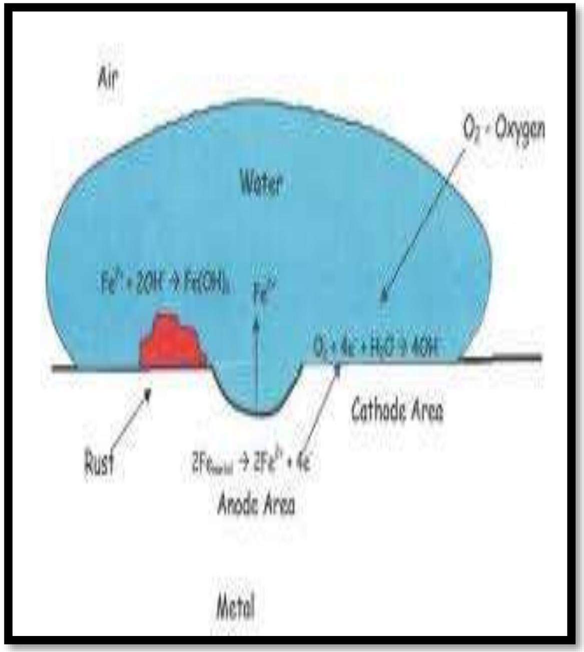
Mechanism of wet corrosion by hydrogen evolution



Absorption of oxygen

Absorption of oxygen: For example, rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen.

- ➢ Usually the surface of iron is coated with a thin film of iron oxide.
- ➢If the film develops cracks, anodic areas are created on the surface.
- ➢While the metal parts act as cathodes. It shows that anodes are small areas, while the rest metallic part forms large cathodes.

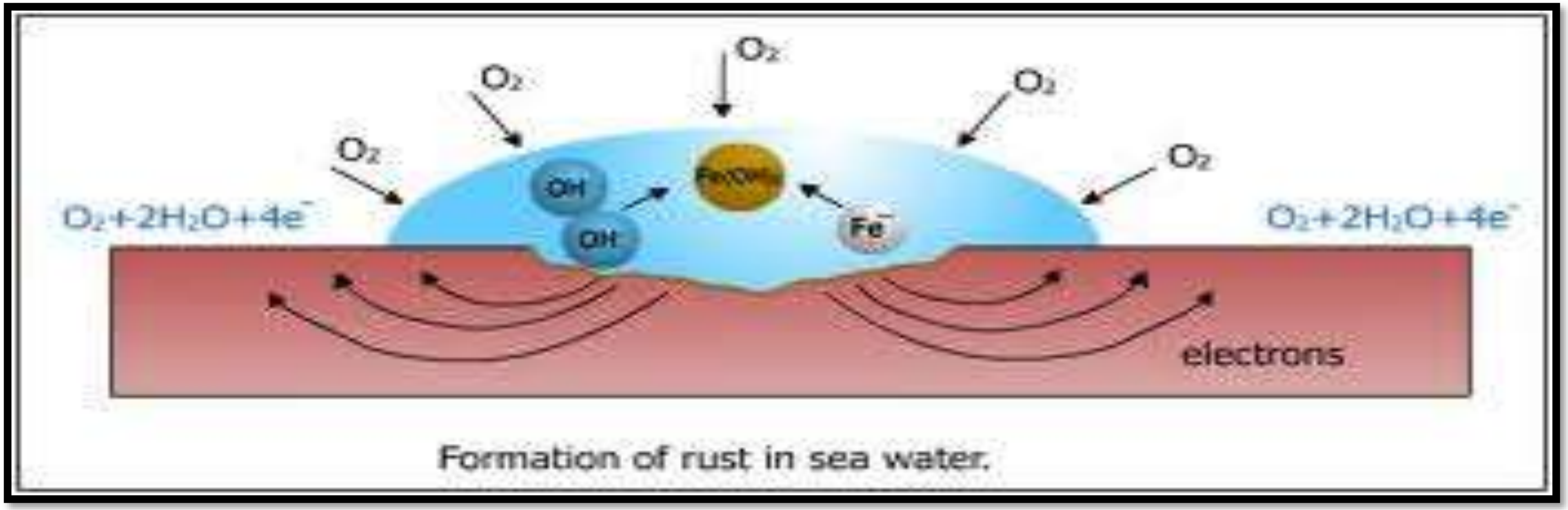


The released electrons flow from anode to cathode through iron metal.

.

At anode: $Fe \text{ ----}\rightarrow Fe_2^{+} + 2e^{-}$ (Oxidation)
At cathode: $\frac{1}{2} O_2 + H_2O + 2e^{-} \text{ ---}\rightarrow 2OH^{-}$ (Reduction)
Overall reaction: $Fe_2^{+} + 2OH^{-} \text{ -----}\rightarrow Fe(OH)_2$

The product called yellow rust corresponds to $Fe_2O_3 . 3H_2O$



Formation of rust in sea water.

FACTORS EFFECTING THE CORROSION

- The factors that effect corrosion are

  i) Nature of the metal

  ii) Nature of the environment

Nature of the metal

- The rate and the extent of corrosion depends on the following factors

A) Purity of a metal
B) Position in galvanic series
C) Over voltage
D) Nature of oxide film
E) Nature of corrosion product

Nature of the metal

1. ***Purity of the metal****:* Heterogeneity of the metal is due to the presence of impurities which form tiny electrochemical cells at the exposed parts. The anodic parts get corroded.

2.***Electrode potentials:*** metals with higher reduction potentials do not corrode easily. They are noble metals like gold, platinum and silver. Whereas the metals with lower reduction potentials readily undergo corrosion (e.g.. Zn, Mg, Al etc.).

3.Position of metal in Galvanic series*:* Metals which possess low reduction potentials and occupy higher end of galvanic series undergo corrosion easily.

When two metals are in electrical contact in presence of an electrolyte, then the metal which is more active undergoes corrosion.

The rate of corrosion depends on the difference in their position in Galvanic series. Greater the difference more will be the extent of corrosion at anode.

4.Relative areas of anodic and cathodic cells: When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the areas of the cathodic and anodic parts. *i.e*, the relative areas o of corrosion is influenced by cathodic to anodic cells.

5. ***Physical state of metal***: Metals with small grain size have more tendencies to undergo corrosion. Metal with more stress/strain also undergoes corrosion easily.

6. ***Hydrogen over voltage:*** when a cathode reaction is hydrogen evolution type, the metal with lower hydrogen over voltage on its surface is more susceptible for corrosion, since the liberation

of hydrogen gas is easy at this condition. Hence the cathodic reaction is very fast which in turn makes anodic reaction fast. Hence the rate of corrosion increases. Higher the over voltage, lesser is the corrosion.

7. ***Nature of surface film**:* If the corrosion product formed is more stable, insoluble and non porous, it acts as protective layer and prevents further corrosion (E.g.. Ti, Al and Cr). If the corrosion product is porous, volatile and soluble, it further enhances the corrosion (Fe, Zn and Mg).

Nature of the environment

1. Temperature: the rate of corrosion reactions increases with increase in temperature.

2. Humidity in air: the moisture or humidity present in atmosphere furnishes water to the electrolyte which is essential for setting up of an electrochemical cell. The oxide film formed has the tendency to absorb moisture which creates another electrochemical cell.

3. Presence of impurities: Atmosphere is contaminated with gases like CO_2, SO_2, H_2S; fumes of H_2SO_4, HCl etc. and other suspended particles in the vicinity of industrial areas. They are responsible for electrical conductivity, thereby increasing corrosion.

4. pH value: pH value of the medium has the greater effect on corrosion. Acidic pH increases the rate of corrosion.

5. Amount of oxygen in atmosphere**:** As the percentage of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell. The decay of metal occurs at the anodic part and the cathodic part of the metal is protected.

6. Velocity of ions which flow in the medium: As the velocity of the diffusion of the ions in the medium increases, the rate of corrosion increases .

CORROSION CONTROL METHODS

The various measures taken for corrosion protection are

I) CATHODIC PROTECTION

II) SURFACE COATINGS

CATHODIC PROTECTION

- The method of protecting metals and alloys from corrosion making them completely cathode.

- To achieve this auxilary anode is provided in the corroding medium which is connected to the structure.

- Cathodic protection is of two types

i) Sacrificial anodic method

ii) Impressed current cathodic method

Cathodic Protection

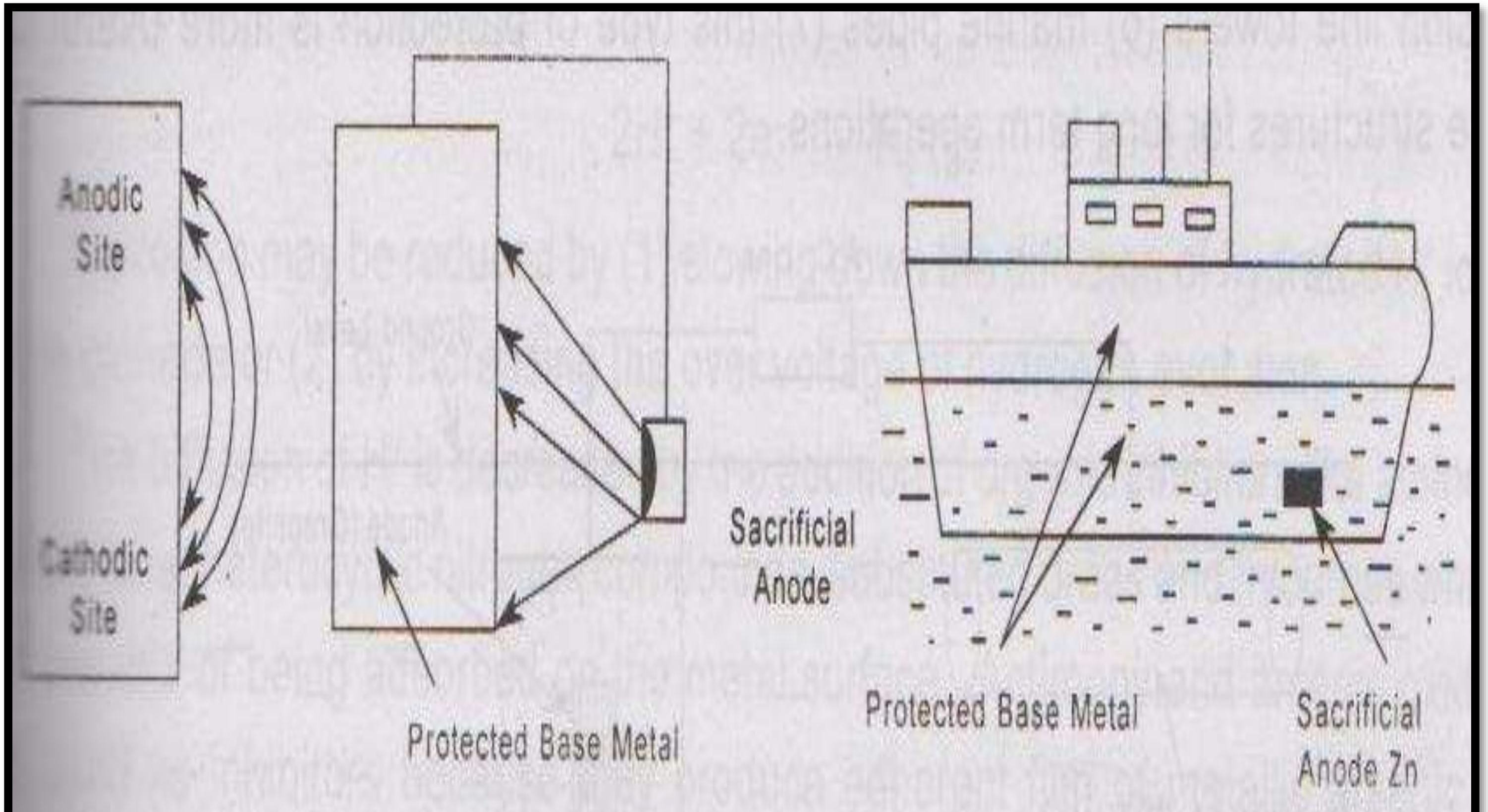
Force the metal to be protected to behave like cathode.

(i) **Sacrificial anodic protection**:

- Metal to be protected from corrosion connected to more anodic metal
- Commonly used metals Mg, Zn, Al and their alloys

Eg. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.

Eg. The underground water pipelines and water tanks are also protected by sacrificial anode method. By referring to the electrochemical series, the metal with low reduction potential is connected to the base metal which acts as anode.



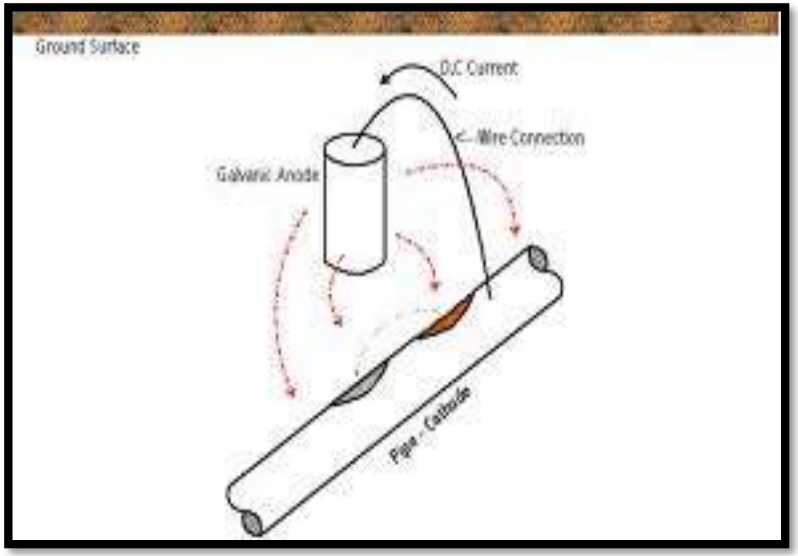
Unprotected metal being corroded

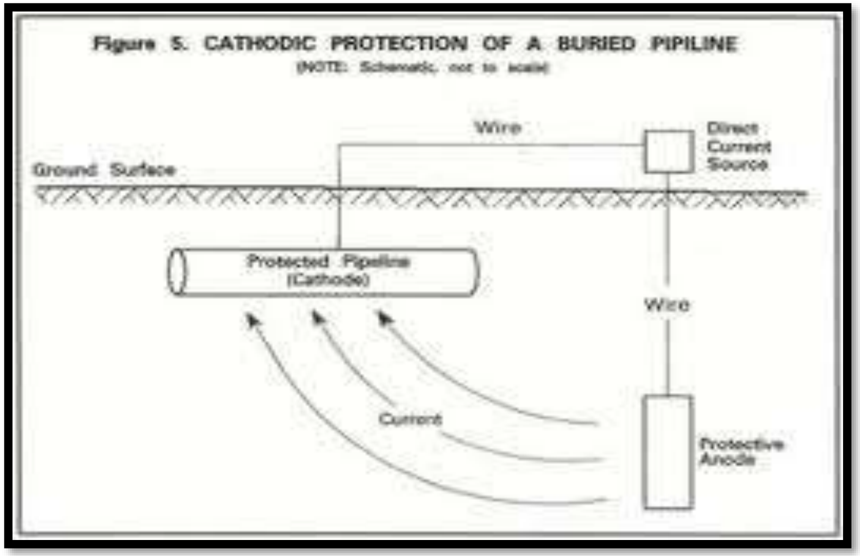
(b) Sacrificial anodic protection

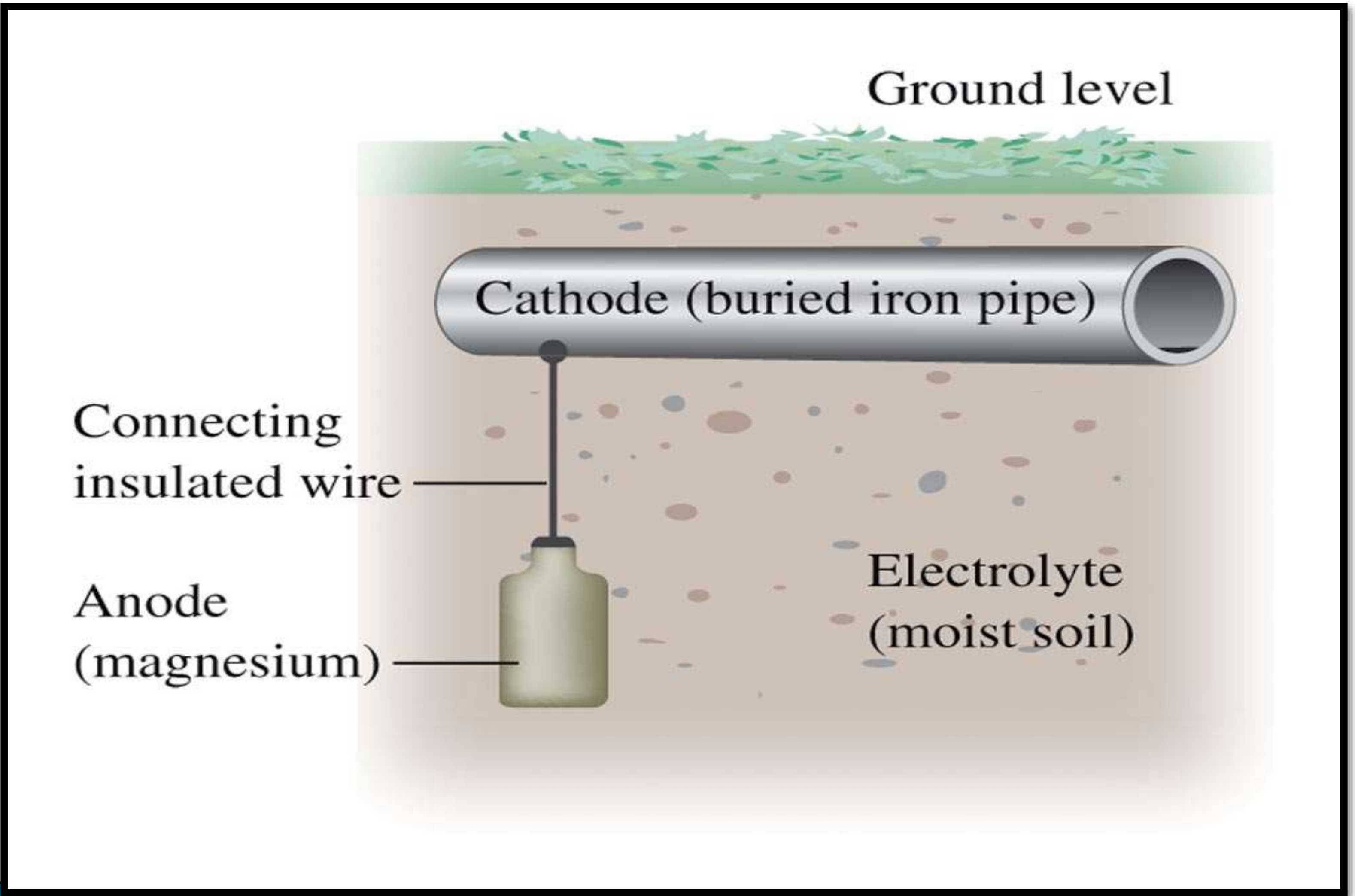
(c) Protection of ship-hull below water line by

Impressed current method:

- Direct current is applied in opposite direction to nullify the corrosion current
- Converts the corroding metal from anode to cathode.






Ground level
Cathode (buried iron pipe)
Connecting insulated wire
Anode (magnesium)
Electrolyte (moist soil)

SURFACE COATINGS

- The metal surface is covered with a coating to protect it from corrosion.
- These may be

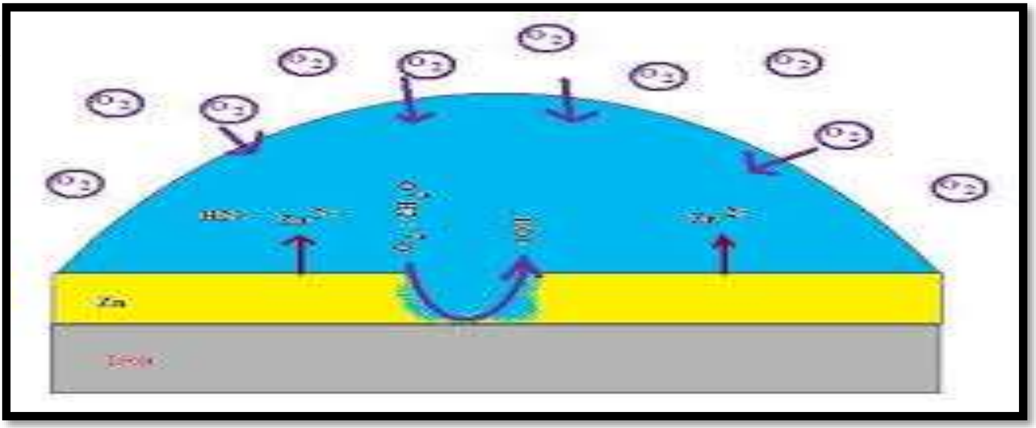
  i) Metallic

  ii) Organic

METALLIC COATINGS

The metals used for coatings may be placed under two categories

i) metals which are anodic to the metal i.e., metals above it in galvanic series.



ii) metals which are cathodic to the metal i.e., metals below it in galvanic series.

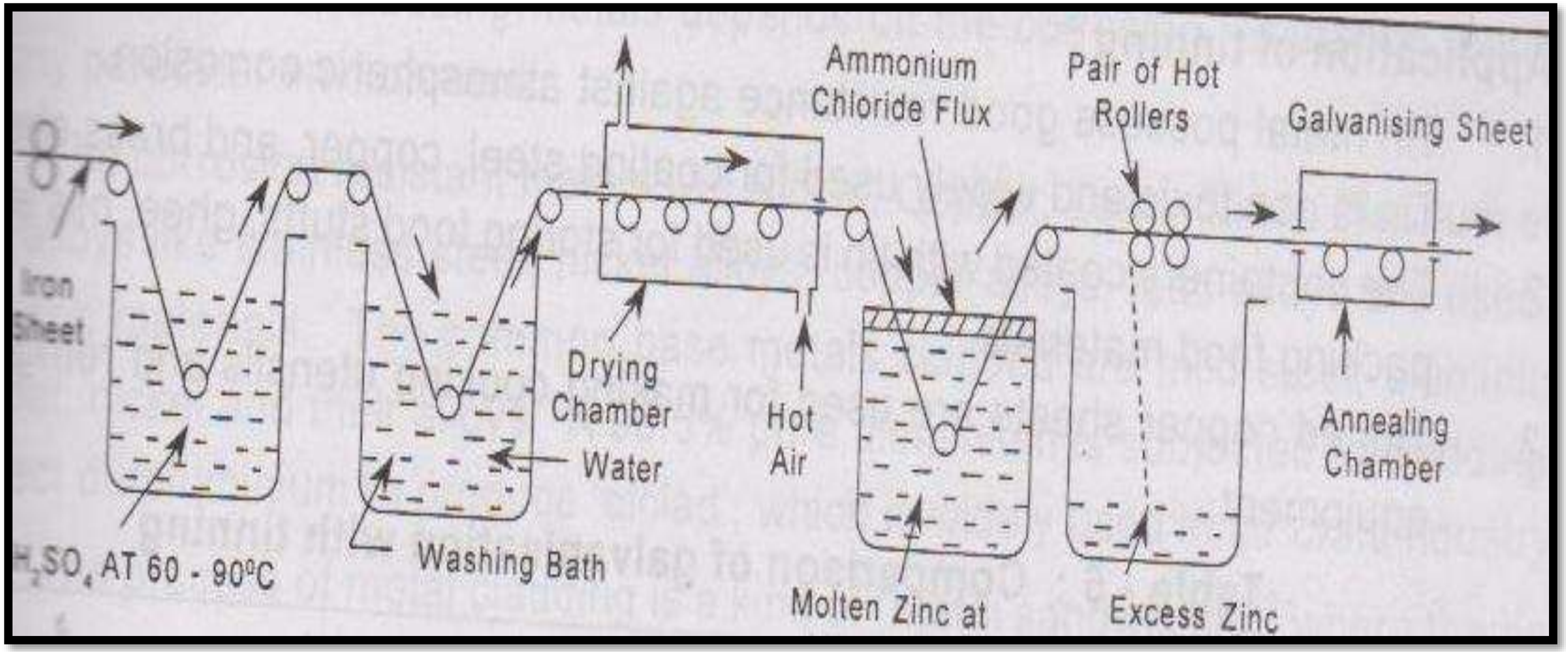
Methods of applications of metal coatings:

- Hot dipping: This technique is most widely used to control corrosion. Hot dipping is used for producing a coating for low melting metals such as Zn, Sn, pb ,Al.
- on Iron, steel, copper which are having high melting point usually underwent into corrosion due to their oxidising property.
- The process in general consisting of immersed a metal in a bath of its molten coating& covered by a molten layer.
- The flux cleans the base metal& prevent oxidation of metal coating with molten solution.
- Hot dipping is widely applied either by (1)GALVANIZING (2)TINNING

Galvanizing

- It is the process in which iron or steel is protected from corrosion by coating with a thin layer of zinc.
- Iron or steel is first cleaned by pickling with dil. H_2SO_4 solution for 15-20 mts at 60^0-90^0c. The steel is then washed well and dried .
- Then the metal sheet is dipped in bath of molten Zinc maintained at 425^0-430^0c.
  The surface of bath is kept covered with a $Zncl_2$ flux to prevent oxide formation.
- Then the metal sheet is passed through a pair of hot rollers which removes excess of Zinc and maintain uniform thickness of Zinc on metal sheet.

- The sheet is subjected to annealing process at 65^0c and cooled slowly.



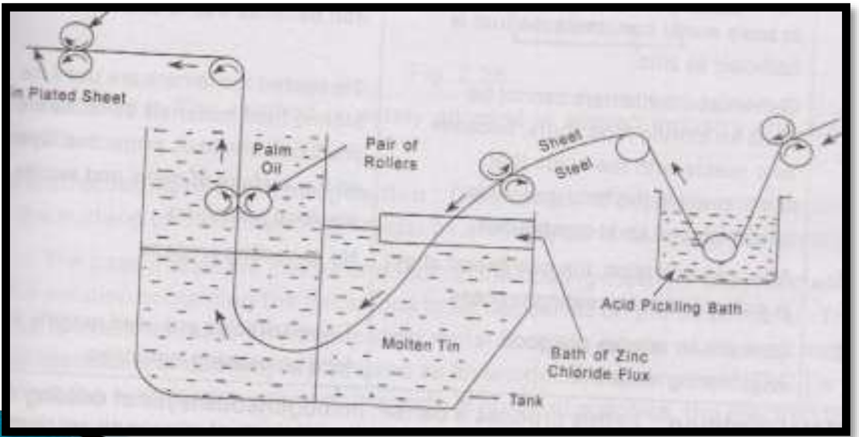
Uses of Galvanization: It is used to protect Iron used for roofing sheets, wires, pipes, nails, bolts, screws, buckets, and tubes.

Defects :Galvanised utensils are not used for cooking because of solubility of Zn.

TINNING

- Tinning is the process of coating of tin over the Iron sheet or steel articles
- A cleaned iron sheet is passed through a bath of molten flux, then passes through a tank of molten tin and finally through a layer of palm oil which protect hot tin coated surface against oxidation.

Uses: (1)It is widely used for coating of steel, copper, brass & bronze etc . It is used to store food stuff, ghee oils, kerosene& pickels and used for refrigerators equipment.



ELECTROPLATING

- Deposition of coating metal on the base metal by passing direct current through an electrolytic solution which contain the soluble salts of the coating material.

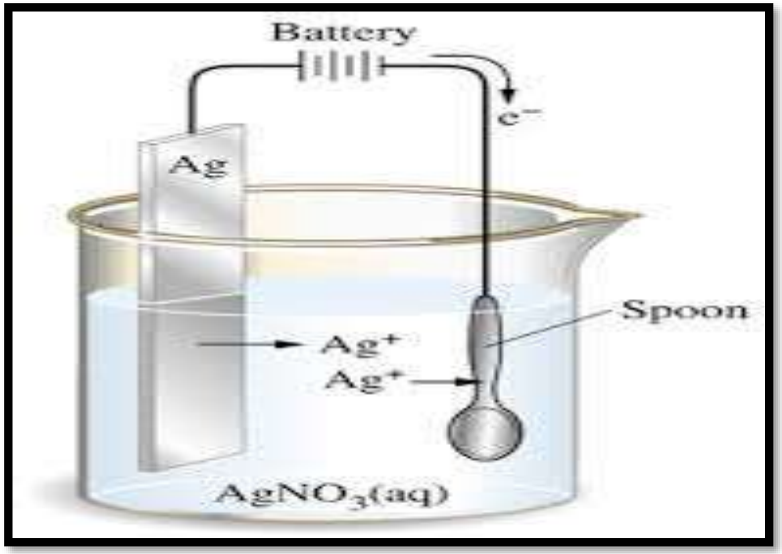
- Pure metal is made as cathode and base metal as anode.
- Electrochemically coat metal is deposited on base metal.
- This metal gives smooth, fine and uniform coating
- It depends on

(i) Temperature

(ii) Current density

(iii) Electrolyte Concentration

(iv) Nature of base metal (v) Time



Applications of Electroplating

- It is most important & frequently used technique in industries to produce metallic coating
- Both metals & non metals can be electroplated.
- In metals the electroplating increases resistance to corrosion, chemical attack, hardness, wear resistance and surface properties.
- In non metals electroplating increases strength and decorates the surface of non metal like plastics, wood, glass.

Electroless Ni plating:

- Pre treatment of surface:
- (1) CO, Ni, steel and Al can be directly plated.
- (2)Pb, Cd and Sn are first electroplated with Ni prior to electroless plating.
- (3)Non conductors are activated in $Sncl_2$ & HCl followed by dipping in $Pdcl_2$,Hcl.on drying thin pd layer is formed.

Organic paints

ORGANIC COATINGS

- Organic coatings protect the surface as they act as physical barriers between the metal to be protected and the corroding environment and are decorative.

- The extent of protection given by the organic coatings depends on

A) Impermeability to gases ,salts and water

B) Chemical inertness to the corrosive environment

C) Good surface adhesion

The Organic & Natural paint co.

PAINTS

- Paints form a protective layer over the surface of the metal to prevent corrosion.

The main constituents of the paints are

- Pigment
- Vehicle
- Thinner
- Driers
- Fillers
- Plasticizers
- Anti skinning agents

Pigment

- It is a solid constituent that obscures the surface and provides a decorative color.
- A liquid binds the pigment to the surface and protects it from decay.
- It usually comprises of 60 to 80% of the weight of the paint film.
- Increases the life of paint film since it prevents the entry of ultra violet rays.
- E.g.; lead oxide, red lead, lead chromate etc.,

Vehicle

- Film forming constituent of the paint.
- They hold the pigment on the metal surface.
- They give metal adhesion to the metal surface.
- They impart durability and toughness to the film.
- They isomerize , polymerize and condense to form characteristic tough, elastic ,coherent, highly cross linked structured macromolecular film.
- E.g.: mustard and sunflower oil etc.,

Thinners

- Viscosity is reduced by the addition of thinners.
- It is a volatile solvent helps to adjust the consistency of the paint.
- Thinner being volatile evaporates.
- They remain permanently in paints and varnishes.
- They improve elasticity of the film.
- They suspend the pigments in the paints.

E.g. Turpentine, mineral spirits, xylol, kerosene.

Fillers

- They are inert materials.
- They are used to improve the properties of the paints.
- They reduce the cost of paints.
- They serve to fill the voids in the film.
- Increases the random arrangement of pigment particles.
- Improves the durability of the film.
- E.g.: talc, chalk, silica etc.,

Driers

- Drying of the oil film is accelerated or catalyzed by driers.
- To reduce the drying time a drier is added.
- They are oxygen carrier catalyst.
- To improve the drying quality of oil film.
- This is done by condensation , oxidation and polymerization.

E.g. linoleates , borates, resinates etc.,

Plasticizers & Anti skinning agents

- They remain permanently in paints and varnishes.
- They improve elasticity of the film.
- To prevent cracking of the film.
- Anti skinning agents prevent the gelling and skinning of the paint film.

E.g.: tricresyl phosphate, tri phenyl phosphate,
di butyl tartarate etc.,


Thank
You

Ceramics

Ceramics are types of hard materials that undergo extreme heating of the materials in order to come up with the desired styles and designs.

Humans have created ceramics that date back in 24,000 BC.

“Ceramic” can be used as an adjective, or as a noun to describe the clay object once it has been fired.

Ceramics are classified as inorganic and nonmetallic materials that are essential to our daily lifestyle.

How Ceramics Are Made?

- Ceramic objects are made by combining naturally occurring raw materials, such as clay, earthen minerals, and water, and shaping them into forms using handbuilding, wheel-throwing, or mold casting techniques. Once shaped, the object is fired in a kiln at a high temperature.
- Firing ceramics make them hardened and heat resistant.
- Ceramic objects can be built by hand using slab, coiling, and pinching techniques. Potters also use wheel throwing to create symmetrical pottery and slip casting to create multiples of one object.

Ceramic Processing

- Ceramic processing is used to produce commercial products that are very diverse in size, shape, detail, complexity, and material composition, structure, and cost.
- Ceramics are typically produced by the application of heat upon processed clays and other natural raw materials to form a rigid product.
- Ceramic products that use naturally occurring rocks and minerals as a starting material must undergo special processing in order to control purity, particle size, particle size distribution, and heterogeneity.
- These attributes play a big role in the final properties of the finished ceramic.

Ceramic Processing

- Chemically prepared powders also are used as starting materials for some ceramic products.
- The next step is to form the ceramic particles into a desired shape. This is accomplished by the addition of water and/or additives such as binders, followed by a shape forming process. Some of the most common forming methods for ceramics include extrusion, slip casting, pressing, tape casting and injection molding. After the particles are formed, these "green" ceramics undergo a heat-treatment (called firing or sintering) to produce a rigid, finished product.
- Some ceramic products such as electrical insulators, dinnerware and tile may then undergo a glazing process.
- Some ceramics for advanced applications may undergo a machining and/or polishing step in order meet specific engineering design criteria.

Ceramic Properties

The properties of ceramic materials, like all materials, are dictated by the types of atoms present, the types of bonding between the atoms, and the way the atoms are packed together. This is known as the atomic scale structure.

Most ceramics are made up of two or more elements. This is called a compound. For example, alumina (Al_2O_3), is a compound made up of aluminum atoms and oxygen atoms.

The atoms in ceramic materials are held together by a chemical bond. The two most common chemical bonds for ceramic materials are covalent and ionic.

For metals, the chemical bond is called the metallic bond. The bonding of atoms together is much stronger in covalent and ionic bonding than in metallic. That is why, generally speaking, metals are ductile and ceramics are brittle.

Ceramic Properties

In general, most ceramics are:

- hard,
- wear-resistant,
- brittle,
- refractory,
- thermal insulators,
- electrical insulators,
- nonmagnetic,
- oxidation resistant,
- prone to thermal shock, and
- chemically stable.

CLASSIFICATION OF CERAMICS

Based on the raw materials and application ceramics can be classified into 2 types:

1) **Traditional ceramics**

- Bricks, pottery, glass, porcelain, tiles, cement, and concrete are our classic, time-tested ceramics.
- Ceramics like this are ancient materials—ones our ancestors would recognize—that have gradually found more and more uses as the centuries have worn on.

1) **Advanced engineering ceramics**

- Advanced ceramics are ones that have been engineered (mostly since the early 20th century) for highly specific applications.
- Most modern engineered ceramics are metal oxides, carbides, and nitrides, which means they're compounds made by combining atoms of a metal with oxygen, carbon, or nitrogen atoms.

Traditional types of ceramic pottery

Clay is one of the widely available raw materials for creating ceramic objects. Different types of clay and combinations of clay with different variations of silica and other minerals result in different types of ceramic pottery.

There are four basic types:

1. Earthenware,
2. Stoneware,
3. Porcelain,
4. Bone china

Earthenware

Earthenware is considered the softest form of pottery, being fired at the lowest heat. It absorbs water, porous as well as scratched easily.

A usual composition of this is 25% ball clay, 32% quartz, 28% kaolin as well as 15% feldspar.

The best examples of fine art earthenware are Chinese clay warriors, also called the Terracotta Army.

To make it waterproof, they wrapped it in a glass-like liquid known as vitreous, and then they are re-fired it in the kiln.

Clay has iron that used for the making of earthenware that provides a shade that ranges from buff to cream, dark red, black, or grey, in accordance to the amount available as well as the oxygen content in the kiln during the process of firing.

This type of pottery can be as thin as porcelain and less tough, strong, but more porous than stoneware. In general, this type of pottery is fired at high temperatures of 1000 to 1200 degree Celsius.

Stoneware

This type of pottery is dense and has a character that resembles stone after being heated; this is why it called stoneware.

This pottery is impermeable or waterproof and normally opaque.

In the natural condition, it is grey; however, it turns brown due to the firing process, and different colors might be then used in the type of glazes.

In general, this type of pottery is fired at high temperatures of 1000 to 1300 degrees Celsius.

This is utilized in the making of commercial ware. On the other hand, it is also preferred by renowned artists in the making of fine art pottery.

Porcelain

The disparity between stoneware and porcelain is vague.

Stoneware varies from porcelain as it opaque and usually just partially vitrified. It is fired at high temperatures.

Ceramists from china define porcelain as a pottery item that provides a ringing tone once tapped. On the other hand, in the west, porcelain is set apart from stoneware by its translucent feature once held to the light.

Porcelain is broken down into various classifications such as:

1. **Hard-paste or also known as true porcelain:** It has added mineral materials to the clay, normally mica. It is fired at high temp and results to tougher and harder objects.
2. **Soft-paste:** This is the least or low type of porcelain. It is regarded as a fragile or low type of porcelain. The best thing about it in spite of being low quality is that it does not require a fixed mineral to be made. Kaolin is combined with bone quartz, ash, soapstone as well as glass to yield this kind, with ball clay added into the mixture. It is also created under high temperatures.

Bone China

This replaces true porcelain in today’s time. It is considered the toughest type of porcelain. It is also very resistant to chip damage. It has remarkable physical strength and normally generates a white and translucent result. It has bone ash, kaolin, phosphates as well as feldspar.

Later, ceramicists tweaked the usual formula by putting in powdered bone ash to create bone china- a typical form of porcelain that is less prone to damage like chipping. It comes with an ivory-white appearance.

Bone china is clear or white. When done firing, they are both white and usually fired at a high temperature of 1200 – 1450 degrees Celsius, which is a bit higher compared to stoneware.

Advanced engineering ceramics

1. Silicon nitrides and tungsten carbides are designed for making exceptionally hard, high-performance cutting tools
2. Tungsten carbide, silicon carbide, and boron nitride, which are hard, cutting-tool ceramics
3. Aluminum oxide (alumina) and silicon dioxide are used in making integrated circuits ("microchips")
4. Lithium-silicon oxide is used to make the heat-protective nose cones on space rockets.
5. High-temperature superconductors are made from crystals of yttrium, barium, copper, and oxygen.
6. Ceramic matrix composite (CMC):
    - Some are composite materials, in which the ceramic forms a kind of background material called the matrix, which is reinforced with fibers of another material (often carbon fibers, or sometimes fibers of a totally different ceramic).
    - Examples include silicon carbide fibers in a silicon carbide matrix (SiC/SiC) with boron nitride at the interface between them—a material used in cutting-edge gas-turbine jet engines.

Types of ceramic materials

Glass Ceramics

- Made by controlling the crystallization, it has properties the same to glass with the ceramics' toughness and strength.
- Properties: zero porosity, mechanical strength, durability, high temperatures, translucency, and biocompatibility.This material is also high chemical durability as well as superconductivity.
- Examples: These types' ceramics are used to make parts in the making of cookware,bakeware, and cooktops. This material is also often applied to scientific and industrial equipment as well as medical devices

Fired Bricks

- Bricks are often made by heating minerals similar to clay, and sand is considered ceramics. This ceramic is common in homes.
- Properties: The properties of this ceramic are extensively different based on their manufacture as well as composition. In general, this ceramic is tough, brittle, heavy as well as can survive higher temperatures.
- Example Used: Some good use of this ceramic include chimneys, fireplaces,as well as walls. They are also often used in landscaping.

Types of ceramic materials

Silicon

Silicon is also a popular type of ceramics and is often considered superior because of its chemical properties. This Ceramic is very abundant as they make up about 90% of the Earth’s crust. Sand And clays, which are used to make common ceramics, are often based on silicon abide. Like for instance, the silica ceramic is used to create fired bricks,and the kaolinite material is used in making porcelains are silicate materials.

Properties of these types of Ceramics: This material has a brittle and hard crystalline solid as well as a semiconductor.

Example of Uses: Extreme purity crystalline silicon like polycrystalline silicon is used in the making of solar panels, and semiconductor devices such as integrated circuits. High quality silicon minerals are used to create ceramics, glass and are used as an aggregate in cement. They are considered the most common raw materials utilized in the field of construction.

Silicon Carbide

Other types of ceramics are Silicon carbide, which is a high quality semiconductor material that has carbon and silicon that naturally occurs as the extremely rare mineral moissanite.

Properties: These types of ceramics are tough and extremely hard ceramic, as well as a semiconductor, which takes place in approximately 250 forms of crystalline. This ceramic is naturally colorless but frequently colored by impurities like iron. This shows low thermal development.

Example of Uses: This ceramic usually use in cutting tools, furnaces,brake disks, abrasives, heating elements as well as lighting, electrical power systems. The natural type of silicon carbide is prized as a jewel because it has the same appearance and hardness to diamonds. It is an artificial substitute that is harder compared to zirconia.

Types of ceramic materials

Titanium Carbide

This is a heat resistance and extremely hard types of ceramic which has a black color.

Properties: The types of ceramics are heat resistance, extremely hard, as well as corrosion and wear-resistant.

Example of Applications: These ceramics usually utilizes in tool bits, machine parts, heat shields as well as watch mechanisms

Tungsten Carbide

This is a material manufactured with the same parts of carbon and tungsten, which is hard and dense.

Properties: These types of ceramics are dense, hard, tough, andstrong with low electrical resistivity.

Example of Applications: Industrial equipment, cutting tools as well as sports equipment.

Engineering Material

Plastics/ Plastic Material

Definition: Organic materials which can be moulded into any desired form, when subjected to heat and pressure in presence of a catalyst.

Terms resin and plastics are now-a-day considered synonyms. However, both are different.

Resins: are the basic binding material which form a major part of th plastics and which has undergone polymerisation reaction during preparation.

Unique properties of plastics

- Lightness in weight
- Good thermal and electrical insulation
- Corrosion resistance
- Easy workability
- Adhesiveness
- Low fabrication cost
- Decorative surface effect
- Easy moulding
- Insect resistant
- Capable to being made to order
- Absorbent of vibrations and sound

- Low thermal expansion coefficient
- Chemical inertness
- Transparency
- Low maintenance cost
- Low softening points
- Ability to take variety of colours, shades, etc.
- Good shock absorption capacity
- High resistance to abrasion
- Impermeable to water
- Good strength and toughness
- Excellent in finish

Uses of Plastics

- Making electrical goods and appliances
- Aeronautical engineering
- Making furniture
- Making floor and wall linings
- Making special types of paints
- Heat and sound insulation
- Making windscreens, laminated glasses, table tops
- Preparing decorative laminates and mouldings

- Making overhead tanks, water pipes
- Making household articles
- Making synthetic fibres
- Making adhesives
- As water softening agents
- Making films for waterproofing, damp proofing and curing of concrete

Preparation of plastics

Prepared using- Polymerisation reaction it is of 2 types:

1. Addition Polymerisation: involves repeated addition of monomers to yield long chains of polymer.
2. Condensation Polymerisation: involves condensation/combination of 2 monomers resulting in loss of small molecules like H_2O, HCl, NH_3 etc. to yield a polymer.

Compounding/ Moulding Constituents of a Plastic

- The finished polymer article doesn’t solely consists of polymeric material alone
- It is usually a mixed with 4-10 ingredients each of which imparts a useful property to the finished artifact. This is called a mix.

Compounding: it means mixing the ingredients in specific proportion to the virgin resin as per the requirement.

Mixing: it means bringing into contact 2 or more components and subjecting them to forces so as to make them distribute uniformly throughout the total volume to make the mass homogenous.

Compounding Ingredients

- Resin
- PLasticizers
- Fillers
- Lubricants
- Catalysts/Accelerators
- Stabilizers
- Colouring agents

Compounding Ingredients

Resins:

Function: binder- holds different constituents together.

Example: thermosetting resins, supplied as linear low molecular weight polymers because at this stage they are mould able and convert into cross linked structures during moulding.

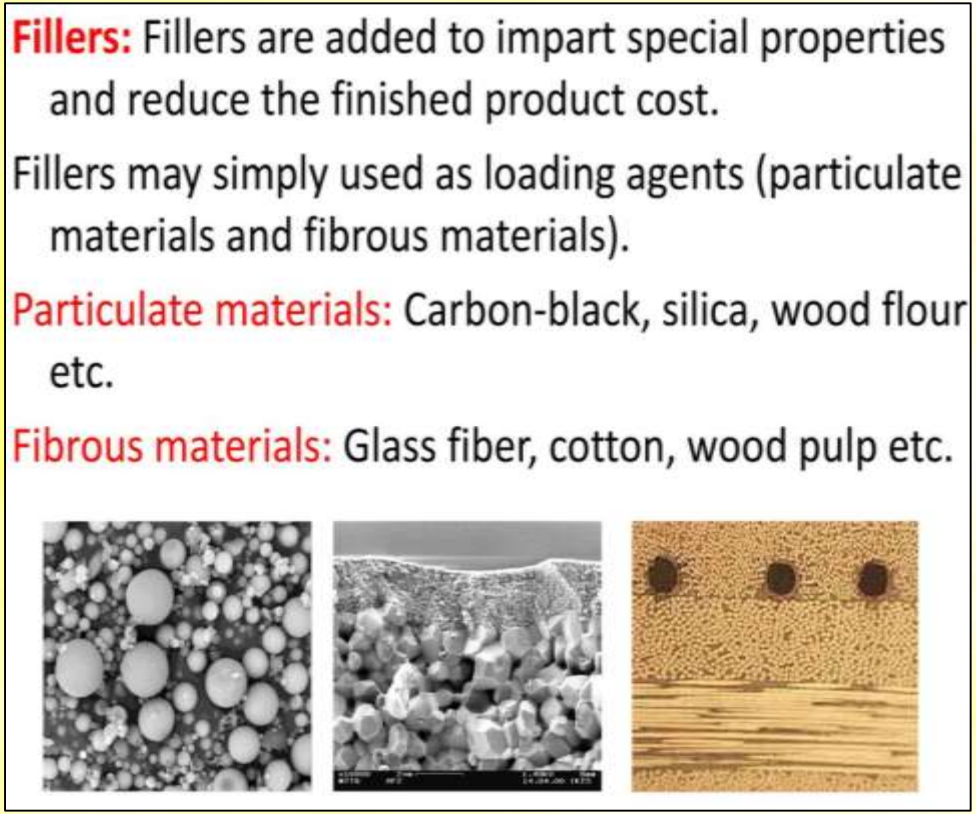
Plasticizers:

Function: Increase plasticity and flexibility by neutralising the intermolecular forces of attraction between polymeric molecules thereby imparting greater freedom of movement movement

Disadvantage: reduce strength and chemical resistance

Example: vegetable oils (non-drying), camphor, esters of stearic and phthalic acid, phosphates of tricresyl, tributyl triphenyl.

Compounding Ingredients- Fillers



Fillers: Fillers are added to impart special properties and reduce the finished product cost.

Fillers may simply used as loading agents (particulate materials and fibrous materials).

Particulate materials: Carbon-black, silica, wood flour etc.

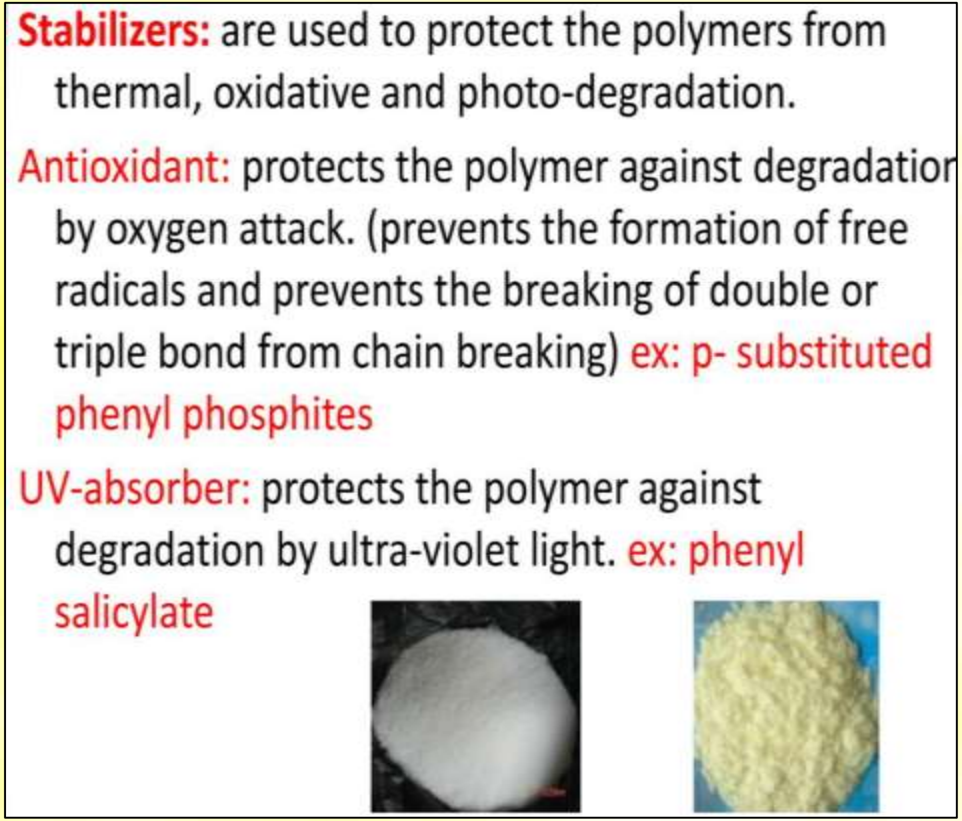
Fibrous materials: Glass fiber, cotton, wood pulp etc.

Examples: Special properties

- Extra hardness: Carborundum, Quartz, mica
- Impervious to x-rays: Barium salts
- Heat and corrosion resistance: asbestos
- Mechanical strength: reinforcing fillers (carbon black to natural rubber imparts tensile strength and abrasion resistance)

The percentage of fillers varies and can be up to 50% of the total moulding mixture

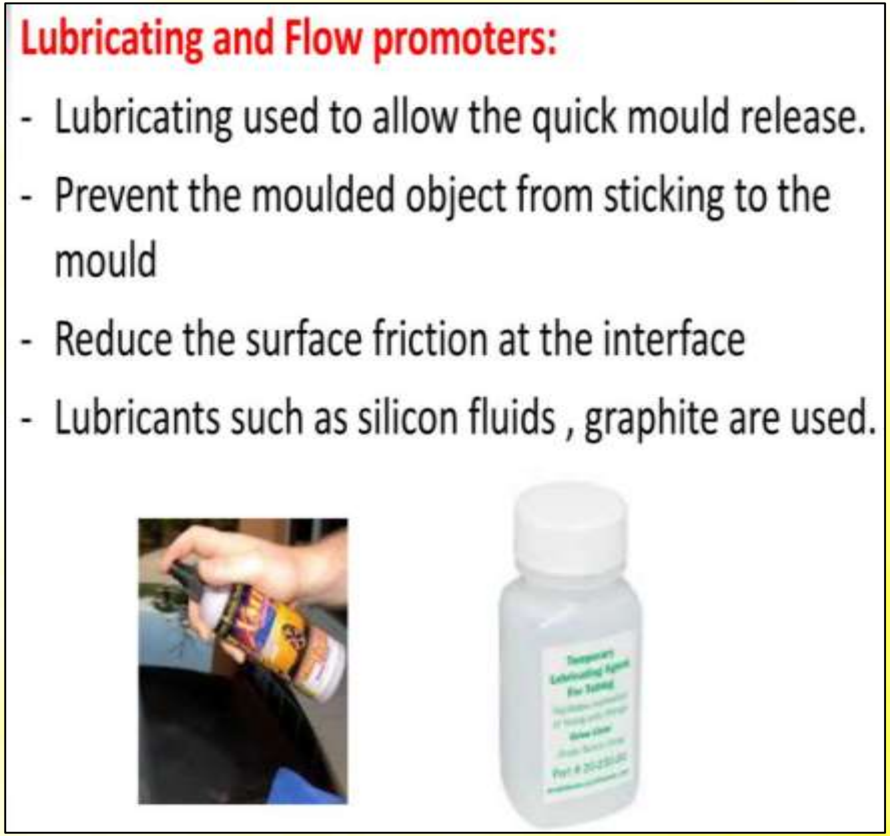
Compounding Ingredients



Stabilizers: are used to protect the polymers from thermal, oxidative and photo-degradation.

Antioxidant: protects the polymer against degradation by oxygen attack. (prevents the formation of free radicals and prevents the breaking of double or triple bond from chain breaking) ex: p- substituted phenyl phosphites

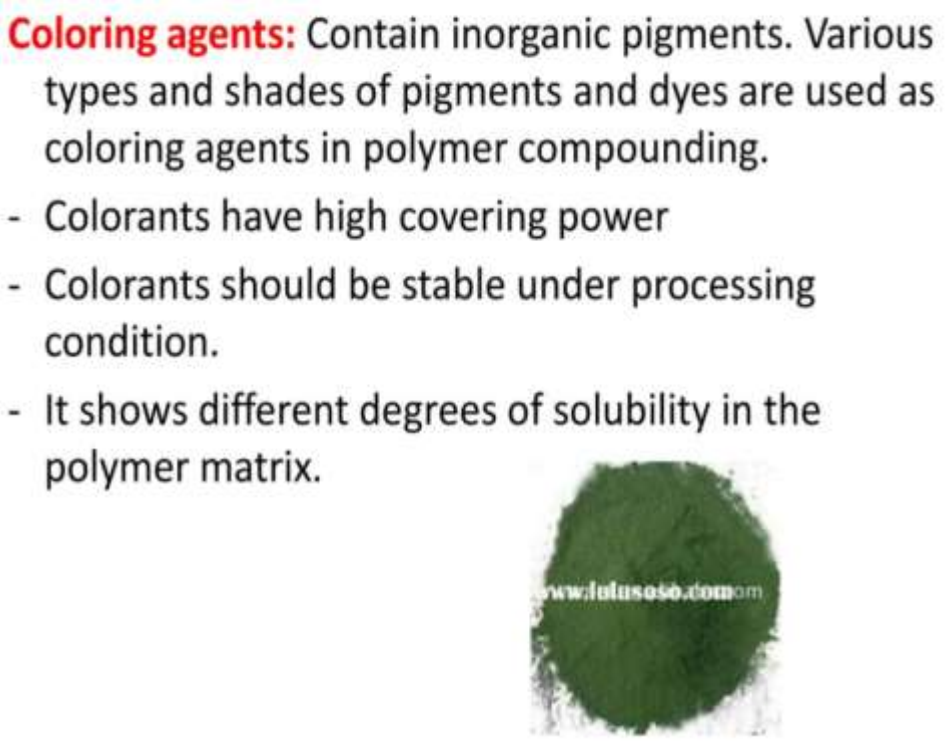
UV-absorber: protects the polymer against degradation by ultra-violet light. ex: phenyl salicylate



Lubricating and Flow promoters:

- Lubricating used to allow the quick mould release.
- Prevent the moulded object from sticking to the mould
- Reduce the surface friction at the interface
- Lubricants such as silicon fluids , graphite are used.

Compounding Ingredients



Coloring agents: Contain inorganic pigments. Various types and shades of pigments and dyes are used as coloring agents in polymer compounding.

- Colorants have high covering power
- Colorants should be stable under processing condition.
- It shows different degrees of solubility in the polymer matrix.

POLY VINYL CHLORIDE (PVC)

Properties of PVC:

- Colourless
- Odourless
- Chemically inert,
- resistant to light, atmospheric oxygen,
- Acids and alkalis
- Pure resin possesses high softening point(148 ^oC)
- Greater stiffness, high rigidity
- It is brittle

Engineering applications of PVC

Unplasticized PVC

Used for making sheets employed for

- tank-linings
- light fittings
- safety helmets
- refrigerated components
- tyres
- cycle and motorcycle mudguards

Plasticized PVC(adding plasticizers)

Used for making sheets employed

- Rain coats
- Table cloths
- Curtains
- Covering of electrical cables
- Toys, tool handles, toiled good
- Plastic coated cloth
- Thermal insulating foam

TEFLON (Poly Tetra Fluoro Ethane)

Properties of Teflon:

- Extreme tough
- High softening point(350 ºC)
- High chemical resistance to chemicals(except hot alkali metal and hot fluorine)
- Waxy touch, very low coefficient of friction
- Good electrical & mechanical properties
- It can be machined, punched & drilled

Engineering Applications of Teflon

Used for:

- Insulating material(motors, transformers,cables, wires, fittings etc)
- For making gaskets, packings, pump parts, tank linings, chemical carrying pipes, tanks, tubings
- For coating & impregnating glass fibres, cloths
- In non lubricating bearings
- Non sticking stopcocks for burettes

BAKELITE

Properties of Bakelite:

- ➢ Hard
- ➢ Rigid
- ➢ Scratch resistant
- ➢ Infusible
- ➢ Water resistant
- ➢ Resistant to acids, salts, organic solvents
- ➢ Attacked by alkalis
- ➢ Excellent electrical insulator

Engineering Applications of Bakelite

Used for making

Electrical insulator parts like

- Switches
- Plugs
- Switch boards
- Heater Handles

Moulded articles like

- Telephone parts
- Cabinets for radio and television

Also used in:

- Paints and varnishes
- As adhesives(binder) for grinding wheels
- As ion-exchange resins in water softening
- For making bearings, used in propeller shafts for paper industry and rolling mills

FIBRES

- **Fibres are thread like structures that are thin, long and flexible strands**

- **There are two types of fibres:**

1) **Natural fibre- obtained from natural sources**
   Examples- Silk, cotton,wool, jute etc

2) **Synthetic fibre- Which are man made**
   Examples- Rayon, Nylon, acrylic etc

Properties of Nylon Fibres

- Translucent
- Whitish, horn
- High melting point(160-264 ºC)
- High tensile strength
- High temperature stability
- High abrasion resistance
- Insoluble in organic solvents
- Soluble in phenol and formic acid
- Have good strength

- Light, high melting
- Absorb little moisture(drip-dry in nature)
- Very flexible
- Regain original shape after use
- Resistant to abrasion
- On blending with wool, the strength & abrasion resistance increases
- Good physical strength and self lubricating properties

Engineering applications of Nylon

Used as:

- ➢ Thread in bristles for toothbrushes
- ➢ As gears, fittings & bearings, automotive industry
- ➢ Threads, ropes, filaments, nets
- ➢ Gun frames
- ➢ Surgical sutures
- ➢ Strings for musical instruments
- ➢ In hosiery and knitted garments
- ➢ Used to make ropes for rock climbing & parachutes

Fibre-reinforced plastic(FRP)

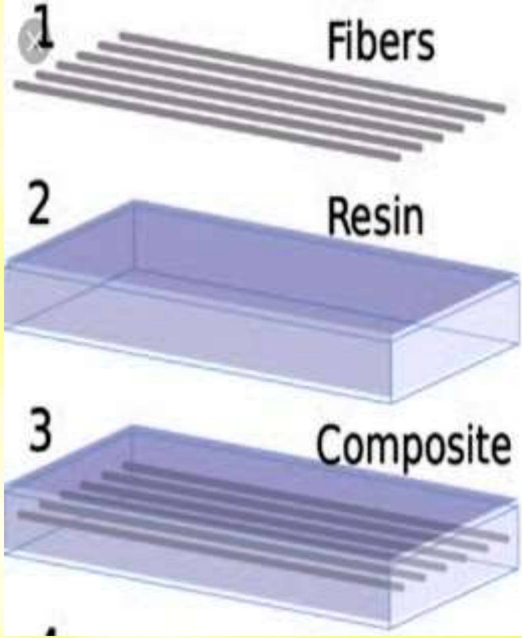
It is a composite material made of a polymer matrix reinforced with fibres

Fibres- They provide strength & stiffness.

- Common fibres used are glass, carbon, aramid, basalt
- Other fibres are paper, wood, asbestos

Matrix- Protects & transfers load between fibres & also supports them under compression loading.

- Common matrices are epoxy, vinyl ester, polyester, Polylactide etc.
- The original plastic without fibre reinforcement is known as matrix or binding agent



Properties of FRPs

- Light weight
- Corrosion resistance
- High tensile strength
- Non magnetic properties
- Specific stiffness
- High specific strength
- Easily constructed
- Ease of handling
- UV radiation stability
- Resistant to chemicals

Examples of FRPs

- GFRP (Glass Fiber Reinforced Polymer)
- CFRP (Carbon Fiber Reinforced Polymer)
- AFRP (Aramid Fiber Reinforced Polymer)

Glass Fibre Reinforced Plastic (GFRP):

- Commonly known as fiberglass
- Is synthetic material made by plastic (forms matrix) & extremely fine fibres of a glass.
  - Fibre: Glass fibre (E- glass, S- glass, R-glass)
  - Matrix: poly ester, epoxy, vinyl ester, poly styrene, polycarbonate etc.
- Glass fibres are made by mixing sand, limestone, folic acid and the mixture is heated about 1260 ^{o}C

Glass Fibre Reinforced Plastic (GFRP):

Advantages:

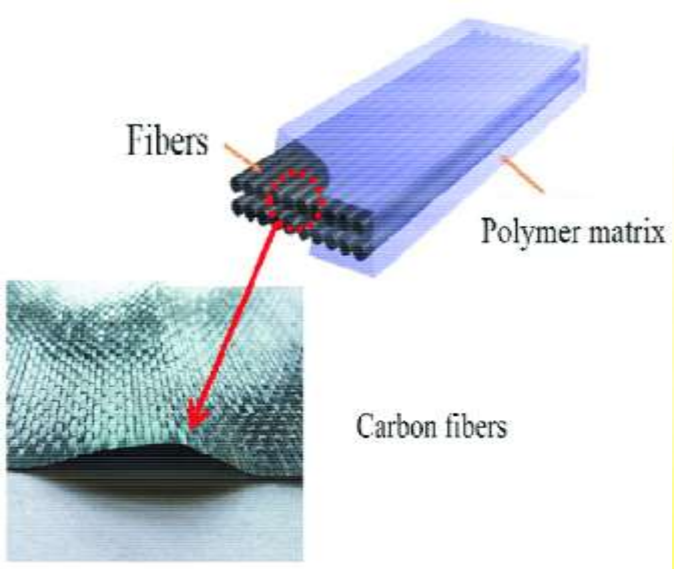
- High tensile strength
- light weight, strong, less brittle
- Heat resistant, weather resistant, insect resistant
- Corrosion resistant, chemical resistant (except HF, H_3PO_4)
- Dimensional stability: will not stretch or shrink
- Low moisture absorption
- Good electrical insulator
- Easy processing: ability to get molded into various complex shapes
- Incombustibility: doesn't support flame or emit smoke or toxic waste when exposed to heat

Applications:

- Manufacturing of automotive bodies: due to its lightweight
- Roofs, domes, pipes
- Boats
- Aquariums, fountains, waterslides, hot tubs, bath tubs, Surf boards, Gliders : due to anti-slip property
- Pump castings
- Storage containers
- for electromagnetic windows
- Screening for cooling towers
- Making aviation equipment and ducts (engine cowlings, bulkheads, storage bins and ground handling equipment)


APPLICATION
SURF BOARD
COMPOUND MATERIAL
WELDING
HEAT PRESERVATION

Carbon Fiber Reinforced Polymer



- CFRP the reinforcement material is carbon fibre
- Carbon fibre: is a long thin strand of carbon atoms which are bonded together in microscopic crystals that are woven together into a fabric
- Carbon fibers are microscopically small and about eight times thinner than a human hair.
- Carbon fibre can be combined with matrix to make almost any shape.
- Matrix: polymer resin such as epoxy, polyester, vinyl ester, nylon
- CFRP is five times lighter than steel and has only about 60% of the weight of aluminium.
- Thus CFRP’s replaces steel and aluminium in a variety of industries.

Carbon Fiber Reinforced Polymers

Properties:

- ➢ Extremely strong
- ➢ Light weight
- ➢ High tensile strength
- ➢ High chemical inertness
- ➢ Good corrosion resistance
- ➢ Low thermal expansion
- ➢ X- ray transparency
- ➢ Low density
- ➢ Vibration resistance
- ➢ Low thermal conductivity
- ➢ Good rigidity
- ➢ Non magnetic
- ➢ Bad conductor of electricity

Applications:

Used in manufacturing of

Automotive field:

- ➢Racing car bodies
- ➢Vehicle parts such as body components

Marine field: Boats, submarines, yacht

Spacecraft & aerospace :

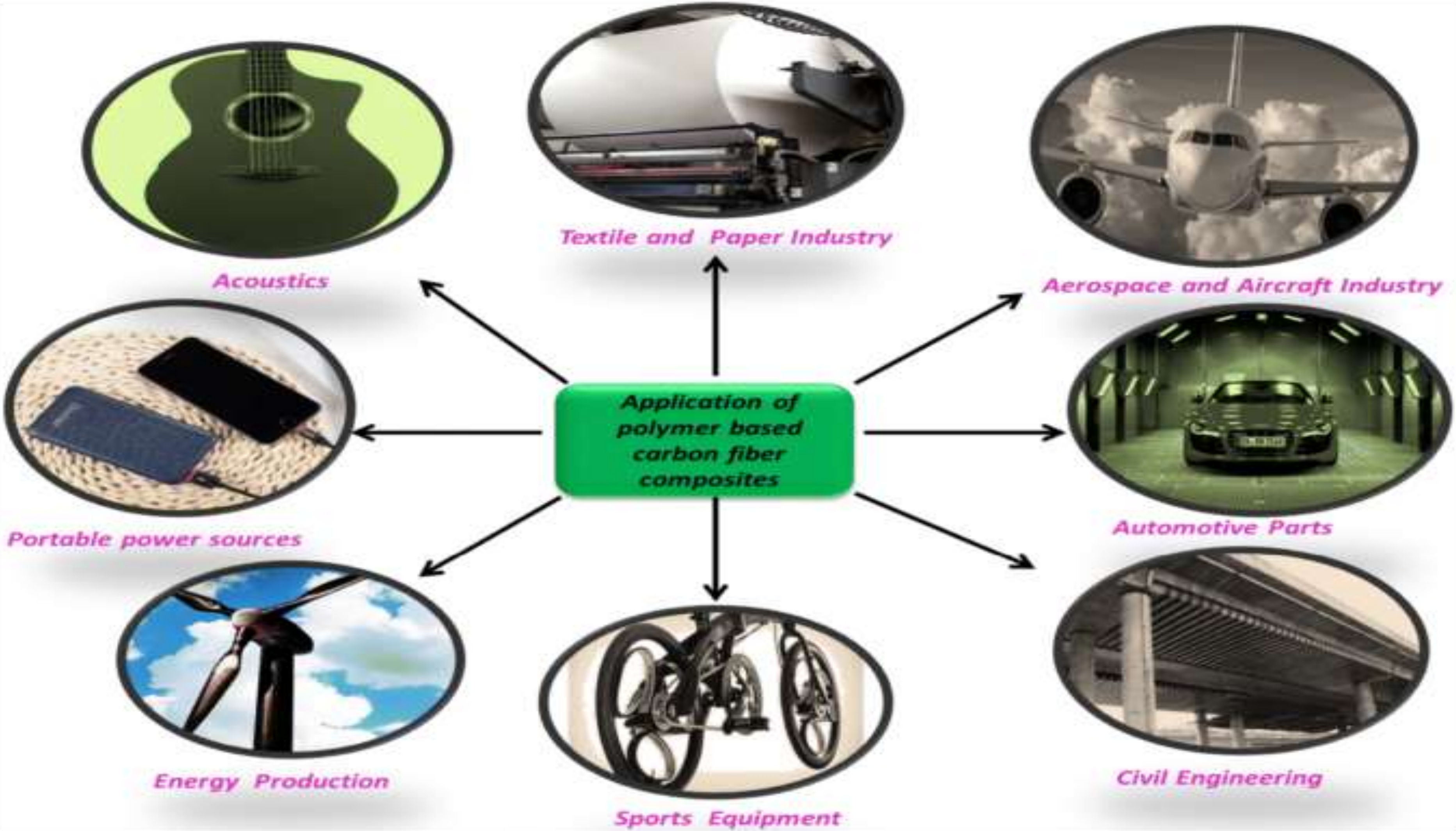
- ➢Main body of the plane, parts of the wings & tail parts

Sports goods:

- ➢Golf club shafts
- ➢Tennis racquets

Others:

- ➢Fishing rods
- ➢Bicycle frames
- ➢Racing car bodies
- ➢Robotic arms



Application of polymer based carbon fiber composites

Textile and Paper Industry

Acoustics

Aerospace and Aircraft Industry

Portable power sources

Automotive Parts

Energy Production

Sports Equipment

Civil Engineering

Aramid fibres

In AFRP the reinforcement material is aramid fibre

Aramid fibres are high strength fibres which are made by aromatic polyamide

Matrix: epoxy, polyester, vinyl ester

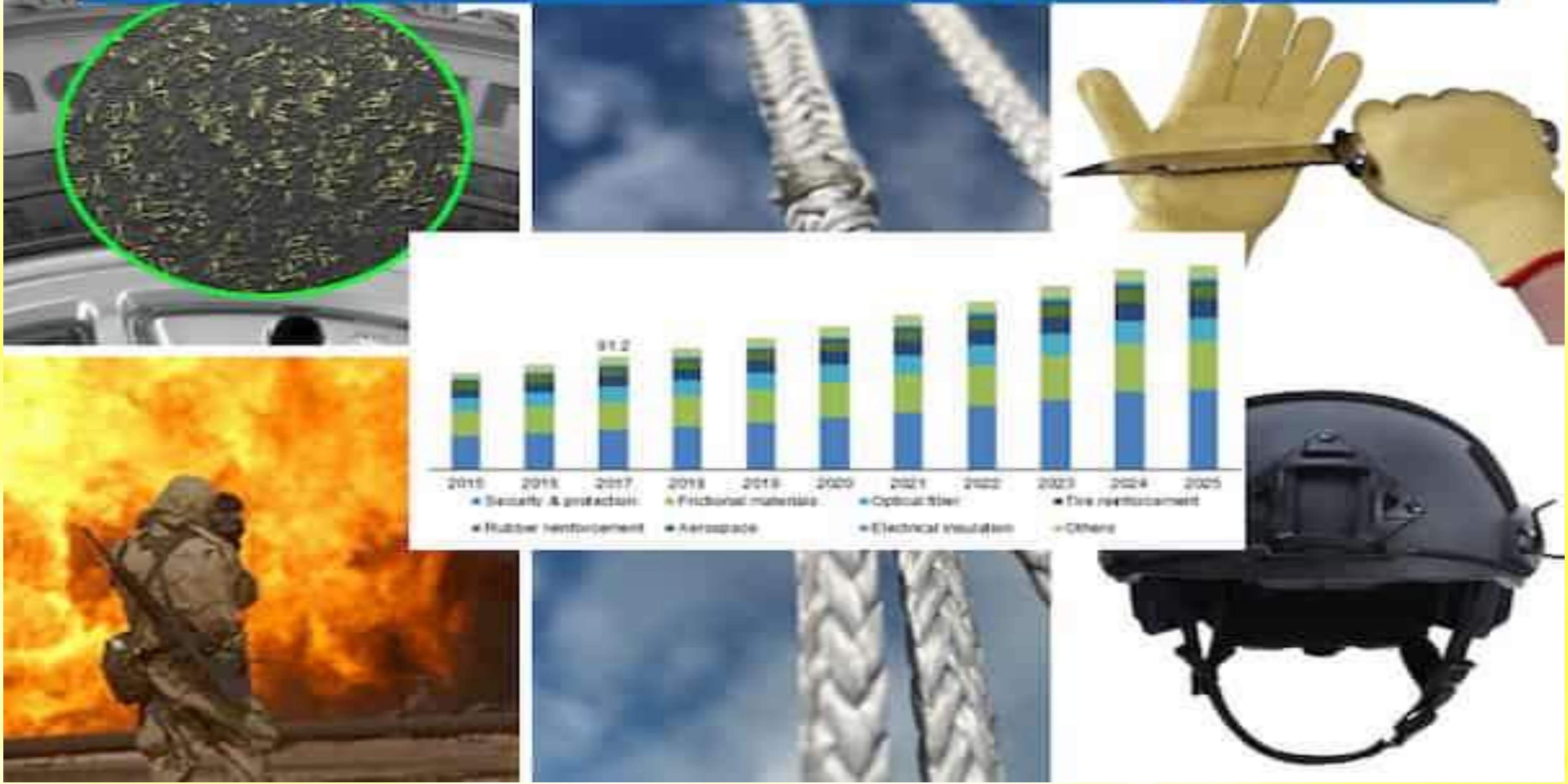
Properties:

- High tensile strength
- Flame resistance
- High chemical resistance
- High compression strength
- High elasticity
- High abrasion resistance
- Low weight

Applications:

- Bullet proof vests
- Fire protection cloths
- Protective gloves, helmets, body armor
- Sports goods
- Aircraft & military vehicles
- Ropes and cables

Aramid- The Ideal Shield for Defence Applications



BULLET / STAB PROOF VESTS

DIVING GLOVES

WALKING BOOTS

MILITARY HELMET

CUT RESISTANT GLOVES

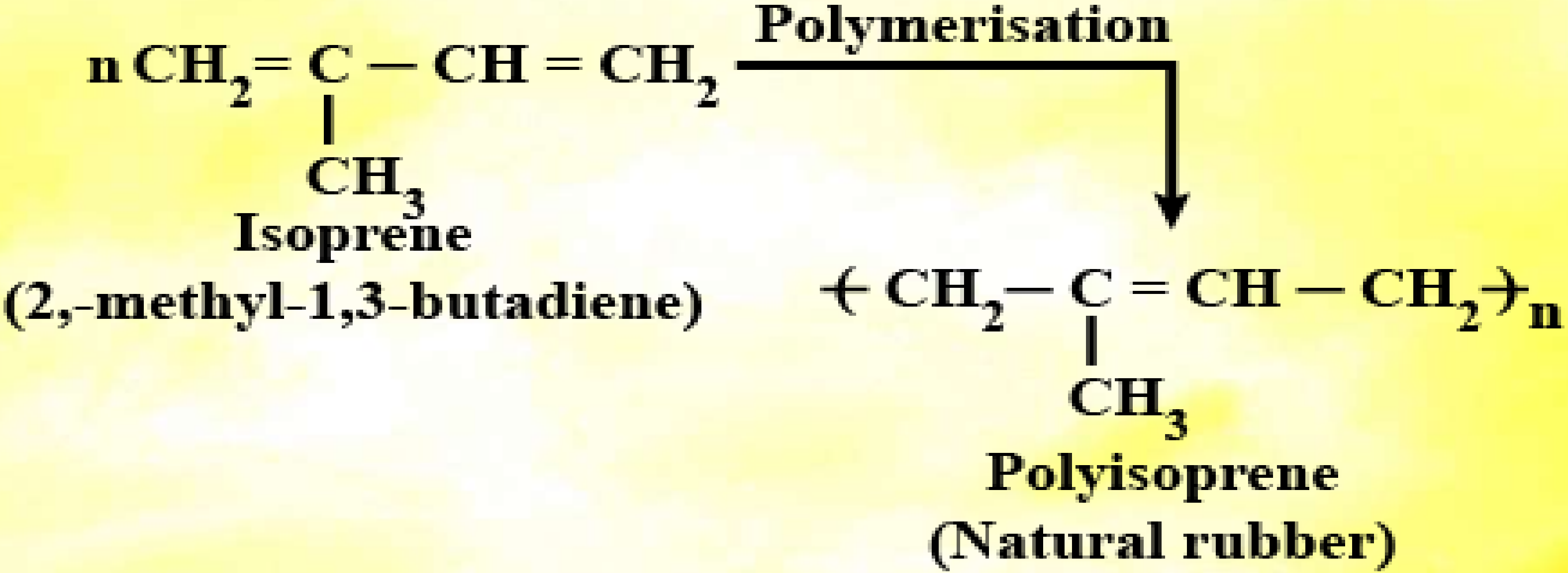
BICYCLE TYRES

CAR TYRES

FIRE PROOF CLOTHING

Natural Rubber

Natural rubber is a natural polymer of organic compound isoprene obtained from the bark of the rubber trees.



$$n\,CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH{=}CH_2 \xrightarrow{\text{Polymerisation}} \left(CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_2 \right)_n$$

Preparation of natural rubber

- Natural rubber is made up of a solid particles suspended in a milky white liquid called latex obtained from the cuts of the bark of a rubber tree.
- Latex is diluted and filtered to eliminate any dirt present in it.
- Acetic acid or formic acid is added to coagulate rubber into a white mass
- The coagulated white mass is washed
- It is allowed to pass through rollers to make it soft and flexible

Properties of natural rubber:

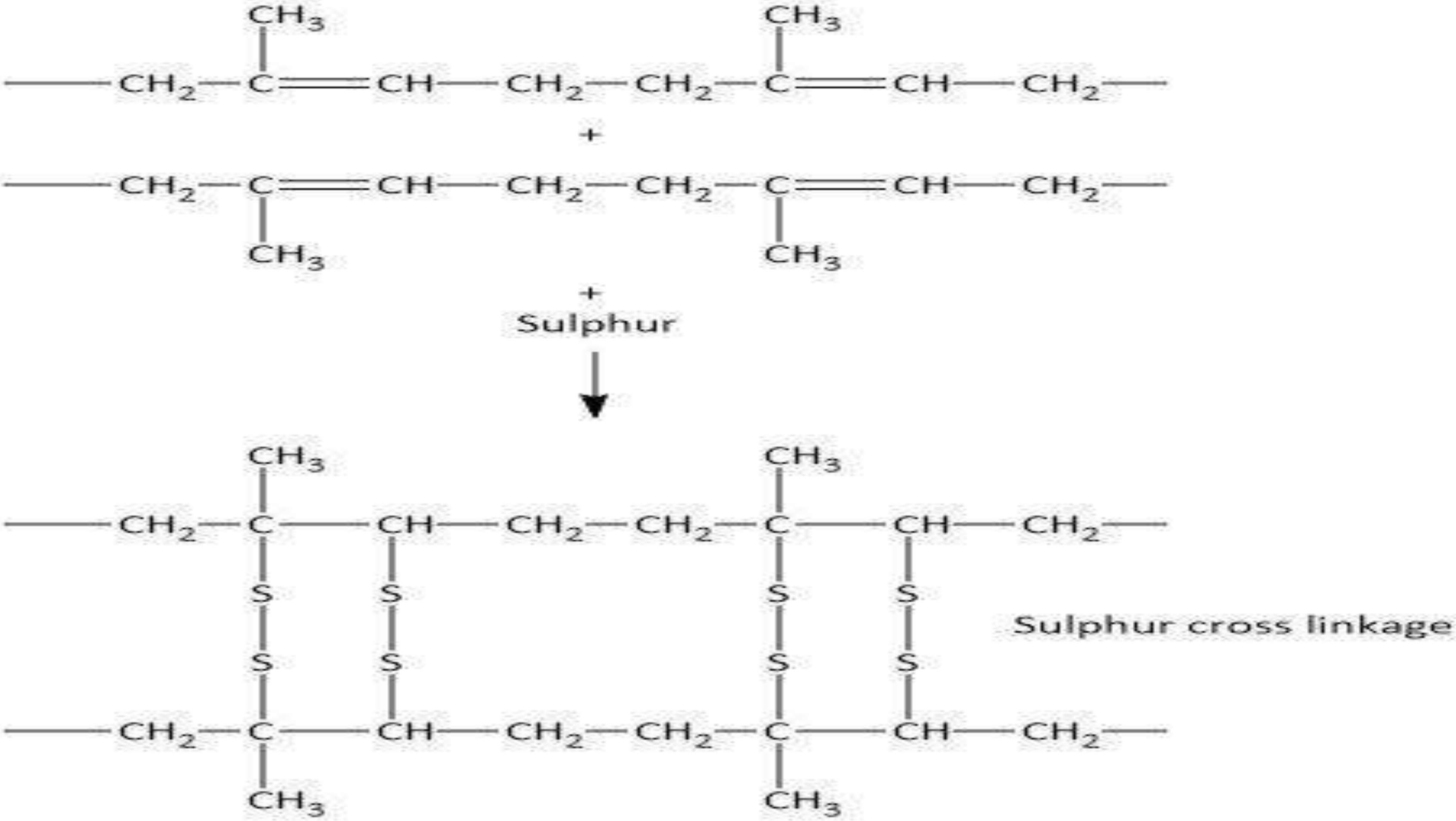
- Soft & sticky
- Flexible
- Low tensile strength
- High elasticity
- Sensitive to heat, light
- Water resistant
- Chemical resistant
- Less resistance to oil, non polar solvents, fats, greases

Vulcanisation of Natural rubber

- Natural rubber is too soft and cannot be used in most of the applications.

  To improve the properties of rubber :

- Natural rubber is heated with sulphur to 140 C
- Sulphur atoms react with the double bonds in the rubber molecule chain to form C-S-S-C cross link between rubber molecules


+
Sulphur
Sulphur cross linkage

Advantages of Vulcanised rubber

- High tensile strength
- Excellent resilience
- Low water absorption
- High resistance to oxidation
- High resistance to abrasion
- High resistance to wear and tear
- Better electrical insulator
- Resistant to organic solvents
- Low elasticity

Applications of vulcanised rubber

- Rubber hoses
- Shoe soles
- Toys
- Erasers
- Tires
- Insulating materials
- Rubber lined tanks
- Conveyor belts
- Suction cups
- Rubber seals
- Hockey pucks

Elastomers

Elastomer is a rubbery material composed of long chain molecules that possess the ability to return to its original shape after being stretched.

The molecules of elastomers held together by weak intermolecular forces.

Elastomers have viscosity as well as elasticity therefore they are known as viscoelasticity.

Following are the examples of the elastomers

- ➢ Natural rubber: They are used in automotive industry and in the manufacture of medical tubes, balloons, adhesives etc
- ➢ Polyurethanes: They are used in the textile industry for manufacturing elastic clothing like lycra.
- ➢ Styrene-butadiene rubber(Buna-S): Used as an adhesive, in footwear industry, in electrical insulation.
- ➢ Neoprene: These are used in manufacture of wet suits and in industrial belts.
- ➢ Silicone rubber: They are used in automotive, electrical, medical, cookware etc

Applications of elastomers

- **Motor vehicles**: Elastomers doesn’t melt easily and offers excellent wear resistance making it efficient in building seals, tyres, interior & exterior parts, engine components.
- **Consumer products**: Elastomers has widest range of products starting from shoe soles to baby pacifiers and many more.
- **Construction**: They are used as adhesives and sealants especially for filling the gaps
- **Industrial products**: Elastomers are hugely used in making industrial tools, appliances, belts, molds, lubricants, etc.
- **Wire & cables**: Elastomers provide good insulation, high resistance to heat & easily reshaped therefore they are used to build wires, telecommunication cables.

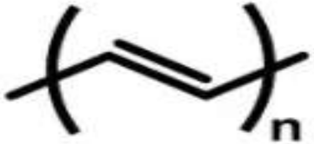
Conducting polymers

Polymers which conduct electricity are called conducting polymers.

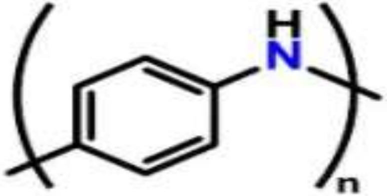
Reason of conduction in the polymer:

- Presence of unsaturated conjugated double bonds in the polymer
- Addition or removal of electrons (doping) into the polymer

Example of Conducting Polymers

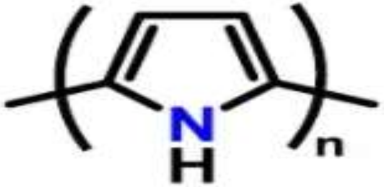


Polyacetylene
(PA)

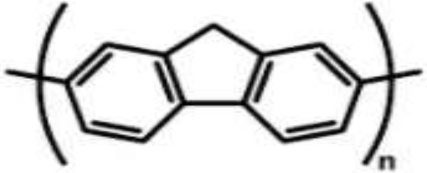


Polyaniline
(PANI)

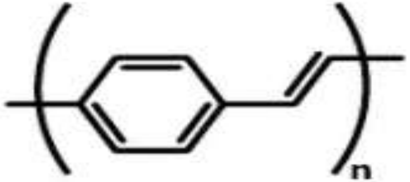
Polythiophene
(PT)



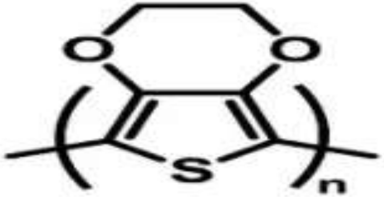
Polypyrrole
(PPy)



Polyfluorenes
(PF)

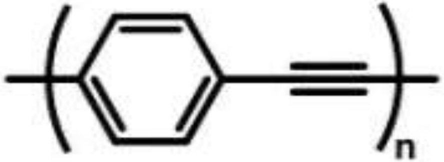


Poly(ρ-phenylene vinylene)
(PPV)



Poly(3,4-ethylenedioxythiophene)
(PEDOT)

Poly(ρ-phenylene)
(PPP)

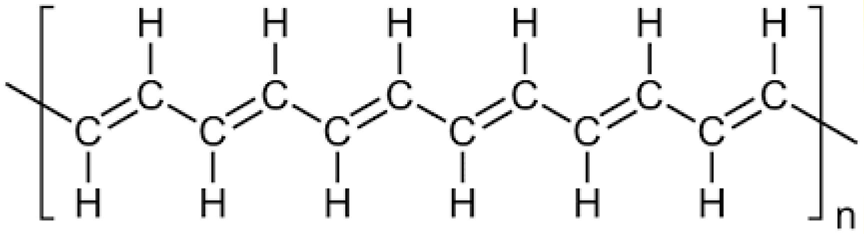


Poly(ρ-phenylene ethynylene)
(PPE)

How can a polymer become conducting?

For a polymer to become electrically conductive, it has to imitate a metal, that is, its electrons need to be free to move and not bound to the atoms.

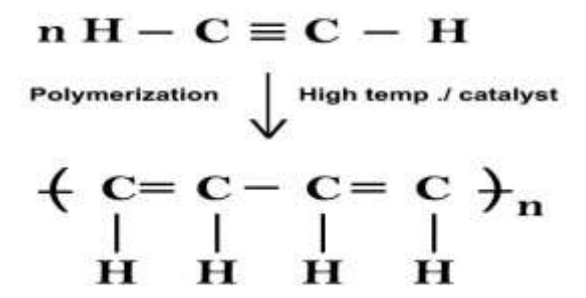
Polyacetylene is the simplest possible conjugated polymer. It is obtained by polymerisation of acetylene. The polymer consists of alternating single and double bonds, called conjugated double bonds.



(In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localised "sigma" (σ) bond which forms a strong chemical bond. In addition, every double bond also contains a less strongly localised "pi" (π) bond which is weaker)

Mechanism of conduction in polyacetylene

Preparation of polyacetylene: Polyacetylene is prepared by passing acetylene gas over Ziegler-Natta catalyst to get polyacetylene.



$$n\,H-C\equiv C-H \xrightarrow[\text{Polymerization}]{\text{High temp ./ catalyst}} \left(\underset{\displaystyle H}{\underset{|}{C}}= \underset{\displaystyle H}{\underset{|}{C}}- \underset{\displaystyle H}{\underset{|}{C}}= \underset{\displaystyle H}{\underset{|}{C}} \right)_n$$

The conductance can be improved by either p-doping or n-doping

Types of doping

p- doping:

- Lewis acids or halogens are added to the polymers having conjugated double bonds
- Oxidation takes place
- Creates positively charged sites on polymer backbone, which are current carriers for conduction.
- Examples for p-dopants:

I_2, Br_2, $AlCl_3$, AsF_5, etc.

n-doping :

- Lewis bases or alkali metals are added to the polymers having conjugated double bonds
- Reduction takes place
- Creates negative charged sites on polymer backbone, which are responsible for the conduction
- Examples for n-dopants:

Li, Na, K, tetrabutyl ammonium, etc.

p-doping

It involves two steps

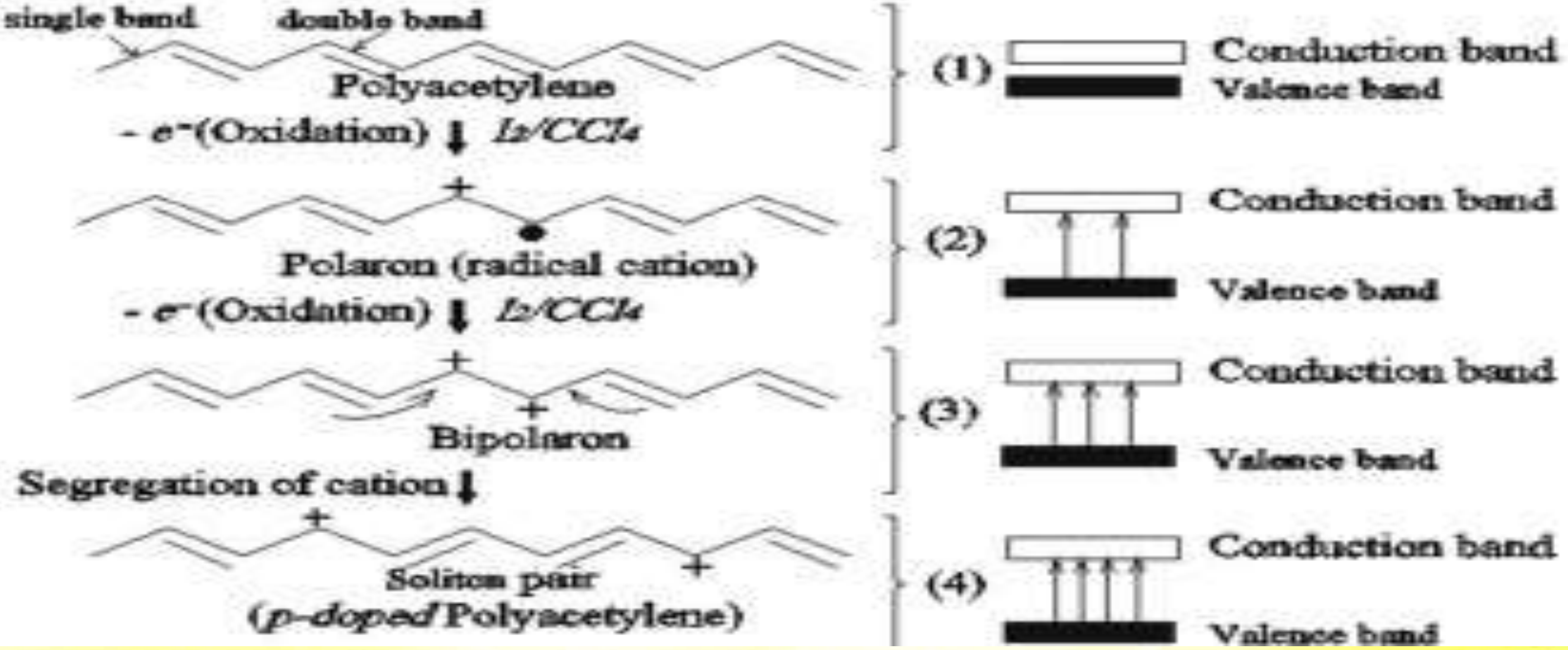
Step I: It involves the oxidation of a polyacetylene with iodine vapour(Lewis acid)

During oxidation the iodine molecule remove an electron from polyacetylene chain creates positive charge called polaron.

Step II: The second oxidation of polaron produces two positive charges on the chain called bipolaron.

This positive charges are mobile due to delocalisation and responsible for conduction.

$$\underbrace{\underbrace{(\mathrm{CH})_x}_{\text{Polyacetylene}} + \underbrace{\mathrm{A}}_{\text{Lewis acid}} \rightleftharpoons \underbrace{(\mathrm{CH})_x^{+}\ \mathrm{A}^{-}}_{\text{p-doped polyacetylene}}}_{\text{Oxidation process}}$$



n-doping

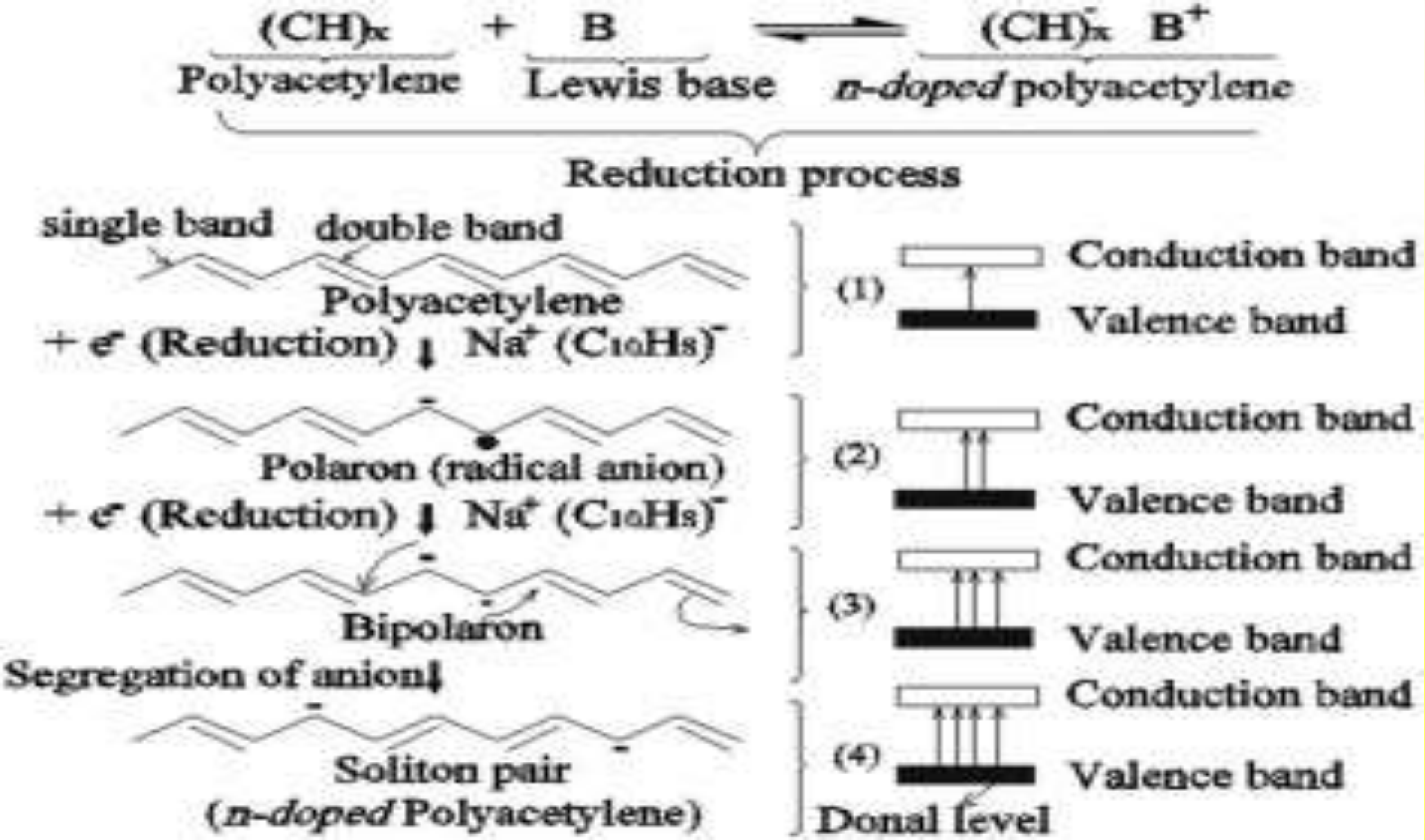
It involves two steps

Step I: It involves the reduction of polyacetylene of with sodium naphthalide

During reduction sodium naphthalide donates an electron to polyacetylene chain creates negative charge on the chain called polaron.

Step II: The second reduction of polaron two produce two negative charges on the chain called bipolaron.

This negative charges are mobile due to delocalisation and responsible for conductance.



$$\underbrace{(CH)_x}_{\text{Polyacetylene}} + \underbrace{B}_{\text{Lewis base}} \rightleftharpoons \underbrace{(CH)_x^- \; B^+}_{n\text{-doped polyacetylene}}$$

Applications of conducting polymers

- Incorporated into commercial displays and batteries
- Printed electronic circuits
- Organic light emitting diodes
- Supercapacitors
- Chemical sensors
- Used in solar cells
- Electromagnetic shielding
- Flexible transparent displays
- Microwave absorbing coating
- Radar-absorptive coating on stealth aircraft

Biodegradable polymers

Polymer that can be decomposed by the action of microorganisms are called biodegradable polymers

These polymers broken into small segments by enzyme catalysed reactions, and microorganisms produce this enzymes.

Examples of biodegradable polymers are polylactic acid, polycaprolactone, polyglycolic acid

Properties biodegradable polymers

- Biodegradable polymers can retain good mechanical integrity until degraded.
- Since biodegradable polymers have extremely strong carbon backbones that are difficult to crack, degradation begins at the end-groups.
- Biodegradable polymers are non toxic
- Degradation rates can be regulated
- Biodegradable polymers are hydrophilic

Uses of biodegradable polymers

Used in

- Controlled drug release systems
- Plasma replacements
- Agricultural materials such as films & seed coatings
- Fast food wrappers & personal hygiene products
- Drug delivery
- Post operative stitches

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What is Spectroscopy?

Spectroscopy is the study of the interaction between matter and radiated energy. Historically, spectroscopy originated through the study of visible light dispersed according to its wavelength, e.g., by a prism. Later the concept was expanded greatly to comprise any interaction with radiative energy as a function of its wavelength or frequency.

Spectrometry is the spectroscopic technique used to assess the concentration or amount of a given chemical (atomic, molecular, or ionic) species. In this case, the instrument that performs such measurements is a spectrometer, spectrophotometer, or spectrograph.

Spectroscopy/spectrometry is often used in physical and analytical chemistry for the identification of substances through the spectrum emitted from or absorbed by them.

Types:

1)Absorption Spectroscopy:

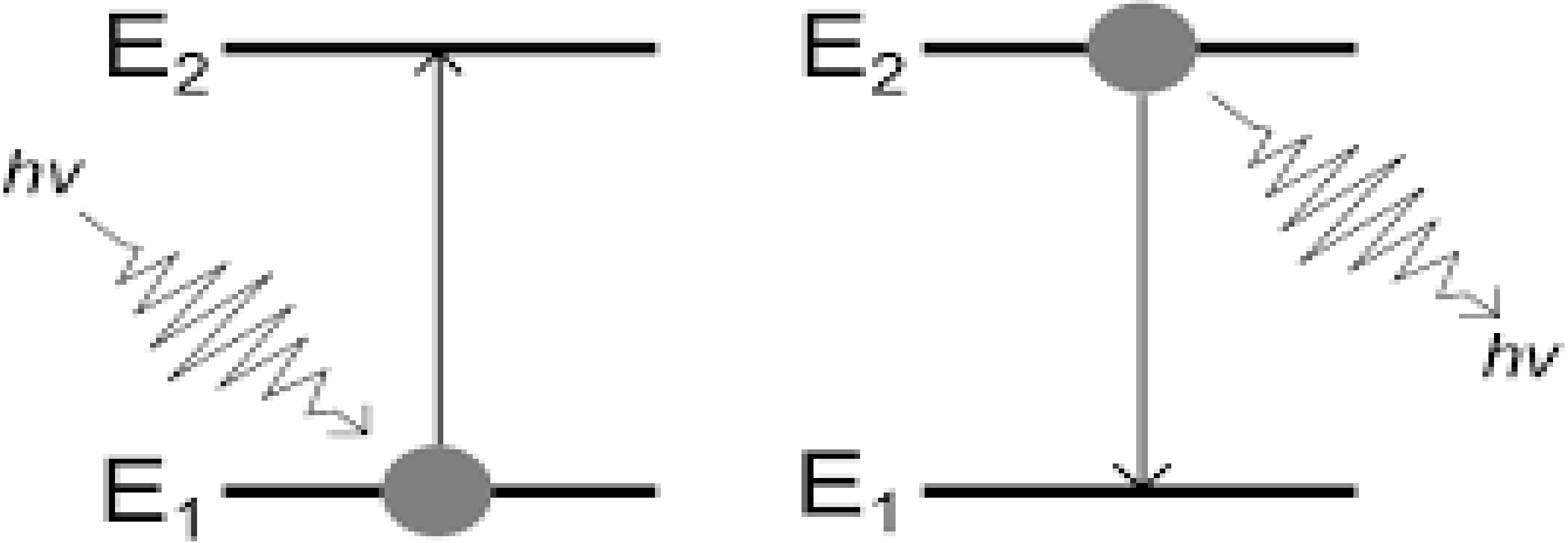
The study of absorbed radiation by molecule , in the orm of spectra.

Eg: UV, IR, NMR, colorimetry,
Atomic absorption spectroscopy

2)Emission Spectroscopy:

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

Eg:flame photometry, flourimetry



ABSORPTION
SPECTROSCOPY

EMISSION
SPECTROSCOPY

Study of spectroscopy

Atomic spectroscopy:

interaction of EMR+ATOMS

Changes in energy take place at atomic level

Eg: atomic absorption spectroscopy, flame photometry

Molecular spectroscopy:

Interaction of EMR + molecules

Changes in energy take place at molecular level

Eg: UV, IR, colorimetry

Results in transitions between vibrational,& rotational energy levels

What are electromagnetic waves?

Electricity can be static, like what holds a balloon to the wall or makes your hair stand on end.

Magnetism can also be static like a refrigerator magnet. But when they change or move together, they make waves - electromagnetic waves.

Electromagnetic waves are formed when an electric field (shown as blue arrows) couples with a magnetic field (shown as red arrows). The magnetic and electric fields of an electromagnetic wave are perpendicular to each other and to the direction of the wave. James Clerk Maxwell and Heinrich Hertz are two scientists who studied how electromagnetic waves are formed and how fast they travel.

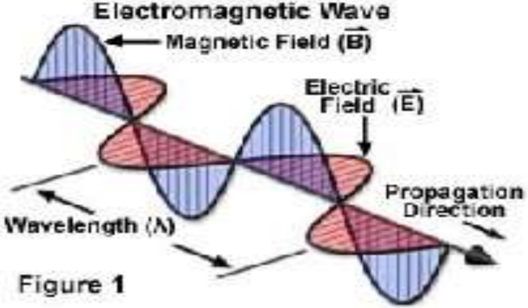
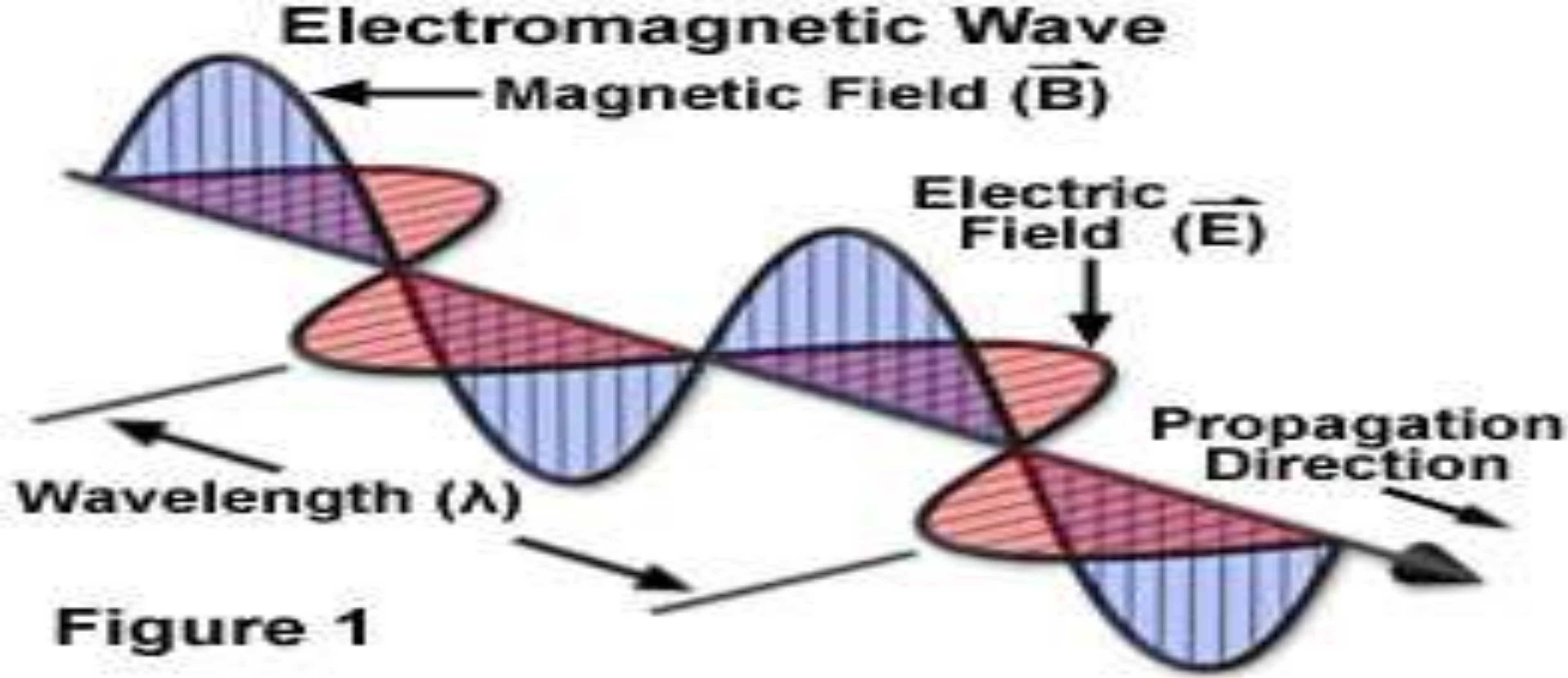


Figure 1

Electromagnetic waves are typically described by any of the following three physical properties: the frequency *f*, wavelength λ, or photon energy *E*.

COMPONENTS OF ELECTROMAGNETIC SPECTRA



Two Components of EM Radiation

- Electrical field (E): varies in magnitude in a direction perpendicular to the direction of propagation
- Magnetic field (M): at right angle to the electrical field, is propagated in phase with the electrical field

- Wavelength (λ), distance from one wave crest to another
- Frequency (ν), No. of crests passing a fixed point/ given time
- Amplitude, height of each peak (watts/sq. meter

- The speed of EM energy “c” 300,000km/second, $c = \nu\lambda$ where λ and ν are inversely related

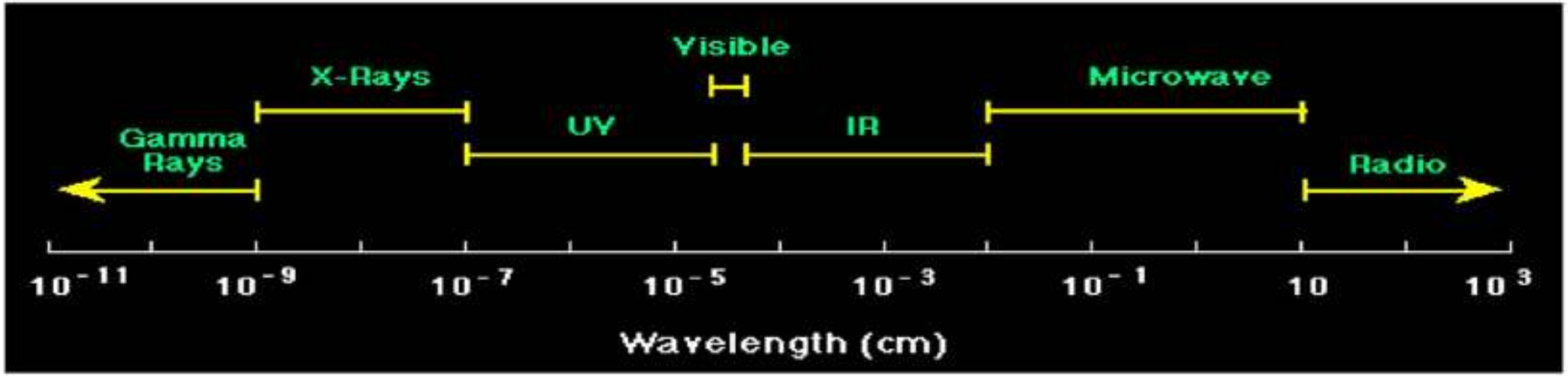
Electromagnetic spectrum

The **electromagnetic spectrum** is the range of all possible frequencies of electromagnetic radiation. The "electromagnetic spectrum" of an object is the characteristic distribution of electromagnetic radiation emitted or absorbed by that particular object.

Electromagnetic radiation

Electromagnetic radiation (**EM radiation** or **EMR**) is a form of energy emitted and absorbed by charged particles, which exhibits wave-like behavior as it travels through space. EMR has both electric and magnetic field components, which oscillate in phase perpendicular to each other and perpendicular to the direction of energy and wave propagation. In vacuum, electromagnetic radiation propagates at a characteristic speed, the speed of light.

- The sun produces a full spectrum of electromagnetic radiation



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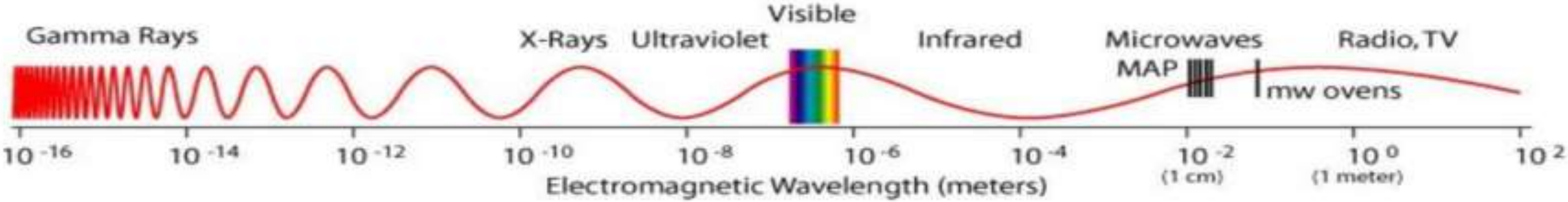

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TYPES OF MOLECULAR ENERGIES AND BORN-OPPENHEIMER APPROXIMATION

A molecule usually possesses four different types of energies. These are…

- Translational energy
- Rotational energy
- Vibrational energy
- Electronic energy

- According to born-oppenheimer approximation, the total energy of a molecule is the sum of translational , rotational, vibrational and electronic energies.

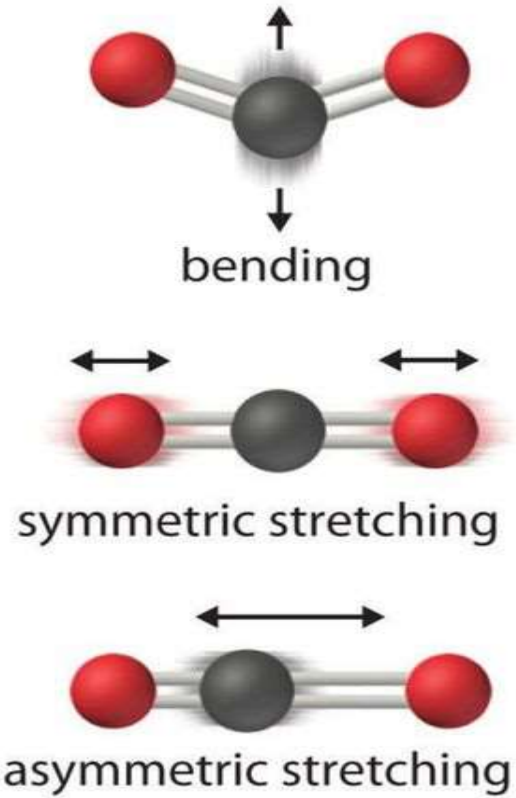
$$E = E_t + E_r + E_v + E_e$$

It is found that the translational energy is neglegibly small.So

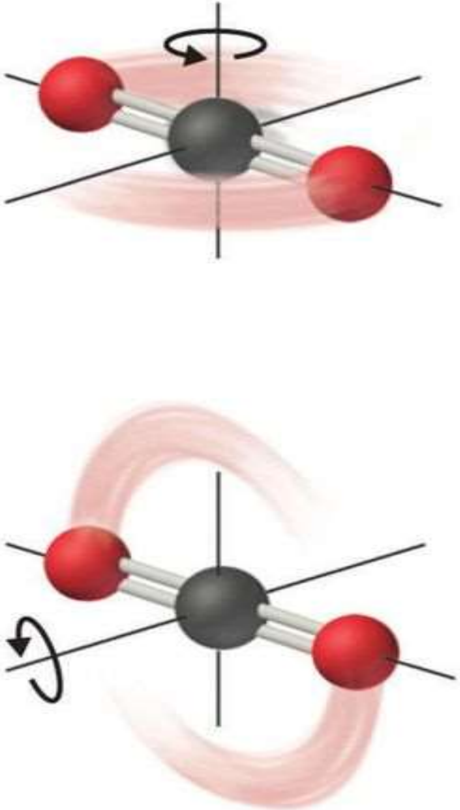
$$E = E_v + E_r + E_e$$

Molecular energies

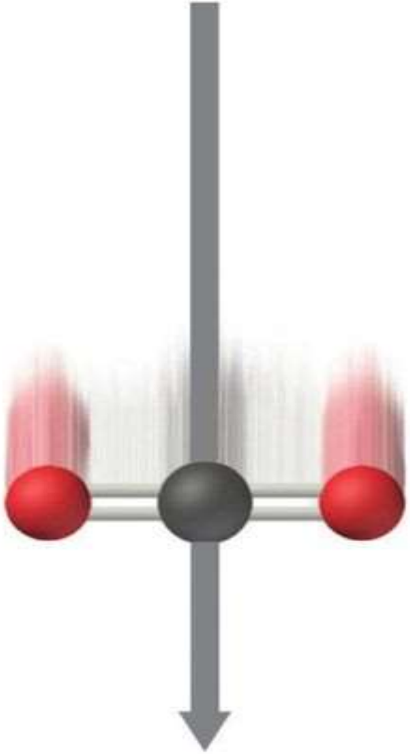
- An isolated molecule possesses:
- translational energy by virtue of the motion of the molecule as a whole
- (ii) rotational energy due to bodily rotation of the molecule about an axis passing through the center of gravity of molecule.
- (iii) vibrational energy due to periodic displacement of its atoms from their equilibrium positions.
- (iv) electronic energy since the electrons associated with each atom and bond are in constant motion.
- the total energy of a molecule can be expressed
- as the sum of the constituent energies, that is
- Etotal = Etrans + Erot + Evib + Eelec



vibrational motion



rotational motion



translational motion

TYPES OF MOLECULAR SPECTRA

- The energy absorbed for any transition is equal to the difference in the energies of the two levels involved.It is found that these energies for transition are in order…
- $E_t << E_r << E_v << E_e$
- Translational energy is considered as continous and we donot observe any translational spectrum.

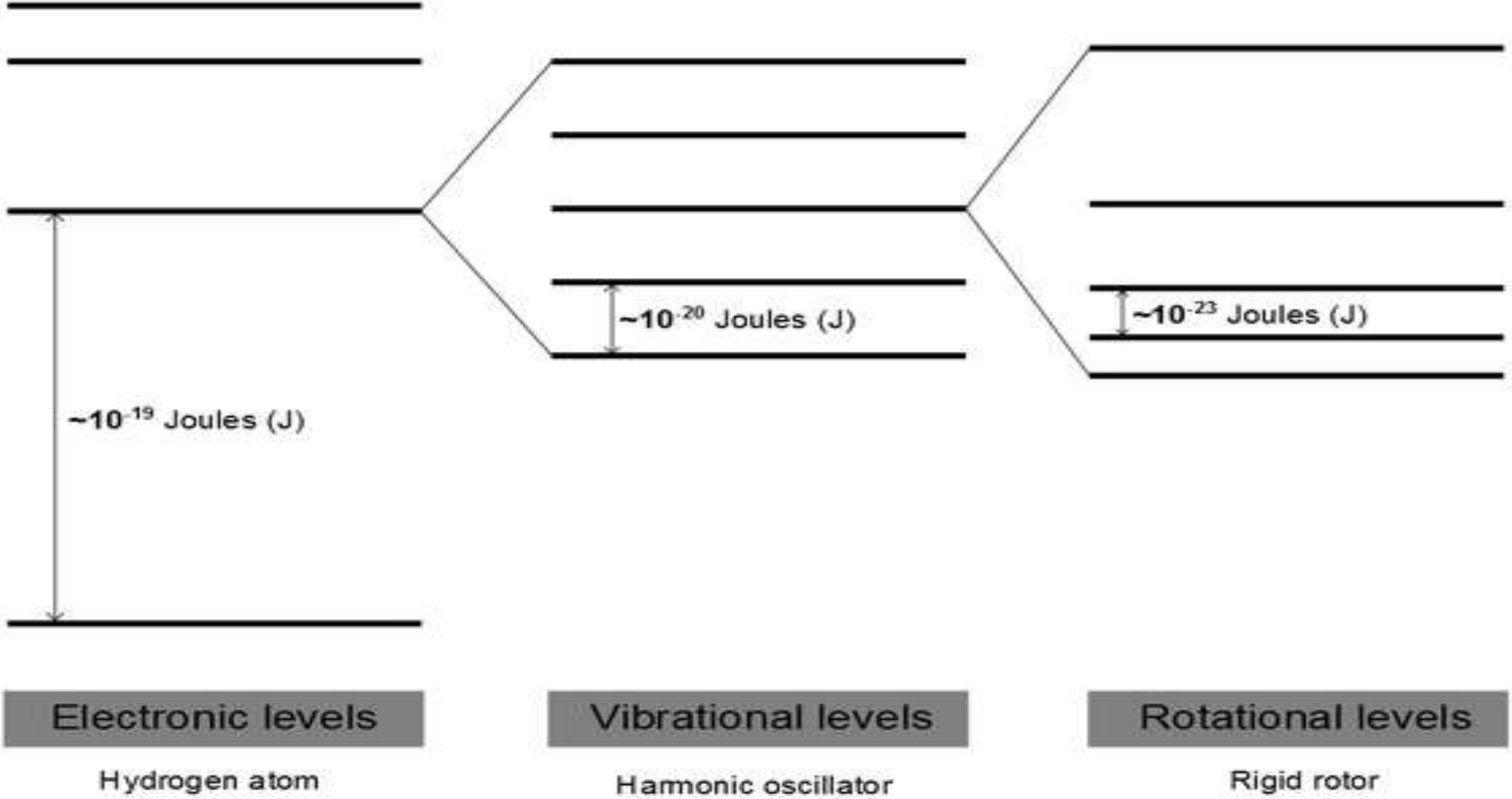
- **Pure rotational (microwave) spectra-** these spectra are observed in far infra-red region or in the microwave region.

- **Vibrational rotational spectra-** such energies are available in the near infra-red region.

- **Electronic band spectra-** for a given electronic transition, a set of bands observed.This set of bands is called a **band group** or a **band system**.Thus whereas atoms give line spectra, molecules give band spectra.These spectra are observed in the visible region and ultra violet region.

Molecular energies

Molecular motions	Absorbed electromagnetic radiations	Energy
Rotation	Microwave, infrared	Low
Vibrations	Infrared	Moderate
Electronic transitions	Visible, UV radiations	High



~10^{-19} Joules (J)

~10^{-20} Joules (J)

~10^{-23} Joules (J)

Electronic levels

Hydrogen atom

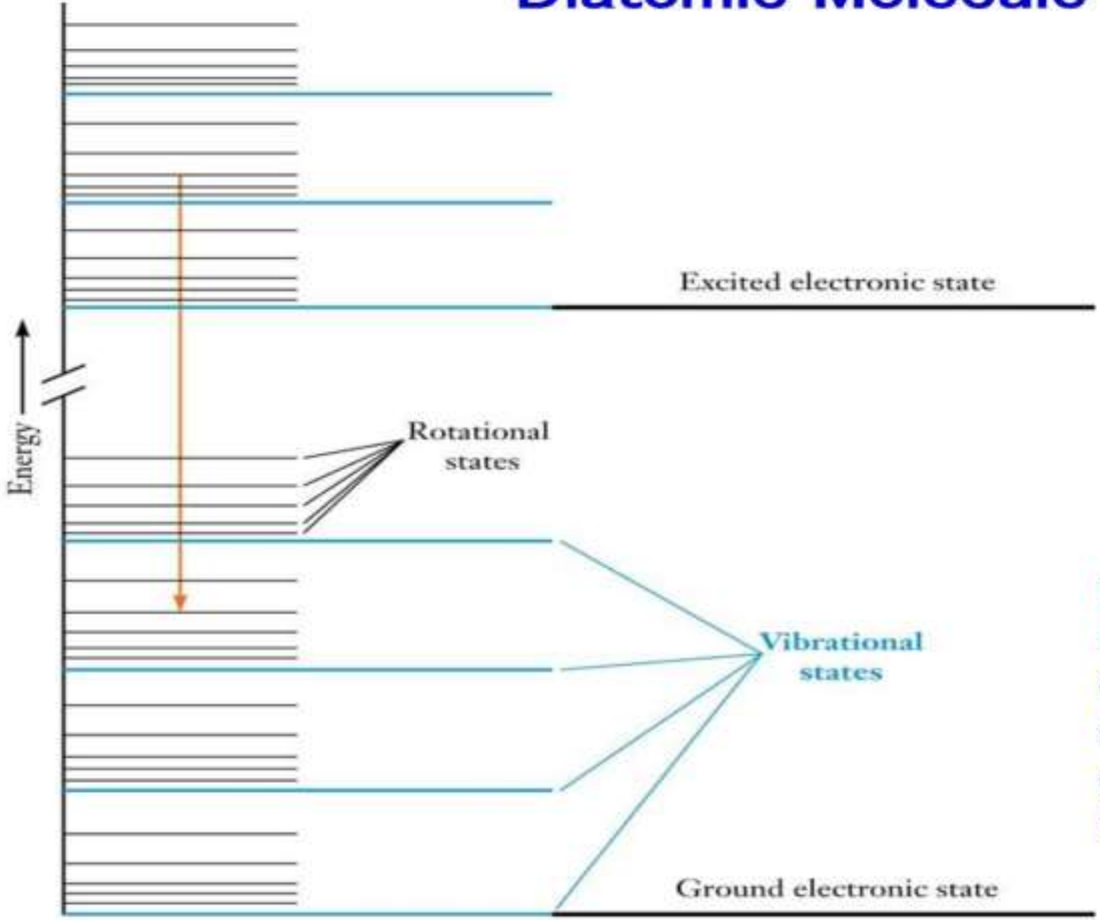
Vibrational levels

Harmonic oscillator

Rotational levels

Rigid rotor

Electronic, Vibrational, and Rotational Energy Levels of a Diatomic Molecule



Exercise: **Indicate the molecular state** **in which it is electronically in the ground state, vibrationally in the first excited state, and rotationally in the ground state.**