TRR GOVT DEGREE COLLEGE(A), KANDUKURU

DEPARTMENT OF CHEMISTRY

STUDY MATERIAL

I B.SC (Hons) CHEMISTRY

MAJOR-1 GENERAL CHEMISTRY

CLASS: SEMESTER-I B. Sc. (HONS) CHEMISTRY,

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MAJOR-1: GENERAL CHEMISTRY

UNIT-I ATOMIC STRUCTURE AND PERIODIC TABLE (9 Hrs.)

Electronic configuration-Aufbau principle, Hund's rule and Pauli's exclusion principle. Periodic law and arrangement of elements in the periodic table, horizontal, vertical, and diagonal relationships in the periodic table. Definition and periodic trends of atomic radii, ionic radii, covalent radii, ionization potential, electron affinity, and electronegativity, Pauling scale, variable valency, inert-pair effect.

ELECTRONIC CONFIGURATION: Electron configuration is the arrangement of electrons in the atomic orbitals (s,p.d.f) around the nucleus of an atom. It describes how electrons are distributed among various energy levels (shells) and sublevels (orbitals) in a specific order according to three rules. Aufbau principle, Pauli exclusion principle ,Hund's rule

It determines chemical properties, valency, magnetism, and periodic position

AUFBAU PRINCIPLE: In the ground state of an atom the electrons occupy the lowest energy orbitals available to them electrons enter the orbitals in the order of increasing energies The lowest energy available orbitals being filled up first Since the energy of an orbitals is determined by the quantum numbers n and 1, the sequence of filling the orbitals proceeds according to the Madelung rule

Orbitals are filled in order of increasing value of n+1.

For example , 4s (n+ 1 =4+0=4) is filled before 3d (n+1=3+2 =5)

For the orbitals having the same value of n + I the orbital having lower value of n is filled up first.

For example, 2p (n+1) = 2+1 =3) is filled before 3s (n+1 = 3+0=3) because 2p has lower value of n

The general order of increasing energies of the orbitals is:

1s<2s<2p< 3s < 3p< 4s< 3d< 4p< 5s< 4d< 5p< 6s< 4f< 5d< 6p< 7s< Sf< 6d< 7p

LIMITATIONS OF AUFBAU PRINCIPLE

1. it does not tell us which electrons are to be removed when an ion is formed from an atom

As per Aufbau principle Electronic configuration of Fe is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

.It has been experimentally confirmed by spectral and magnetic studies that Fe^{2+} has configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^o 3d^6$ and not $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$

It means that ionization results in the loss of 4s electrons in preference to 3d electrons even though the 3d was the last to be added in building up the configuration of Fe atom. It means that in Fe^{2t},3d has lower energy than 4s which is contrary of Aufbau order of filling.

2. Although (n - 1) d subshells and ns subshells lie quite close together, yet the (n - 1) d is somewhat, higher in energy. Accordingly, the predicted Aufbau outer configuration of Cr (Z = 24) is $[Ar]3d^4 4s^2$ but the experimentally supported configuration is [Ar] $3d^5 4s^1$

   The reasons for these deviations lie in the extra stability associated with half-filled or completely filled subshell

HUND'S RULE: In an atom, no electron pairing takes place in the p and d or f orbitals respectively until each orbital of the given subshell contains at least one electron. The unpaired electrons present in the various orbitals of the same subshell should have parallel spins

This is because, presence of the electron each in two orbitals of the same subshell involves lesser inter-electronic repulsion as compared to the electrons in the same orbital. Therefore, it leads to lower energy state.

Exchange Energy: stabilization from parallel spins in different orbitals is due to Exchange energy which lowers the atom's energy. When two electrons have the same spin but are in different orbitals, their wavefunctions overlap more smoothly(quantum exchange symmetry), reducing repulsion slightly. This gives extra stability

Exchange energy $\propto$ number of possible exchange interactions between same-spin electrons

Pairing Energy: energy needed to put two electrons with opposite spins in the same orbital as to overcome the repulsion leads to unstabilty of the atom

N ($2p^3$) [↑] [↑] [↑] is stable [↑↓] [↑] [ ] is unstable and violates Hund rule

PAULI EXCLUSION PRINCIPLE: In an atom, a maximum of two electrons can occupy the same orbital or else No two electrons in an atom can have identical set of four quantum numbers. The two electrons in the same orbital will have identical n, and m but must have different spins (+1/2 and -1/2).

it does not have a straightforward mathematical proof .The principle is deeply connected to the spin-statistics theorem in quantum field theory, which relates particle spin to the symmetry properties of their wavefunctions

If both electrons had the same spin, the spin part would be symmetric, requiring an antisymmetric spatial part. But identical spatial states cannot be antisymmetric, so the total wavefunction becomes zero—making such a configuration forbidden. This is the quantum mechanical expression of the Pauli Exclusion Principle.

Multiple experiments like Atomic Transition Experiments, Neutron and Nucleon Systems etc conducted but found no evidence contradicting the principle, on any possible violations

PERIODIC LAW : The physical and chemical properties of elements are periodic functions of their atomic numbers.

Explanation: Periodicity arises from the repeating pattern of electron configurations and the variation of effective nuclear charge (Zeff), distance or principal quantum number n Shielding & penetration of s,p,d,f orbitals , Subshell shape , exchange & pairing energies, and relativistic effects.

Example: Na (Z=11) and K (Z=19) both have ns^1 outer configurations and hence similar properties.

In the periodic table, elements with similar properties occur at intervals of 2,8, 8,18, 18 and 32. These numbers are called as magic numbers

ARRANGEMENT OF ELEMENTS IN THE PERIODIC TABLE, HORIZONTAL, VERTICAL:

The modern periodic table consists of horizontal rows (periods) and vertical column (groups)

Periods : There are seven periods numbered as 1, 2, 3, 4, 5, 6 and 7.

- Each period consists of a series of elements having same valence shell.
- Each period corresponds to a particular principal quantum number of the valence shell present in it.
- Each period starts with an alkali metal having outermost electronic configuration as ns 1 .
- Each period ends with a noble gas with outermost electronic configuration ns 2 np 6 except helium having outermost electronic configuration as 1s 2 .
- Each period starts with the filling of new shell.
- The number of elements in each period is twice the number of atomic orbitals available in shell that is being filled.
- Elements within a period have the same number of electron shells but different numbers of electrons in the outermost shell, resulting in changing chemical behaviour from metals to metalloids to nonmetals

Periods	Number of elements	Called as
(1)st n = 1	2	Very short period
(2)nd n = 2	8	Short period
(3)rd n = 3	8	Short period
(4)th n = 4	18	Long period
(5)th n = 5	18	Long period
(6)th n = 6	32	Very long period
(7)th n = 7	32	Very long period

Period 1: Contains only 2 elements: Hydrogen and Helium.

Smallest elements with only one electron shell.

Hydrogen is a unique nonmetal, Helium is a noble gas with a full outer shell.

Period 2: Contains 8 elements. Li to Ne

Involves filling of the 2nd electron shell (n=2).

Shows transition from reactive metals (like lithium) to nonmetals (like fluorine).

First appearance of p-block elements.

Elements vary from metals to metalloids to nonmetals.

Period 3: Contains 8 elements. Na to Ar

Completion of the third electron shell (n=3).

Similar to period 2 but atoms are larger with more electron shielding.

Includes important elements like sodium, magnesium, chlorine, and argon.

Period 4: Contains 18 elements. K to Kr

Filling of the 4th shell including the d-block or transition metals.

Exhibits variable oxidation states and complex chemistry.

Includes biologically and industrially important metals like iron, copper, and zinc.

Period 5:Contains 18 elements. Rb to Xe

Similar to period 4 but with larger atoms.

Includes the lightest synthetic element technetium.

Rich in transition metals with diverse chemistry.

Period 6: Contains 32 elements. Cs to Rn

Filling of 6th electron shell including the lanthanide series (f-block).

Lanthanides show similar chemical properties.

Includes heavy metals like lead and bismuth.

Period 7: Contains 32 elements. Fr to U_{uo} (118)

Includes the actinide series (f-block).

Mostly radioactive and synthetic elements.

Completes the current known periodic table with the heaviest elements like uranium and oganesson.

Each period corresponds to the filling of electron shells that determine the chemical properties of the elements, gradually changing from metals on the left to nonmetals and noble gases on the right.

Groups :

There are eighteen groups numbered as 1, 2, 3, 4, 5,..... 13, 14, 15, 16, 17, 18.

Group consists of a series of elements having similar valence shell electronic configuration

This common valence electron count gives rise to similar chemical properties within a group.

For example:

- Group 1 elements (alkali metals) have 1 valence electron and are highly reactive metals.
- Group 17 elements (halogens) have 7 valence electrons and are reactive nonmetals.
- Group 18 elements (noble gases) have full outer shells and are mostly inert.
- Groups can be further divided into families like alkali metals, alkaline earth metals, transition metals, halogens, and noble gases.
- Moving down a group, elements have increasing numbers of electron shells, which influences properties like atomic size and reactivity.

Group 1: Alkali Metals

Elements: Li, Na, K, Rb, Cs, Fr

1 valence electron

Highly reactive, especially with water

Soft metals, low melting points

Form +1 ions

Reactivity increases down the group

Group 2: Alkaline Earth Metals
Elements: Be, Mg, Ca, Sr, Ba, Ra

2 valence electrons

Less reactive than Group 1 but still reactive

Harder and higher melting points than alkali metals

Form +2 ions

Reactivity increases down the group

Groups 3-12: Transition Metals

Includes elements like Fe, Cu, Ni, Zn

Variable valence electrons

Hard, high melting points, good conductors

Exhibit multiple oxidation states

Form colourful compounds

Commonly used as catalysts

Group 13: Boron Group
Elements: B, Al, Ga, In, Tl

3 valence electrons

Mix of metals and metalloids

Form +3 ions typically

Boron is a metalloid; others are metals

Group 14: Carbon Group

Elements: C, Si, Ge, Sn, Pb

4 valence electrons

Contains nonmetals, metalloids, and metals

Exhibits multiple oxidation states (+2, +4)

Essential for organic chemistry

Group 15: Pnictogens

Elements: N, P, As, Sb, Bi

5 valence electrons

Variety of nonmetals, metalloids, and metals

Form -3 ions or covalent compounds

Important for biological molecules

Group 16: Chalcogens

Elements: O, S, Se, Te, Po

6 valence electrons

Reactive nonmetals and metalloids

Form -2 ions

Oxygen is vital for respiration

Group 17: Halogens

Elements: F, Cl, Br, I, At

7 valence electrons

Highly reactive nonmetals

Form salts with metals

Exist as diatomic molecules (e.g., Cl_2)

Group 18: Noble Gases

Elements: He, Ne, Ar, Kr, Xe, Rn

Full valence shells (8 electrons except He with 2)

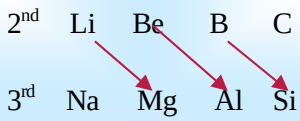
Very low reactivity (inert)

Used in lighting and welding

Each group shares the same number of valence electrons, leading to similar chemical reactivity and bonding patterns. Reactivity trends can vary within groups, often increasing or decreasing as you move down the group due to atomic size and electron shielding effects

DIAGONAL RELATIONSHIPS IN THE PERIODIC TABLE:

Some elements of certain groups of 2^{nd} period resemble much in properties with the elements of 3^{rd} period of next group i.e. elements of 2^{nd} and 3^{rd} period are diagonally related in properties. This phenomenon is known as diagonal relationship



on descending a group, the atoms and ions increase in size. On moving from left to right in the periodic table, the size decreases and hence trends are compensated Thus on moving diagonally, the size remains nearly the same (Li + = 0.76 Å & Mg 2+ = 0.72 Å)

it is sometimes suggested that the diagonal relationship arises because of diagonal similarity in electronegativity values. (Li = 1.0 & Mg = 1.2)

This is more Pronounced in s/p-block elements and in d block elements not significant due to mall size change across periods and complex shielding/oxidation patterns

PERIODIC TRENDS

ATOMIC RADII: Distance from nucleus to outermost electron.

Trend across a Period : Decreases across a period

Reason: Due to increasing of effective nuclear charge (Z_{eff})across a period from left to right with increasing atomic number in the same shell .As a result electrons are pulled towards the nucleus thus distance decreases

Trend across Group : increases down a group

Reason: Due to addition of electrons into the new shell down a group outweighs the effective nuclear charge (Z_{eff}) As a result distance increases form outer most electrons to the nucleus

IONIZATION POTENTIAL : The ionisation potential of an element is defined as amount of energy required to remove the most loosely bound electron from an isolated gaseous atom**.**

Trend across a Period: Increases across a period

Reason: Due to the gradual increase in the effective nuclear charge (Z_{eff}) and simultaneous decrease in the atomic size, the electrons get more and more strongly held to the nucleus. Therefore it is very difficult to remove the electrons. As a result ionisation potential increases

Trend across Group : : Decreases down a group

Reason: In going from top to bottom in a group the effective nuclear charge (Z_{eff}) , the atomic size and shielding effect increases .The increase in atomic size and the shielding effect more than neutralise the effect of the increased charge (Z_{eff}), As a result outermost electrons are loosely held to the nucleus and hence ionisation potential decreases.

ELECTRON AFFINITY : The amount of energy released when a neutral atom in the gaseous state acquires an extra electron to form a negatively charged ions is known as electron affinity

Trend across a Period: Increases across a period

Reason: The atomic size decreases while the nuclear charge increases across a period ,this would increases attraction of addition of electrons by nucleus . As a result electron affinity increases

Trend across Group : : Decreases down a group

Reason: The atomic size as well as the nuclear charge increase on moving down the group. But the overall effect of is that the effective nuclear attraction for the electron decreases. As such nucleus would have less tendency to attract additional electron so that its electron affinity would decrease.

ELECTRONEGATIVITY : Electronegativity is defined as power of an atom in a molecule to attract or pull bond pair of electrons towards itself

Trend across a Period: Increases across a period

Reason: Due to the increasing effective nuclear charge and decreasing atomic size casus pulling of bonding electrons towards the nucleus hence electronegativity increases across a period

Trend across Group : Decreases down a group

Reason: Down the group atomic size and shielding power increases as result nuclear pull towards bonding pair decreases making it harder for the nucleus to attract electrons in a bond .hence electronegativity decreases down a group

Property	Trend across a Period	Trend across Group
ATOMIC RADII	Decreases	Increases
IONIZATION POTENTIAL	Increases	Decreases
ELECTRON AFFINITY	Increases	Decreases
ELECTRONEGATIVITY	Increases	Decreases

PAULING SCALE: Electronegativity is defined as power of an atom in a molecule to attract electrons to itself Pauling derived the scale based on bond dissociation energies (bond strengths) of molecules containing the atoms. The difference in electronegativity between two atoms A and B is related to the excess bond energy of the A-B bond over the average of the A-A and B-B bonds, by the formula

$$|X_A - X_B| = 0.182 \times \sqrt{E_{AB} - \sqrt{E_{AA} \times E_{BB}}}$$

where E_{AB} ,E_{AA} ,E_{BB} are the bond energies of the respective molecules in kcal/mol.

Higher Pauling electronegativity values indicate a stronger ability to attract electrons in a bond. This scale helps predict bond polarity, with large differences in electronegativity leading to ionic bonds and small differences indicating covalent bonds. Pauling's scale is relative and empirical, based on observed chemical behaviour and energy data

Pauling scale: F = 4.0 (highest), Cs = 0.7 (lowest).

VARIABLE VALENCY INERT-PAIR EFFECT.: The ability of an element to exhibit more than one valency due to involvement of (n-1)d and ns electrons

Reason: Close energy levels of ns and (n–1)d or (n–2)f orbitals allow both to participate in bonding.

Stability of half-filled or fully filled orbitals

Inert pair effect in p-block elements causes lower oxidation states to be more stable.

Elements in s-block generally have fixed valencies, whereas d-block elements (transition metals) often show variable valencies due to their complex electron configurations.

Iron (Fe): Exhibits +2 (ferrous) and +3 (ferric) valencies; FeO and Fe_2O_3 are examples.

Copper (Cu): Shows +1 (cuprous) and +2 (cupric) valencies; Cu_2O and CuO are examples.

INERT-PAIR EFFECT:

The reluctance of the outermost ns^2 electrons of heavier p-block elements to participate in bonding is called the Inert Pair Effect.

Causes of Inert Pair Effect

1. Poor shielding by inner d and f electrons increases nuclear attraction on ns electrons.
2. High effective nuclear charge.
3. Relativistic effects stabilize ns^2 electrons in heavy atoms

Consequences of Inert Pair Effect

Heavier elements of p-block show two oxidation states — a higher and a lower one. The lower oxidation state becomes more stable down the group.

Element	Expected O.S.	Observed O.S.	Stable State	Reason
Tl	+3	+1, +3	+1	$6s^2$ inert
Pb	+4	+2, +4	+2	$6s^2$ inert
Bi	+5	+3, +5	+3	$6s^2$ inert

Relationship Between Inert Pair Effect and Oxidation States

Lighter elements: Higher oxidation states are stable (C^{4+}, Si^{4+}).

Heavier elements: Lower oxidation states are stable (Pb^{2+}, Bi^{3+}).

Oxidising and Reducing Nature

Higher oxidation state compounds act as oxidising agents ($Pb^{4+} \rightarrow Pb^{2+}$).

Lower oxidation state compounds act as reducing agents ($Sn^{2+} \rightarrow Sn^{4+}$).

QUESTION BANK

UNIT-1 LONG ANSWER QUESTIONS 10 MARKS

1. Discuss the concept of electronic configuration and explain the rules Aufbau principle, Pauli Exclusion Principle, Hund's Rule?
2. Explain periodic trends of atomic radii, Ionization Potential, Electron Affinity, and Electronegativity?

SHORT ANSWER QUESTIONS 5 MARKS

1. Explain the concept of variable valency with examples
2. Write a short note on the inert pair effect.
3. Explain the diagonal relationship in the periodic table

MAJOR-1: GENERAL CHEMISTRY

UNIT-II IONIC BOND (9 Hrs.)

Properties of ionic compounds, factors favouring the formation of ionic compounds, Lattice energy: definition, factors affecting lattice energy, Born-Haber cycle ionic compound and stability, Covalent character in ionic compounds rules, effects of polarization. enthalpy of formation of polarization and Fajan's rules and effects of polarization.

PROPERTIES OF IONIC COMPOUNDS : An ionic compound is formed by complete transfer of electrons from one atom (metal) to another (non-metal), resulting in electrostatic attraction between oppositely charged ions.
Example: $Na + Cl \rightarrow NaCl$ ($Na \rightarrow Na^+ + e^-$; $Cl + e^- \rightarrow Cl^-$).

Property	Explanation
Physical State	Crystalline solids like NaCl, KBr In the solids state each cation surrounds itself with anions, and each anion with cations. These very large number of ions are arranged in an orderly network called ionic crystal
Melting & Boiling Points	High due to strong electrostatic attraction. Since electrostatic interactions between +ve and-ve ions in the crystal are generally strong, therefore their breakdown requires higher energies and hence ionic compounds have higher melting and boiling points
Electrical Conductivity	Conduct in molten or aqueous state, not in solid state. In an ionic crystal, the ions are situated in fixed positions in the lattice, that is, they are not mobile. Therefore, ionic solids do not conduct electricity in the solid state. However, in molten state or fusion or in solution the crystal lattice breaks and ions are free to move in an electric field. Thus, they conduct electricity
Solubility	Soluble in polar solvents like water, insoluble in non-polar solvents. Ionic compounds are soluble in highly polar solvents. Water is a good solvent for dissolving ionic compounds because It has a larger dipole moment which provides high hydration energy due to strong ion-solvent dipole interactions. If hydration energy is greater than the lattice energy, the crystal breaks and soluble in water
Brittleness	Ionic crystals are brittle because like charges repel on shifting layers. The constituent units which make up ionic solids are oppositely charged ions. If requisite energy is supplied to the crystal layers, the movement of layers of ions brings ions of like charges near each other and this causes strong repulsions which lead to brittle in spite of their hardness
Structure	Form a three-dimensional ionic lattice. The constituent ions of an ionic solid possess an orderly arrangement in a definite geometric pattern which repeats itself throughout the crystal. Crystals are always bound by plane faces and these faces always meet at some fixed angles. For any particular substance, the angle between corresponding pair of faces is always the same in all crystals
Heat of Formation	Highly exothermic and stable compound. The electrostatic interaction between oppositely charged ions depends on: (1) ionic radii (ii) charges on the ions For a given ionic charge, Heat of formation increases with decrease in interionic distance for crystals In short, smaller the structure stable is the substance
Isomorphism	If two different ionic compounds are having similar crystalline structures then, these are known as Isomorphism to each other. $MgSO_4 .7H_2O$ $FeSO_4 .7H_2O$ $ZnSO_4 .7H_2O$

FACTORS FAVOURING THE FORMATION OF IONIC COMPOUNDS:

Ionisation Energy: Lower the ionisation energy, greater will be the tendency of the metal atom to form cation and hence, greater will be the tendency of formation of ionic bond.

$$Na \rightarrow Na^{+} + e^{-} \quad -119 \text{ kcal/mol}$$

Electron affinity: Higher the electron affinity higher will be the anion. Hence, ease the formation of ionic bon On moving down a group the electron affinity decreases and therefore, the tendency of ionic bond formation also decreases.

$$Cl + e \rightarrow Cl^{-} + 85 \text{ kcal}$$

Lattice energy: Lattice energy $\propto$ strength of ionic bond

Electronegativity: High electronegativity difference between atoms (<1.7) greater ionic character

LATTICE ENERGY:

Definition: The energy released when one mole of an ionic crystalline solid is formed from its constituent gaseous ions. Or The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions

Example: $Na^{+}(g) + Cl^{-}(g) \rightarrow NaCl(s) + Energy$

FACTORS AFFECTING LATTICE ENERGY :

Lattice energy (L.E.) $\alpha \ \frac{1}{r}$ r = r+ + r- r = interionic distance

L.E. α Z+ , Z

$Z_{+} \Rightarrow$ charge on cation in terms electronic charge

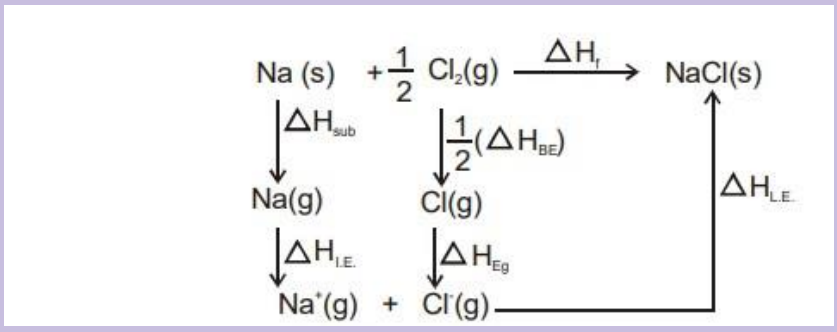
$Z_{-} \Rightarrow$ charge on anion in terms electronic charge

Factor	Effect
Charge on Ions	Higher charge increases lattice energy.
Ionic Radii	Smaller ions will have higher lattice energy.
Interionic Distance	Shorter distance more stronger attraction.
Dielectric Constant	Polar medium reduces lattice energy.

BORN-HABER CYCLE : The Lattice energy of ionic crystal can be determined by two different paths interrelating different thermochemical quantities which is based on Hess's law

Hess's Law $\Rightarrow$ the net enthalpy changes of a chemical reaction or of any process always remain same whether the reaction takes place in one step or many steps

Born Haber Cycle for NaCl (s)



Steps involved:

1. Sublimation of $Na(s) \rightarrow Na(g)$ $\Delta H_{sub} = +108$ kJ/mol

Sublimation energy of the metal Since energy is required for the process (endothermic), its value is taken as a positive

2. Ionization of $Na(g) \rightarrow Na^+(g) + e^-$ $\Delta H_{IE} = +496$ kJ/mol

Ionization energy, i.e., energy required for the removal of an electron from an isolated gaseous atom, M. The process is endothermic and is taken as a positive

3. Dissociation of $Cl_2(g) \rightarrow \frac{1}{2}Cl_2(g) = Cl(g)$ $\Delta H_{DE} = +122$ kJ/mol

Dissociation energy of X2 gas into atoms. This process is endothermic, and its value is taken as a positive

4. Electron affinity by Cl(g): $Cl(g) + e^- \rightarrow Cl^-(g)$ $\Delta H_{EA} = -349$ kJ/mol

Electron affinity, i.e., amount of energy released when a neutral gaseous atom gains an electron. The process is exothermic, and its value is taken as a negative

5. Lattice Formation of NaCl(s): $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ $\Delta H_{LE} =$

Lattice energy: it is amount of energy released when one mole of gaseous positive and negative ion condenses to form an ionic solid quantity. The process is exothermic, and its value is always negative

6. Heat of formation of NaCl solid $Na(s) \rightarrow \frac{1}{2}Cl_2(g)$ $\Delta H_f = -410$ kJ/mol

Heat of formation, it is defined as the amount of energy released when one mole of a substance is formed from its element Energy is released in the process and its value is taken as a negative

According to Hess's Law

$\Delta H_f = \Delta H_{sub} + \Delta H_{IE} + \Delta H_{DE} + \Delta H_{EA} + \Delta H_{LE}$

$\Delta H_{LE} = \Delta H_f - (\Delta H_{sub} + \Delta H_{IE} + \Delta H_{DE} + \Delta H_{EA})$

$= -410 - (108+496+122-349)$

$= -410-377$

$= -787$ kJ/mol

IONIC COMPOUND AND STABILITY

Lattice energy is a key factor in the stability of ionic compounds. It is the energy released when oppositely charged ions come together to form an ionic solid from their gaseous states, or equivalently, the energy required to separate one mole of an ionic solid into its gaseous ions.

Lattice Energy Affects Stability

Higher lattice energy means ions are held together more strongly by electrostatic forces, making the ionic compound more stable.
More stability means higher melting and boiling points, making the compound less likely to decompose or dissolve easily

Ionic Charge :Lattice energy increases with greater charges on the ions e.g., MgO with Mg^{2+} and O^{2-} has higher lattice energy than NaCl with Na^+ and Cl^-

Ionic Size: Smaller ions allow ions to pack more closely, resulting in stronger attractions and higher lattice energy.
Fluoride ions (F^-) are smaller than iodide ions (I^-). MgF_2 has a higher lattice energy than MgI_2 due to smaller anion size leading to closer ionic packing and stronger attraction

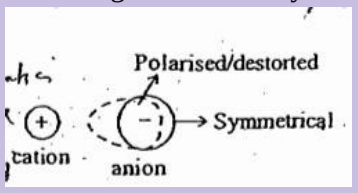
Lower lattice energy indicates weaker attractions between ions, leading to less stability and lower melting points. Larger ions decrease lattice energy due to increased distance between their centres

NaCl has a higher lattice energy (-788 kJ/mol) compared to KCl (-701 kJ/mol). This is because Na^+ ions are smaller than K^+ ions

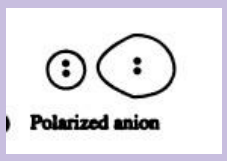
COVALENT CHARACTER IN IONIC COMPOUNDS RULES,

Even ionic compounds possess some covalent character due to polarization of the anion by the cation.
More distortion of anion, more will be polarisation then covalent character increases
Polarization: Deformation of the electron cloud of anion by cation.

Polarizing Power: Ability of cation to distort anion.



Polarisability: Tendency of anion to get distorted.



When two opposite charged ions (cation and anion) of the ionic molecule come closer to each other, the cation attracts the electron cloud of the outermost shell of the anion towards itself and hence, the symmetrical shape of the anion gets distorted (i.e. deformed or polarised). This phenomenon is called polarisation of anion

FAJAN'S RULES : He gave qualitative ideas to offer simple approach to the problem of partial covalent character in ionic compounds.

1. **<u>Small, highly charged cations</u>**. Small, highly charged cations have higher polarizing effects on anions than large, lowly charged cations. In other words covalent character in ionic compounds increases with decrease in size of the cation or increase in charge on the cation.
   Size of cation ↑ Polarisation ↓ Covalent character ↓
   Charge of cation↑ Polarisation ↑ Covalent character ↑

2. **Large, highly charged anions**. Covalent character induced in ionic compound due to polarization of the anion increases with an increase in size and charge on the anion. The electron cloud on the large-sized anion is less strongly held by its nucleus and hence it is easily polarized by the approaching cation.

Negative charge on anion ∞Polarisability of anion

Size of anion ∞ Polarisability of anion

3. **Cation configuration (pseudo noble gas configuration**). Cations with pseudo noble gas configuration (i.e., 18 electron outer shell) have higher polarizing power than cations with noble gas configurations. In ns^2 np nd^1 configuration d-electrons shield the nucleus poorly with the consequence that such a cation will exert a higher nuclear charge on the interacting anion

Cu [Ne] $3s^2$ $3p^6$ $3d^{10}$ = 18 electrons Pseudo inert gas configuration

EFFECTS OF POLARIZATION.:

Bond Character Changes:

Reason: Greater polarization means more electron sharing, hence, more covalent character

Example: $AlCl_3$ (aluminium chloride) is more covalent, while NaCl remains mostly ionic

Because Al^{+3} (High +ve charge)polarizes much more than Na^+ does

Melting and Boiling Points

Reason: Compounds with more covalent character (from more polarization) have lower melting/boiling points than expected for purely ionic compounds.

Example: AgCl melts at a lower temperature than NaCl because Ag^+ is a good polarizer

Solubility

Reason: More covalent compounds tend to be less soluble in water (a polar solvent).

Example: AgCl is much less soluble in water than NaCl

Colour Properties

Reason: Polarization affects the way compounds absorb light and display color.

Example: PbI_2 (lead(II) iodide) is yellow and insoluble in water Pb^{2+} (small, high charge) strongly polarizes the large I^- ion

QUESTION BANK

UNIT-2 LONG ANSWER QUESTIONS 10 MARKS

1. Define lattice energy. Explain the factors affecting lattice energy
2. Discuss the factors that favour the formation of ionic compounds and how lattice energy influences stability
3. Describe the Born-Haber cycle with its application to the formation of an ionic compound

SHORT ANSWER QUESTIONS 5 MARKS

1. What are Fajan's rules?
2. Define ionic bond and give two examples
3. Write short notes on polarization.

MAJOR-1: GENERAL CHEMISTRY

UNIT-III COVALENT BOND (9 Hrs.)

Valence Bond theory: Hybridization of atomic orbitals and geometry of molecules - $BeCl_2$, BF_3, CH_4, $PC1_5$, and SF_6
VSEPR model: Effect of bonding and nonbonding electrons on the structure of molecules - NH3, H2O, SF_4, ICl_2 and XeF_4
Molecular orbital theory: LCAO method, construction of M.O. diagrams for homo nuclear and hetero nuclear diatomic molecules (N_2, O_2, CO and NO**)**

VALENCE BOND THEORY

Heitler–London Theory (1927): They showed that a covalent bond forms when:

- Two half-filled atomic orbitals (each with one electron) overlap.
- The electrons pair up with opposite spins.
- The overlapping wave functions interfere constructively, lowering the energy.

This was the first quantum explanation of a chemical bond — the foundation of Valence Bond Theory (VBT)

Valence Bond Theory (VBT) is a fundamental theory in chemistry that explains how covalent bonds form between atoms. Developed by Linus Pauling and John C. Slater in 1931.

Key Principle
VBT assumes that covalent bonds are formed when half-filled atomic orbitals from two atoms overlap. And each overlapping orbital contains one unpaired electron with opposite spins.
and the strength of a bond is proportional to the amount of orbital overlap.

Postulates:

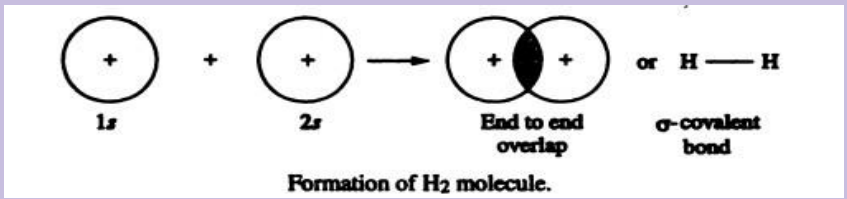
1. A covalent bond is formed when half-filled atomic orbitals of two atoms overlap with each other
   The overlapping region contains shared electrons that contribute to bond formation ,Greater overlap leads to stronger bonds
2. Each overlapping atomic orbital must contain an unpaired electron with opposite spin. The electrons in the overlapping orbitals must have antiparallel spins (in accordance with Pauli's exclusion principle).The electron density is maximum in the region between the two bonding nuclei
3. The overlapping atomic orbitals must have nearly the same (comparable) energy. Bond formation releases energy, making the molecule more stable than isolated atoms. The overlap leads to a decrease in potential energy

4. Covalent bonds are directional in nature. The direction of the bond is determined by the orientation of the overlapping orbitals

Types of Orbital Overlap

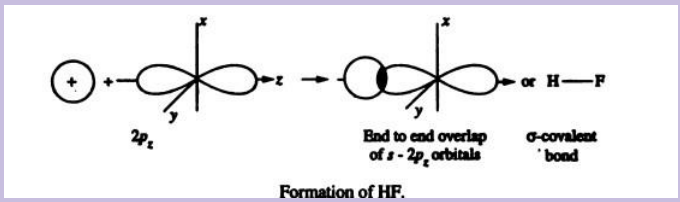
Sigma (σ) Bonds: Formed by head-on (axial/end-to-end) overlap of atomic orbitals along the internuclear axis

s-s overlap: Two s orbitals overlap (e.g., H_2)



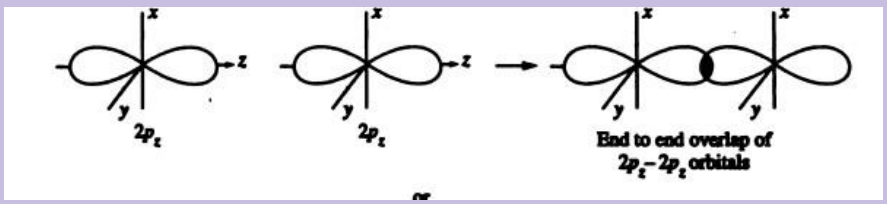
Formation of H_2 molecule.

s-p overlap: One s and one p orbital overlap (e.g., HF)



Formation of HF.

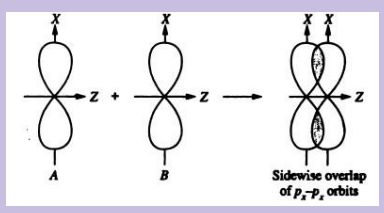
p-p axial overlap: Two p orbitals overlap along their axes (e.g., Cl_2)



Characteristics

- Strongest type of covalent bond
- Allows free rotation around the bond axis
- Cylindrically symmetrical about the internuclear axis
- Found in all single bonds
- Involves in Hybridization

Pi (π) Bonds : Formed by lateral (side-by-side/sideways) overlap of parallel p orbitals perpendicular to the internuclear axis



Characteristics

- Weaker than sigma bonds due to less effective overlap
- Restricts rotation around the bond axis
- Found in double and triple bonds (in addition to sigma bonds)
- The electron density is above and below the internuclear axis
- Do not involve in Hybridization

The Need of Hybridization

methane (CH_4) :

- Carbon's ground state configuration: $1s^2\ 2s^2\ 2p^2$
- It has two unpaired electrons in the 2p orbitals → so we would expect carbon to form only two bonds.
- But experimentally, carbon forms four identical bonds (C–H) of equal length and equal energy, arranged tetrahedrally (109.5°).

Simple overlap of unhybridized orbitals can't explain equal bond energies or geometry

Hybridization says: "Before bonding, atomic orbitals on the central atom mix to form new, equivalent orbitals called hybrid orbitals."

This mixing:

- Gives equal energy orbitals ie explains why all four C–H bonds in CH_4 are identical.
- The resulting orbitals orient themselves symmetrically ie explains specific geometries like linear, trigonal planar, tetrahedral, etc.

So, hybridization is basically a mathematical adjustment to make VBT consistent with experimental evidence.

Is hybridization "real"?

Not exactly. It's a conceptual model, not a physical process that literally "mixes" orbitals in space.

Conditions for Hybridization

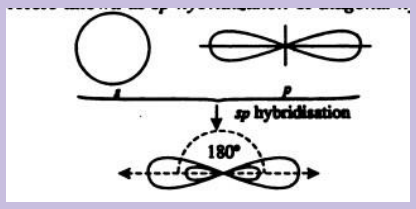
1. Only atomic orbitals of the same atom can undergo hybridization
2. Orbitals participating must have comparable energy (e.g., 2s and 2p)
3. Full, half-filled, or even empty orbitals can participate
4. Number of hybrid orbitals formed = Number of atomic orbitals mixed
5. Electrons from the original orbitals fill the hybrid orbitals following Pauli's exclusion principle and Hund's rule

Characteristics of Hybrid Orbitals

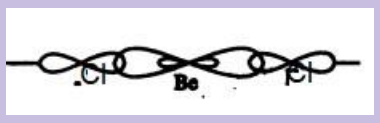
1. All hybrid orbitals of a given type are equivalent in energy and shape
2. Hybrid orbitals have specific orientations in space
3. Hybrid orbitals provide better overlap than pure atomic orbitals, forming stronger bonds
4. Hybrid orbitals participate only in sigma bond formation
5. Hybrid orbitals have different shapes from the original atomic orbitals

$BeCl_2$:

- Beryllium (Be, Z = 4):
- Ground state: No unpaired electrons in valence shell $1s^2\ 2s^2$
- Excited state: One electron promoted from 2s to 2p → $1s^2\ 2s^1\ 2px^1$
- One 2s orbital + one 2p orbital mixes to give Two identical and equivalent sp hybrid orbitals
- Each sp orbital is 50% s and 50% p in character
- Two sp hybrid orbitals orient themselves at 180° to minimize repulsion



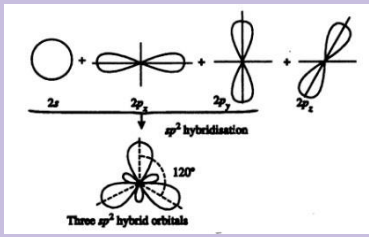
- Each sp hybrid orbital of Be (containing one unpaired electron) overlaps with the half-filled 3p orbital of a Cl atom
- Two σ (sp-p) bonds are formed



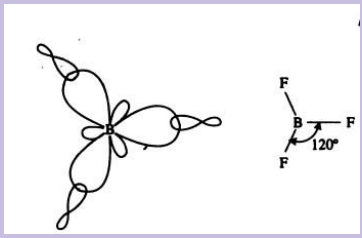
- Molecular geometry Linear
- Bond angle: Cl-Be-Cl = 180°
- Hybridization: sp
- Cl ←—— Be ——→ Cl
  180° (Linear)

BF_3 :

- Boron (Be, Z = 5):
- Ground state: one unpaired electron in valence shell $1s^2\ 2s^2 2px^1$
- Excited state: One electron promoted from 2s to 2p → $1s^2\ 2s^1\ 2px^1 2py^1$
- One 2s orbital + two 2p orbital mixes to give Three identical and equivalent sp^2 hybrid orbitals
- Each sp^2 orbital is 33.33% s and 66.67% p in character
- Three sp^2 hybrid orbitals arrange themselves in a plane at 120° to minimize repulsion
- The unhybridized 2pz orbital remains perpendicular to this plane



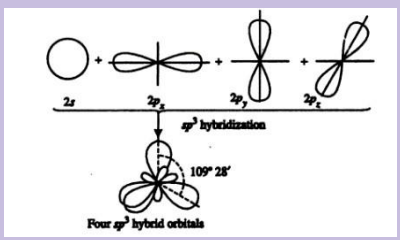
- Each sp^2 hybrid orbital of B overlaps with the half-filled 2p orbital of a F atom
- Three σ (sp^2-p) bonds are formed



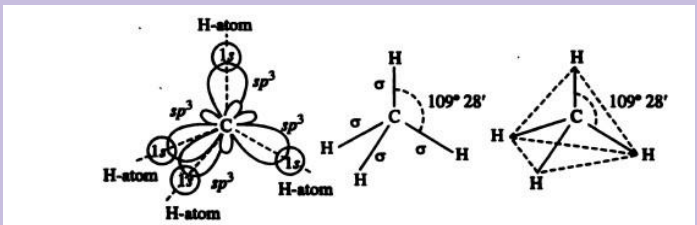
- Molecular geometry: Trigonal Planar
- Bond angle: F-B-F = 120°
- Hybridization: sp^2

CH_4 :

- Carbon (C, Z = 6)
- Ground state: Two unpaired electrons in valence shell $1s^2\ 2s^2\ 2px^1\ 2py^1$
- Excited state: One electron promoted from 2s to 2p → $1s^2\ 2s^1\ 2px^1\ 2py^1\ 2pz^1$
- One 2s orbital + three 2p orbital mixes to give four identical and equivalent sp^3 hybrid orbitals
- Each sp^3 orbital is 25% s and 75% p in character
- Four sp^3 hybrid orbitals arrange themselves to point toward the four corners of a tetrahedron
- This arrangement minimizes electron-electron repulsion
- The bond angle between any C-H is $108^0.28'$



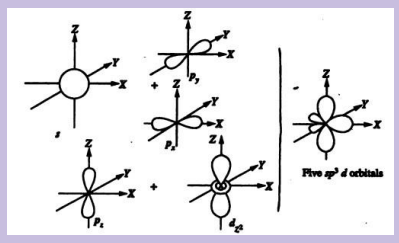
- Each sp^3 hybrid orbital of C (containing one unpaired electron) overlaps with the 1s orbital of a H atom
- Four σ (sp^3-s) bonds are formed



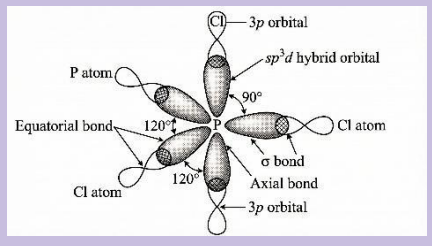
- Molecular geometry: Tetrahedron
- Bond angle: H-C-H = $108^0.28'$
- Hybridization: sp3

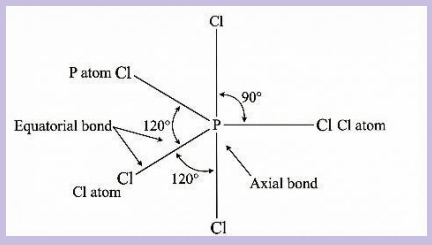
PCl_5:

- Phosphorus (P, Z = 15)
- Ground state: Three unpaired electrons in valence shell [Ne] $3s^2$ $3px^1$ $3py^1$ $3pz^1$
- Excited state: One electron promoted from 2s to 3d→ [Ne] $3s^2$ $3px$ $^13py^1$ $3pz^1$ $3d^1$
- One 2s orbital + three 2p orbital+ one $3d_{z2}$ mixes to give five identical and equivalent sp^3d hybrid orbitals
- Five sp^3d hybrid orbitals arrange in trigonal bipyramidal geometry
- Three equatorial positions in the same plane, 120° apart
- Two axial positions Above and below the equatorial plane, 180° apart
- Axial positions are perpendicular (90°) to the equatorial plane



- Each sp^3d hybrid orbital of P overlaps with the half-filled 3p orbital of a 5 Cl atoms
- Five σ (sp^3d-p) bonds are formed





- Molecular geometry: trigonal bipyramidal
- Equatorial-equatorial 120°
- Axial-equatorial 90°
- Axial-axial 180°
- Hybridization sp^3d

SF_6 :

- Sulphur (S, Z = 16)
- Ground state: Two unpaired electrons in valence shell [Ne] $3s^2$ $3px^2$ $3py^1$ $3pz^1$
- Excited state: One electron promoted each from 2sand 2p to 3d→ [Ne] $2s^1$ $3px^1$ $3py^1$ $3pz^1$ $3d^2$
- One 2s orbital + three 2p orbital+ two $3d_{z2}$, $3d_{x2-y2}$ mixes to give six identical and equivalent sp^3d^2 hybrid orbitals
- Six sp^3d^2 hybrid orbitals themselves arrange toward the six corners of a regular octahedron
  - Four orbitals in a square plane (equatorial)
  - One orbital above and one below this plane (axial)
  - All positions are equivalent in an octahedron

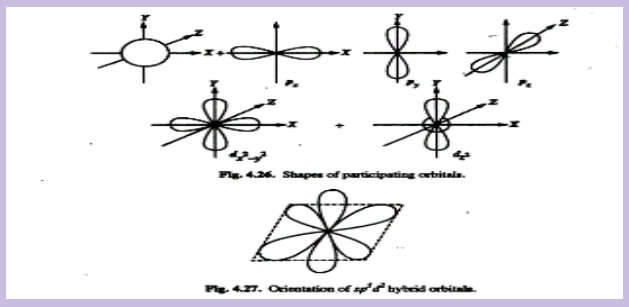
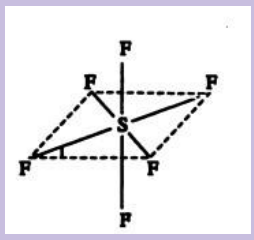


Fig. 4.26. Shapes of participating orbitals.

Fig. 4.27. Orientation of sp^3d^2 hybrid orbitals.

  - Each sp^3d^2 hybrid orbital of S overlaps axially with the half-filled 2p orbital of a F atom
  - Six σ (sp^3d^2-p) bonds are formed



- Molecular geometry: Regular octahedral
- Adjacent F-S-F angles 90°
- Opposite F-S-F angles 180°
- Hybridization sp^3d^2

Merits of Hybridization

1. Predicts the shape of molecules accurately — linear (sp), trigonal planar (sp^2), tetrahedral (sp^3), etc
2. Gives clear bond angles consistent with observations (e.g., 109.5° in CH_4).
3. Explains why all bonds in CH_4, BF_3, etc., are identical in length and strength, despite originating from different orbitals (s and p).
4. Provides 3D picture of bonding directions
5. Extends naturally to explain molecules with expanded octets (PCl_5 → sp^3d, SF_6 → sp^3d^2).

Demerits of Hybridization

1. Hybridization doesn't quantitatively predict bond energies or lengths; it's qualitative and descriptive
2. Modern quantum studies show that in PCl_5 and SF_6, 3d orbitals contribute very little to bonding — the actual bonding is better explained by delocalized molecular orbitals (3-center 4-electron model).
3. Works well for small, simple molecules, but fails for transition metal complexes and molecules with delocalized π systems
4. Can't predict paramagnetism (like in O_2) or electronic transitions
5. Treats bonds as localized and fixed, ignoring the dynamic, delocalized nature of real electron density in molecules

VSEPR :

Nyholm and Gillespie (1957) developed and refined the VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons. this theory is based on the repulsive interactions of the electron pairs in the valence shell of the atoms

- The shape of a molecule depends upon the number of valence shell electron pairs [bonded or nonbonded) around the central atom.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- A multiple bond is treated as if it is a single electron pair, and the two or three electron pairs of a multiple bond are treated as a single super pair.
- Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.
- The repulsive interaction of electron pairs decreases in the order:

Lone pair (lp) - Lone pair (Ip) > Lone pair (Ip) - Bond pair (bp) > Bond pair (bp) - Bond pair (bp)

Why this ordering?

- A lone pair sits close to the nucleus → very dense electron cloud → occupies large volumes → pushes everything away.

- A bond pair is shared between two nuclei → stretched → less concentrated → weaker repulsion.
- A multiple bond (double/triple) is denser than a single bond → behaves "larger" than a single bond → repels more strongly than a single σ bond**.**

NH3:

No of Bond Pairs : 3

No of Lone Pairs : 1

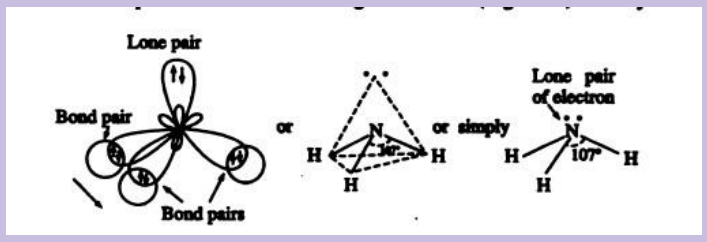
Parent geometry : Tetrahedral (sp3 Hybridization)

Actual shape : Trigonal pyramidal

Reason: The lone pair sits close to N and pushes the three N–H bonds downward

Repulsion Order: LP–BP > BP–BP

Effect : This compression gives a bond angle of 107°, slightly less than tetrahedral 109.28°.



H_2O:

No of Bond Pairs : 2

No of Lone Pairs : 2

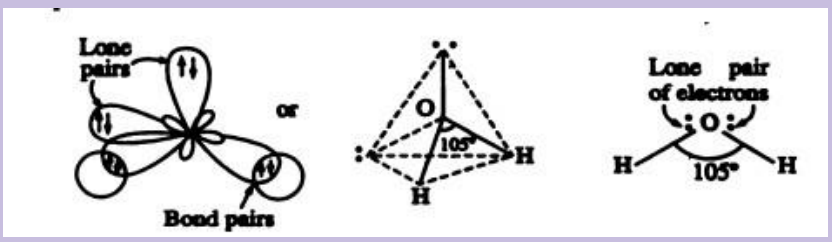
Parent geometry : Tetrahedral (sp3 Hybridization)

Actual shape : V or bent shape

Reason: Two lone pairs create strong repulsive forces on Oxygen atom

Repulsion Order: LP–LP > BP–BP

Effect : Water's H–O–H angle shrinks to 104.5° less than tetrahedral 109.28°



SF_4 :

No of Bond Pairs : 4

No of Lone Pairs : 1

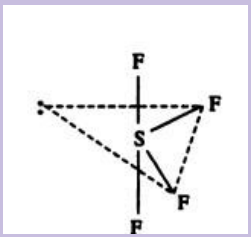
Parent geometry : Trigonal bipyramidal (sp^3d Hybridization)

Actual shape : Seesaw shape

Reason: In Trigonal Bi Pyramidal the lone pair always occupies an equatorial site. Lone pair in equatorial squeezes the two axial S–F bonds. The molecule bends slightly and becomes a "distorted seesaw"

Repulsion Order: LP–LP > BP–BP

Effect :



ICl_2^- :

No of Bond Pairs : 2

No of Lone Pairs : 3

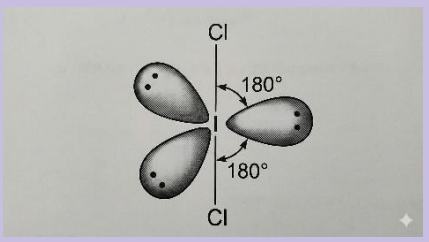
Parent geometry : Trigonal bipyramidal (sp^3d Hybridization)

Actual shape : Linear shape

Reason: In Trigonal Bi Pyramidal the lone pair always occupies an equatorial site. Lone pairs cancel distortions in that plane. Only two axial positions remain for bonds with 180° apart

Repulsion Order: LP–LP > BP–BP

Effect : two bond pairs fall into perfect linear geometry



XeF_4

No of Bond Pairs : 4

No of Lone Pairs : 2

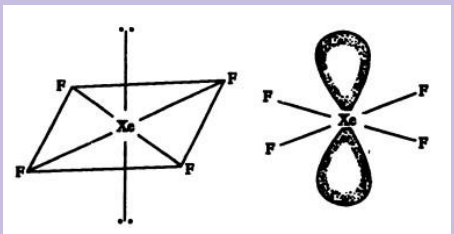
Parent geometry : Octahedral (sp^3d^2 Hybridization)

Actual shape : Square Planar

Reason: All sites start equivalent in an octahedron. But with two lone pairs, VSEPR places lone pairs opposite each other (180°) to minimize LP–LP repulsion (strongest) This sets the lone pairs on the "top" and "bottom," leaving a square of four F atoms in a perfect plane

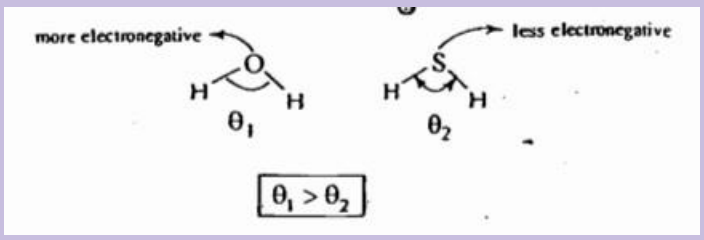
Repulsion Order: LP–LP > BP–BP

Effect : Two lone pairs positioned opposite cancel distortions gives a square planar structure

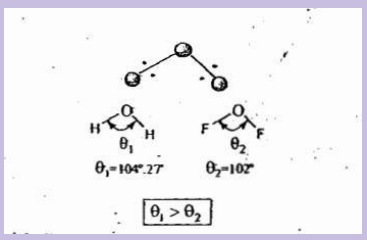


Secondary Effects of VSEPR

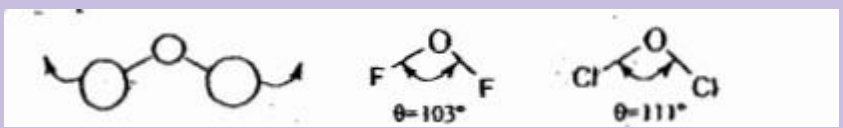
1. The repulsion between electron pair increases with increase in electronegativity of central atom and hence the bond angle decreases. The bond pairs are closer and thus by shortening the distance between them, which in turn increases the repulsion. Hence the bonds tend to move away from each other. e.g., H_2O, H_2S



2. However, the bond angle decreases when the electronegativities of bonded atoms are more than that-of central atom. There is increase in the distance between bond pairs since they are now closer to bonded atoms .Due to this, they tend to move closer resulting in the decrease in bond angle. e.g. H_2O, F_2O



3. However, the bond angle increases with increase in the size of ligand atoms, which surround the central atom. These is more repulsion between bigger ligand atoms and hence they tend to move away from each other Thus bond angle increases.



MOLECULAR ORBITAL THEORY:

To explain the formation of the covalent bond in molecules/ions and their behaviour like relative bond strength, magnetic property etc., a new approach was developed by Hund and Mulliken in 1932 and later by Lennard Jones and Coulson. This approach is known Molecular Orbital Theory

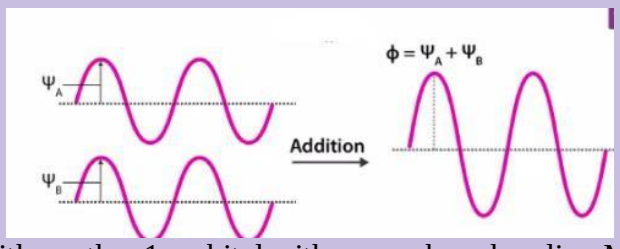
LCAO METHOD:

Molecular Orbitals (MOs) which are associated with the entire molecule and result from the linear combination of atomic orbitals (LCAOs) of constituent atoms of the molecule/ion

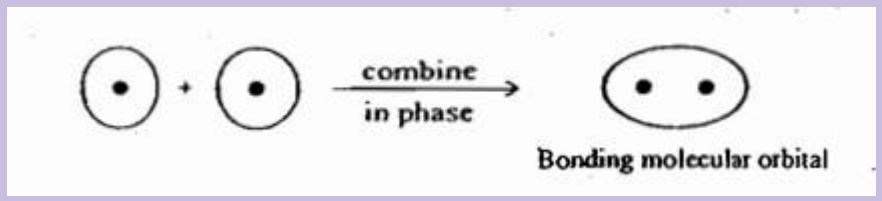
Suppose Ψ_A and Ψ_B represent the wave function of the electrons in the A.Os. of the atoms A and B respectively. Then linear combination of these A.Os. may be done in two ways

$\Psi_{bonding} = \Psi_A + \Psi_B$ (++ combination)

This additive combination of AOs when sign of wave functions are same gives bonding molecular orbital for which the wave function is denoted by $\Psi_{bonding}$ .This is also called constructive interaction

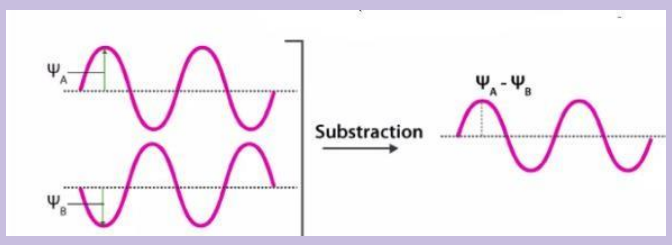


for example if 1s orbital with another 1s orbital with same phase bonding MO formed

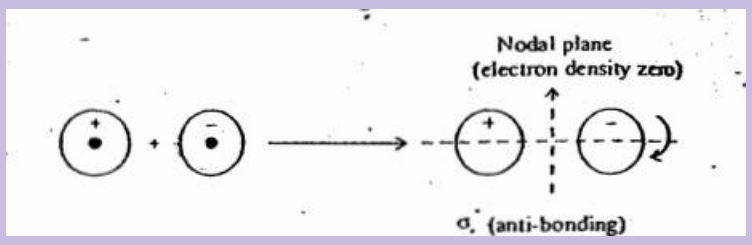


$\Psi_{anti\ bonding} = \Psi_A - \Psi_B$ (+- combination)

This subtractive combination of AOs when sign of wave functions are opposite gives anti bonding molecular orbital for which the wave function is denoted by $\Psi_{anti\ bonding}$ .This is also called destructive interaction



for example if 1s orbital with another 1s orbital with opposite phase anti bonding MO formed



The probability density in bonding and antibonding molecular orbitals is given by the square of the wave function

$\Psi^2_{bonding} = (\Psi_A+\Psi_B)^2 = \Psi^2_A + \Psi_B^2 + 2\,\Psi_A\,\Psi_B$ ……. Eq 1

$\Psi^2_{anti\text{-}bonding} = (\Psi_A-\Psi_B)^2 = \Psi^2_A + \Psi_B^2 - 2\,\Psi_A\,\Psi_B$ ……. Eq 2

From equation (1) it is clear that the probability density of bonding molecular orbital is greater than the sum of the probability densities $\Psi^2_A + \Psi_B^2$ of isolated atoms by the factor $2\,\Psi_A\,\Psi_B$. Thus the probability density of electrons in bonding MO is greater than that in either of atomic orbital Ψ^2_A or Ψ_B^2 But in case of antibonding MO the probability density is lesser than the sum of probability densities of isolated atoms $\Psi^2_A + \Psi_B^2$ by the factor $2\,\Psi_A\,\Psi_B$ (equation-2). Thus the probability density of electrons in ABMO's is lesser than that in either of atomic orbitals Ψ^2_A (or) Ψ_B^2

Example :

The formation of a o($2p_z$) BMO by the linear- additive combination of two $2p_z$.atomic orbitals as represented below

$2p_z$ AO + $2p_z$ AO $\sigma 2p_z$ BMO

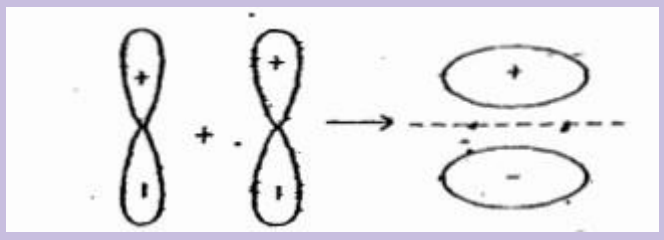
The formation of a o($2p_z$) BMO by the linear- subtractive combination of two $2p_z$.atomic orbitals as represented below

The corresponding AMBO o^*2p_z is obtained by the linear substrative combination of two 2p atomic orbitals as represented below

$2p_z$ AO + $2p_z$ AO o^*2p_z ABMO

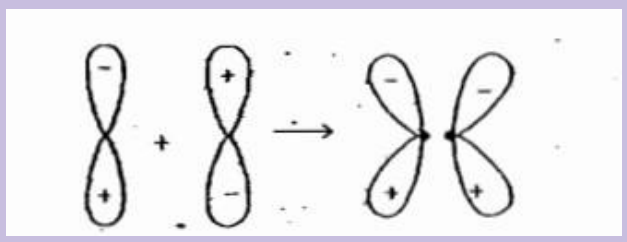
The combination of $2p_x$ and $2p_y$ atomic orbitals:

Suppose a $2p_x$ orbital of an atom overlaps with a $2p_y$ orbital of another atom overlapping is positive but it is side to side and not end to end as in the case of $2p_z$ orbital The resulting molecular orbitals are called π molecular orbitals The formation of BMO's designation as $\pi_{2px}\,\pi_{2py}$
as showing below



$2p_x$ AO + $2p_y$ AO $\pi_{2px}\,\pi_{2py}$ BMO

Similarly the ABMO are which are in high energy similarly charge nuclei are not effectively surrounded by the electronic charge (-ve) and therefore repel each other considerably. as showing below



$2p_x$ AO - $2p_y$ AO $\pi^*_{2px}\,\pi^*_{2py}$ ABMO

Postulates of Molecular Orbital Theory :

1. The atomic orbitals (AOs) combining linearly together to form the molecular orbitals (MOs) lose their identity and the number of atomic orbitals is equal to the number of molecular orbitals formed.
2. The linear combination of the AOs may occur in two different ways, i.e. the additive combination gives bonding molecular orbitals (BMOs) and the subtractive combination gives antibonding molecular orbitals (ABMOs)
3. The bonding MO has lower energy and hence greater stability than the antibonding MO which is higher un energy and less stable obtained from two AOs
4. The bonding MOs are denoted by σ,π, etc. symbols while the antibonding MOs by σ * ,π * etc. symbols.
5. MOs are the energy states of the molecules/ions in which the electrons are filled according to Pauli ,Hund's and Auf-bau principles
6. The order of energy of MO for Total electrons >14

   $\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2pz} < \pi_{2px} = \pi_{2py} < \pi^*_{2px} = \pi^*_{2py} < \sigma^*_{2pz}$

7. The order of energy of MO for Total electrons ≤ 14

   $\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \pi_{2px} = \pi_{2py} < \sigma_{2pz} < \pi^*_{2px} = \pi^*_{2py} < \sigma^*_{2pz}$

8. The bond order is $= \frac{1}{2}(N_b - N_a)$

   N_b = No of electrons in bonding MO , N_a = No of electrons in bonding ABMO

CONDITIONS FOR THE COMBINATION OF ATOMIC ORBITALS :

1. The combining atomic orbitals must have the same or nearly the same energy i.e. his means that 1s orbital can combine with another 1s orbital but not with 2s orbital
2. The combining atomic orbitals must have the same symmetry i.e. 2pz orbital of one atom can combine with 2pz orbital of the other atom but not with the 2px or 2py orbitals because of their different symmetries.
3. The combining atomic orbitals must overlap to the maximum extent. Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.
4. S-P MIXING : the 2s and 2pz orbitals have the same symmetry (σ). if their energies are close enough (as in N, C, B), they "mix" or hybridize slightly. this mixing pushes the lower even lower σ_{2s} and pushes the higher σ_{2Pz} higher, even above the orbitals.

   With Mixing $\pi_{2px} = \pi_{2py} < \sigma_{2pz}$ (Total electrons $\leq$ =14)

   Without mixing $\sigma_{2pz} < \pi_{2px} = \pi_{2py}$ (Total electrons >14)

MO diagram for N_2

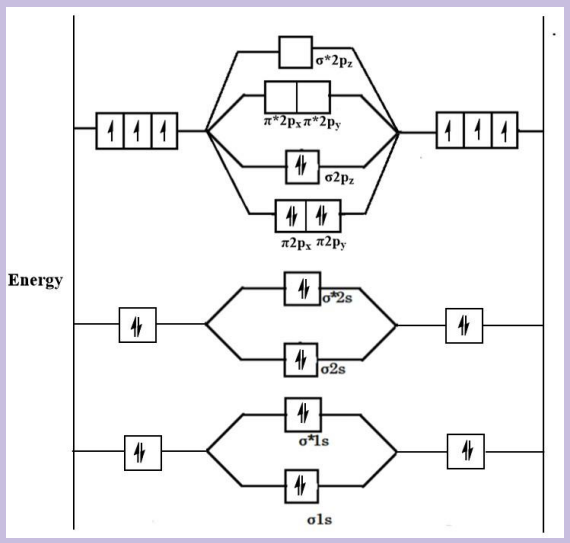
Total Electrons: 14 (7 from each N).

Key Feature: Strong s-p mixing. The σ_{2pz} is pushed above the $\pi_{2px} = \pi_{2py}$

Configuration: $\sigma_{1s}^2 < \sigma^*_{1s}^2 < \sigma_{2s}^2 < \sigma^*_{2s}^2 < \pi_{2px}^2 = \pi_{2py}^2 < \sigma_{2pz}^2 < \pi^*_{2px} = \pi^*_{2py} < \sigma^*_{2pz}$

Bond Order: $= \frac{1}{2}(N_b - N_a) = = \frac{1}{2}(10 - 4) = 3$ (Triple Bond)

Magnetism: Diamagnetic (All paired).



MO diagram for O_2

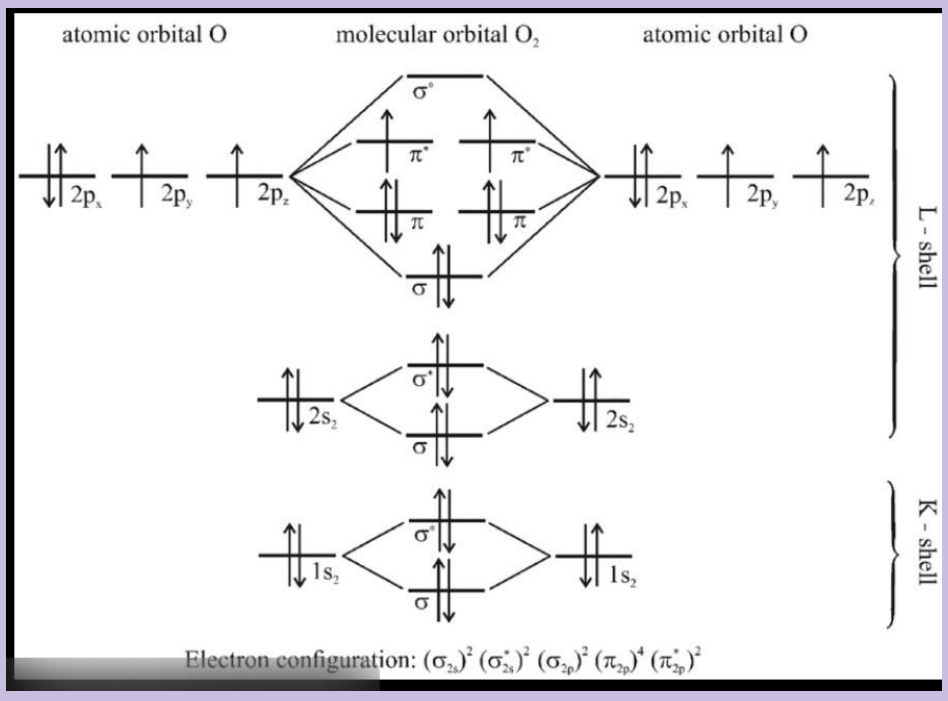
Total Electrons: 16 (8 from each O).

Key Feature: No s-p mixing due to Total electrons >14 hence The σ_{2pz} is below the $\pi_{2px} = \pi_{2py}$

Configuration: $\sigma_{1s}^2 < \sigma^*_{1s}^2 < \sigma_{2s}^2 < \sigma^*_{2s}^2 < \sigma_{2pz}^2 < \pi_{2px}^2 = \pi_{2py}^2 < \pi^*_{2px}^1 = \pi^*_{2py}^1 < \sigma^*_{2pz}$

Bond Order: $= \frac{1}{2}(N_b - N_a) = = \frac{1}{2}(10 - 6) = 2$ (Double Bond)

Magnetism: paramagnetic due to two unpaired electrons in π^*



MO diagram for CO

Total Valence Electrons: 10 (4 from C and 6 from O). iso electronic to N_2

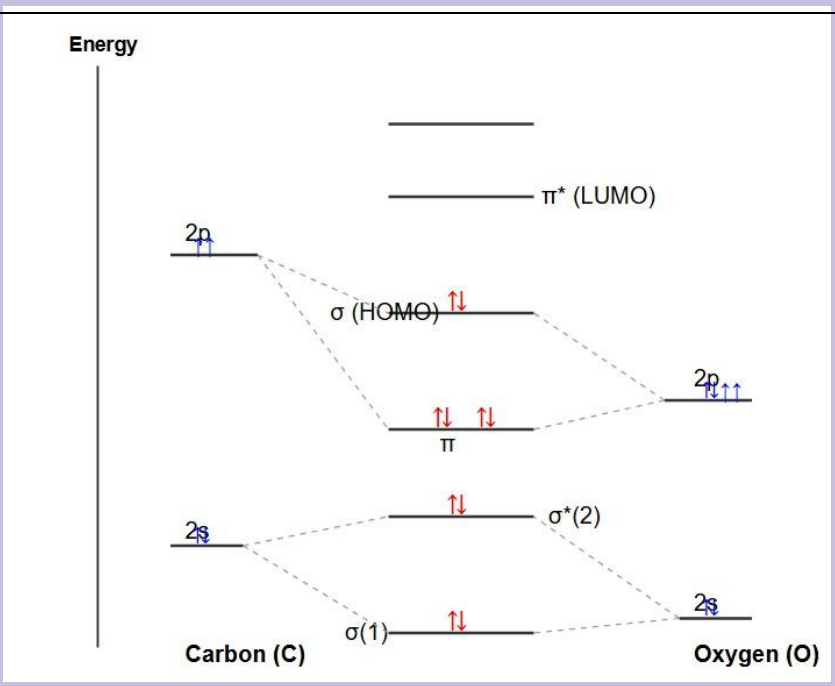
Key Feature: s-p mixing due to Total electrons $\leq$14 hence The σ_{2pz} is pushed above the $\pi_{2px} = \pi_{2py}$

Electronegativity difference. Oxygen orbitals are lower in energy

Configuration: $\sigma_{2s}^2 < \sigma^*_{2s}^2 < \pi_{2px}^2 = \pi_{2py}^2 < \sigma_{2pz}^2 < \pi^*_{2px} = \pi^*_{2py} < \sigma^*_{2pz}$

Bond Order: $= \frac{1}{2}(N_b - N_a) = = \frac{1}{2}(8 - 2) = 3$ (Triple Bond)

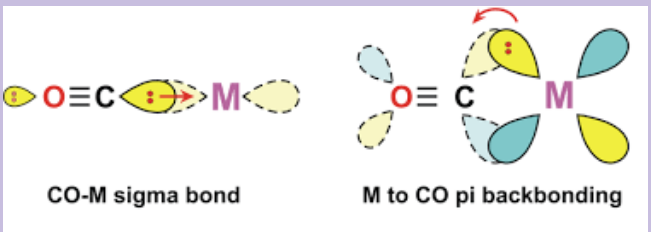
Magnetism: Diamagnetic (All paired).



In CO molecule the carbon has more affinity towards to Metal carbonyls rather than oxygen due to Carbon's 2s/2p are higher in energy (less electronegative) and Oxygen's 2s/2p are lower in energy (more electronegative) Because oxygen is more electronegative, its orbitals are pulled down, making

$E_{2p}C > E_{2p}O$

When orbitals with different energies combine the MO closer in energy to carbon AOs gets more carbon character and the MO closer in energy to oxygen AOs gets more oxygen character since the HOMO is the highest filled orbital, it closer to carbon's atomic p orbital .The HOMO is mostly carbon in character. And higher-energy lone pair more available for donation



MO diagram for NO

Total Valence Electrons: 11 (5 from N and 6 from O).

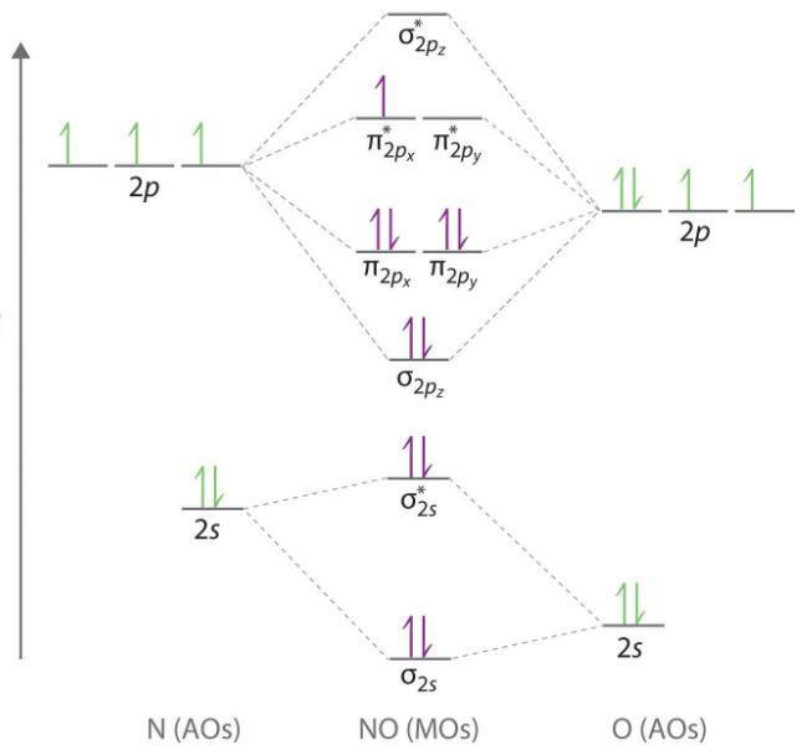
Key Feature: No s-p mixing due to Oxygen has more Z_{eff} high nuclear charge it pushes down the 2s orbital of N there by increasing energy gap between 2s and 2p of N and resists s-p mixing and hence resulting MO's are low in energy under control of Oxygen

Due to Electronegativity difference. Oxygen orbitals are lower in energy

Configuration: $\sigma_{2s}^2 < \sigma^*_{2s}{}^2 < \sigma_{2pz}{}^2 < \pi_{2px}{}^2 = \pi_{2py}{}^2 < \pi^*_{2px}{}^1 = \pi^*_{2py} < \sigma^*_{2pz}$

Bond Order: $= \frac{1}{2}(N_b - N_a) \quad = = \frac{1}{2}(8 - 3) = 2.5$

Magnetism: paramagnetic due to one unpaired electrons in π^*



QUESTION BANK

UNIT-3 LONG ANSWER QUESTIONS 10 MARKS

1. Define Valence Bond Theory and describe the concept of hybridization with examples like BF_3, CH_4, and PCl_5
2. Explain the Molecular Orbital Theory and draw the MO diagrams for N_2, and CO molecules.
3. Discuss the types of hybridization and their relation to molecular geometry with examples
4. Discuss the VSEPR theory and predict the shapes of NH_3, H_2O, SF_4, ICl^{-2}, and XeF_4 molecules

SHORT ANSWER QUESTIONS 5 MARKS

1. What are sigma and pi bonds?
2. Apply VSEPR model to predict the geometry of NH_3 and H_2O molecules
3. How MOT explains magnetic behaviour of molecules
4. Give differences between VBT and MOT
5. Define hybridization and give examples

MAJOR-1: GENERAL CHEMISTRY

UNIT-IV METALLIC AND HYDROGEN BONDS (9 Hrs.)

Metallic bond: Metallic properties, free electron theory, band theory of metals. Explanation of conductors, semiconductors, and insulators.

Hydrogen bonding: Intra and Inter-molecular hydrogen bonding, influence on the physical properties of molecules, Van der waals forces, dipole-dipole interactions.

METALLIC PROPERTIES:

An element is said to be metal if it loses its outer most electrons easily to form cation

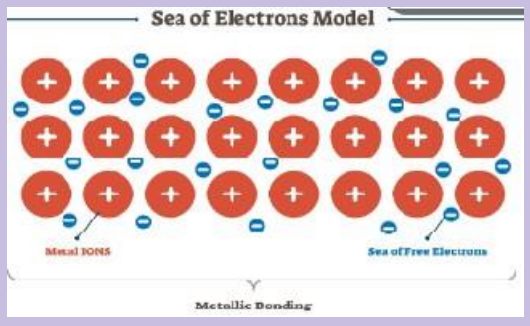
1. They are good conductor of electricity.
2. They are good conductor of heat.
3. They possess a unique lustre as their surface is good reflector of light and appears shining.
4. They can be beaten into sheets (malleable) and can be drawn into wires (ductile) .
5. They have high tensile strength.
6. They possess elasticity.

These specific properties of metals cannot be explained by covalent and ionic bonds as former needs different atoms and later needs valence electrons hence they are ruled out

The metallic bond is the force of attraction between the fixed positive metal ions (kernels) and the delocalized mobile electrons that surround them.

Free Electron Theory (Drude-Lorentz Theory) or Electron Sea Model:-

- As the ionization energy of these metals is low so that some of these metals easily loose electrons from their outermost shell and form cation. These cations are called kernels
- Since nucleus is present in these +vely charged Kernels, therefore they are heavy and hence, occupy fixed position in metal lattice
- The electrons which are lost by metals are free to move in the space present between Kernels
- As a result the positive ions (kernels) are submerged in a "sea" or "pool" of these negative electrons Thus, this model is called electron sea model or electron gas model.
- The metal is held together by the electrostatic attraction between the positive kernels and the negative electron sea



The Free Electron Theory to able to explain the metallic properties

Property	Explanation via Free Electron Theory
Electrical Conductivity	Because the electrons are free (delocalized), applying a voltage pushes them towards the positive terminal. They drift like a fluid.
Thermal Conductivity	When you heat one end, the free electrons gain kinetic energy and move rapidly to the cooler end, transferring heat quickly.
Malleability & Ductility	The bond is non-directional. If you hit a metal with a hammer, layers of ions slide over each other, but the "sea" of electrons adjusts immediately to keep holding them together. The bond doesn't break; it just shifts.
Lustre (Shine)	Mobile electrons absorb light energy and oscillate, then immediately re-emit it as visible light.
High Tensile strength	Because Strong electron cloud glues cations tightly and they can resist stretching without breaking
Elasticity	Because metal ions can move from one lattice site to another .They can recover their original form soon after the removal of the deforming force

Limitations of free electron theory:-

- This theory cannot explain why certain metals behave as semiconductor in solid state.
- It cannot explain specific heat, temperature dependence of conductivity

BAND THEORY OF METALS:

- This theory is an extension of the molecular orbital theory. When numerous metal atoms come together, their atomic orbitals overlap to form distinct "bands" of energy rather than single energy levels
- Valence Band: The band containing the valence electrons. It is the highest filled energy range.
- Conduction Band: The energy band above the valence band. It is effectively "empty" or partially filled. Electrons must be here to move and conduct electricity.
- Forbidden Zone (Energy Gap or Band Gap, E_g): The energy difference between the valence and conduction bands. No electrons can exist here

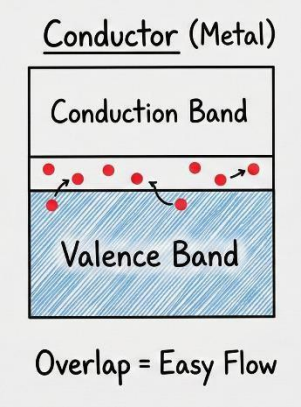
CONDUCTORS, SEMICONDUCTORS, AND INSULATORS

CONDUCTORS

Band Structure: The Valence Band and Conduction Band **overlap**. There is no energy gap ($E_g \equiv 0$).

Electron Movement **:** Electrons can move effortlessly from the valence area to the conduction area.

Effect of Temperature**:** As temperature increases, conductivity **decreases**. (Reason: Vibrating positive ions obstruct the flow of electrons).

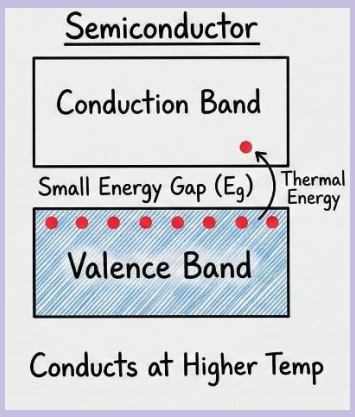


SEMICONDUCTORS (e.g. Silicon, Germanium)

Band Structure: There is a small energy gap ($E_g < 3$ ev) between valence band and conduction band

Electron Movement **:** At room temperature, some electrons gain enough thermal energy to jump the small gap into the conduction band. However at absolute zero (0 K), they act like insulators.

Effect of Temperature**:** As temperature increases, conductivity increases (because more electrons gain the energy to jump the gap)

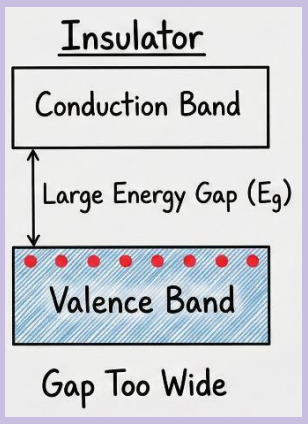


INSULATORS (e.g. Glass, Rubber)

Band Structure: There is a very large energy gap ($E_g > 3$ ev) between valence band and conduction band often much higher like ($E_g > 6$ ev)

Electron Movement **:** The gap is too wide. Ordinary thermal energy is not enough to kick electrons up to the conduction band. The conduction band remains empty.

Result: No flow of current.



Some Intelligentsia thought provoking stuff after you complete the above

1. Why does Magnesium conduct electricity better than Sodium?

Magnesium contributes 2 valence electrons per atom to the "sea of electrons ," while Sodium contributes only 1. More charge carriers more is the conductivity.

2. Why do metals get hot when current flows through them?

The moving electrons collide with the fixed metal ions (kernels), causing the ions to vibrate faster and make them to release heat.

3. According to Band Theory, what happens to the band gap if we turn a semiconductor into a metal?

The band gap would disappear hence complete overlap between conduction and valence bands

4. Beryllium ($1s^2$ $2s^2$) has a completely full valence shell. According to the rules, a full shell means it should be an inert gas or an insulator. Why is it a metal?

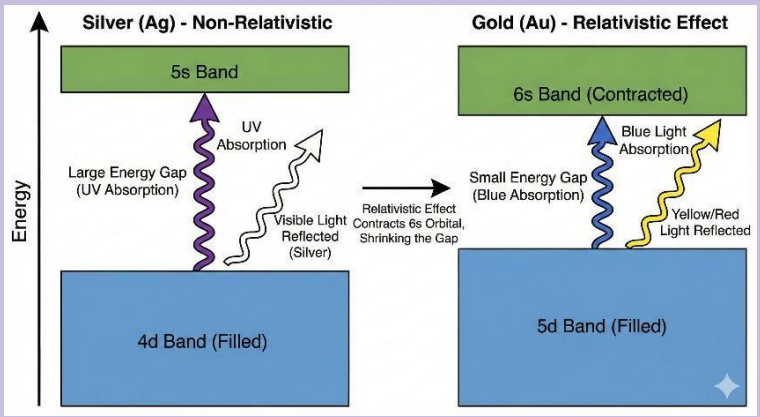
In a single isolated atom, the 2s and 2p energy levels are distinct. However, in a crystal lattice, the energy bands spread out. In Beryllium, the empty 2p band overlaps with the filled 2s band. Because of this overlap, electrons can easily flow from the filled 2s area into the empty 2p area, acting as conduction electrons.

5. If we keep a wooden block and a steel spoon in the same AC room (20^C), why does the metal feel colder?

They are actually at the same temperature our nerves don't measure temperature they measure the rate of heat transfer. Metals have free electrons that act as "heat carriers." When you touch the metal, these electrons rapidly absorb heat from your finger and speed away into the bulk of the metal (High Thermal Conductivity, K). Wood lacks these free carriers, so heat leaves your finger very slowly

6. Silver (Ag) is grey. Copper (Cu) and Gold (Au) are coloured. Why

Gold is a heavy atom with a massive positive charge (+79). The inner 6s-electrons orbit so fast (near the speed of light) their mass increases and orbit start contracts. This contraction stabilizes the 6s orbital and effectively raises the energy of the 5d band. The energy gap for an electron to jump from 5d 6s shrinks to the energy of blue light. Gold absorbs blue and reflects the rest (Yellow). Silver absorbs in the UV range (invisible to us), so it reflects all visible light (White/Grey).



7. Adding impurities to Silicon increases conductivity (doping). But adding impurities to Copper (making an Alloy like Brass) decreases conductivity. Why the opposite behaviour?

In Semiconductors Silicon You are adding charge carriers (electrons) where there were very few.

$$n\uparrow \approx \text{Conductivity} \downarrow$$

In Metal Copper) have millions of charge carriers. Adding extra disrupts the perfect crystal arrangement. These cause the electrons to scatter more often.

$$\text{Mean Free Path } \lambda\downarrow \approx \text{ Resistivity}\uparrow$$

8. Are there any repulsions between electrons when they are dallying around metal kernels

   Yes, electrons do repel each other, but in a metal that repulsion does not destroy the metallic bond. According to quantum mechanics they occupy different quantum states, they do not crowd into the same region of space, which reduces direct repulsion. Hence electrons in a metal are mostly spread out and so strongly attracted to the ion lattice that their repulsion becomes a minor factor.

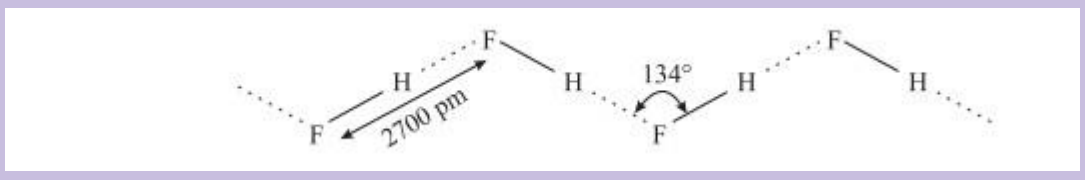
HYDROGEN BONDING

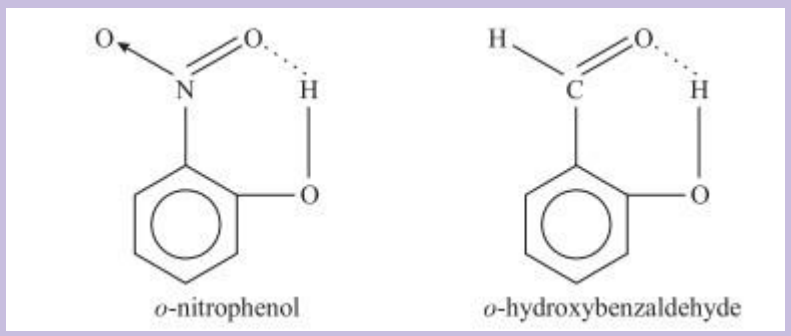
Hydrogen bonding is a specific type of dipole-dipole interaction that occurs when a hydrogen atom covalently bonded to a highly electronegative atom interacts with another electronegative atom possessing lone pair electrons. The most common electronegative atoms involved in hydrogen bonding are nitrogen (N), oxygen (O), and fluorine (F).

The hydrogen bond is often represented as: A−H···B A−H···B where A is the electronegative atom bonded to hydrogen, and B is the electronegative atom with lone pair electrons. This interaction is stronger (20-40 kJ/mol) than typical dipole-dipole forces (3-4 kJ/mol) but weaker than covalent or ionic bonds (>200 kJ/mol)

Electronegativity plays a pivotal role in hydrogen bonding. When hydrogen is bonded to a highly electronegative atom like O, N, or F, the bond becomes polar, with hydrogen acquiring a partial positive charge (δ^+) and the electronegative atom a partial negative charge (δ^-). This polarity facilitates the attraction between the hydrogen atom and the lone pair electrons of another electronegative atom, forming a hydrogen bond.

For example, in water (H_2O), the oxygen atom is more electronegative than hydrogen, resulting in polar O-H bonds. The partial positive charge on hydrogen atoms attracts lone pairs on adjacent oxygen atoms, leading to a network of hydrogen bonds





Strength of Hydrogen Bonds

Hydrogen bonds are relatively strong intermolecular forces, with bond energies ranging from 20 to 40 kJ/mol.

The strength of a hydrogen bond depends on several factors:

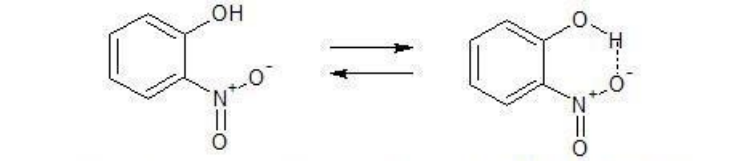
- Electronegativity: Higher electronegativity of the involved atoms increases bond strength.
- Distance: Shorter distances between the hydrogen donor and acceptor enhance bond strength.
- Angle: Linear orientations typically result in stronger hydrogen bonds

INTRA -MOLECULAR HYDROGEN BONDING

The Hydrogen bonding occurs within the same molecule is called Intra(within) molecular hydrogen bonding

The molecule forms ring like (chelation) structure

Examples : Ortho Nitrophenol ,Ortho Nitro benzaldehyde ….



o-nitrophenol forms an intramolecular hydrogen bond MP~ 44 C, BP 215 C

Effects

Molecule becomes more compact.

Boiling point decreases (behaves like an individual molecule, not clustered).

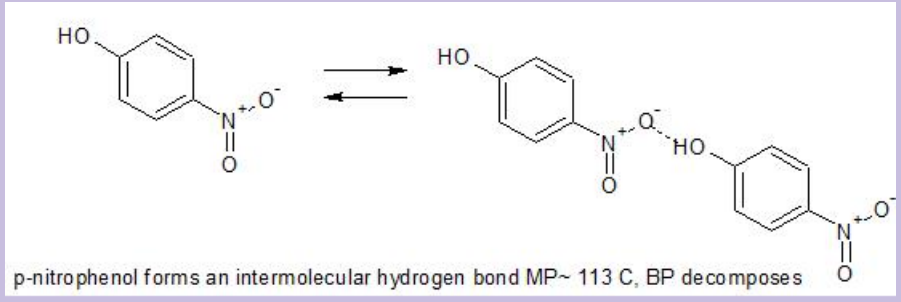
Solubility in water decreases because internal H-bonding reduces interaction with solvent

Intramolecular H-bonding locks the molecule into a ring, reducing external interactions

INTER-MOLECULAR HYDROGEN BONDING

The Hydrogen bond forming between two different molecule is called Inter (between) molecular hydrogen bonding

It causes molecules to cluster together (Association)



p-nitrophenol forms an intermolecular hydrogen bond MP~ 113 C, BP decomposes

Examples : Water, HF, Para Nitrophenol ….

Effects

Molecules associate into clusters

Boiling point increases (more energy needed to break clusters)

Melting point increases

Viscosity increases

Solubility in water increases (H-bonding with water)

INFLUENCE ON THE PHYSICAL PROPERTIES OF MOLECULES

(i) Boiling and Melting Points

Strong intermolecular hydrogen bonds lead to higher boiling and melting points and hence requires more heat energy to separate them into gas

(water > H_2S; alcohols > alkanes)

(ii) Solubility

If a compound can form Hydrogen-bonding with water it dissolves

Example: Alcohols, sugars, amino acids.

Intramolecular H-bonding lowers solubility.

(iii) Viscosity and Surface Tension

Hydrogen bonding leads to network formation, increasing viscosity.(resistance to flow)

Example: glycerol > ethanol > acetone.

(iv) Density Anomalies

In liquid water, hydrogen bonding creates an open structure (more empty volume)hence ice becomes less dense than water

Some Intelligentsia thought provoking stuff after you complete the above

1. Can Carbon form a Hydrogen Bond?

Yes! In terminal alkynes (R-C ≡ C-H). The sp hybridized carbon is electronegative enough (50% s-character) to make the Hydrogen acidic. that's why Acetone + Acetylene shows negative deviation in Raoult's law due to this C-H...O bond**.**

2. HF has the strongest Hydrogen bonding (fluorine is most electronegative), yet water (H_2O) has a higher boiling point (100^C vs 20^C). Why?

HF forms strong bonds, but each HF has only 1 H-atom to donate. It forms a linear chain (1 bond per molecule average). Water has 2 H-atoms and 2 Lone Pairs. It forms a 3D Tetrahedral Cage (4 bonds per molecule).

3. Why does NH_3 form strong Hydrogen bonds (Liquid), but HCl(Gas) does not ?

Nitrogen is small (75 pm), so its lone pair is confined to a tiny volume (High Charge Density).It is large (99 pm) with 3d orbitals available. Its lone pair is spread out over a large volume.(Low Charge Density).Hence NH_3 form strong Hydrogen bonds than HCl

4. Why does ice float on water?

H-bonding creates an open "cage-like" structure in ice, creating empty spaces. This makes ice less dense than liquid water

5. Why is ortho-nitrophenol steam volatile, but para-nitrophenol is not?

Ortho has Intra-molecular bonding (chelation), so it easily escapes into the steam. Para has Inter-molecular bonding (more association or cooperativity), so it stays in the liquid

6. Is the $[F^- —H--- F^-]$ bond in KHF_2 hydrogen bond ?
   No in bifluoride ion $[F^- —H--- F^-]$ the hydrogen is between two fluorine atoms and the bond energy 165 kJ/mol normally hydrogen bond energy is 30-40 kJ/mol .it is an 3 centred 4 electron bond
7. Why is DNA held together by Hydrogen Bonds and not Covalent Bonds?

   If DNA were held by Covalent Bonds, It would be too strong. The DNA strands could never separate to replicate. Life would be frozen .
   If DNA were held by Hydrogen Bond, It is strong enough (in large numbers) to hold the genetic code stable, but weak enough (individually) to be broken by enzymes when the cell needs to divide.

VAN DER WAALS FORCES

Van der Waals forces are weak, short-range intermolecular attractions arising from electron motion.

They are present in all molecules and dominate when stronger forces are absent.

These arise due to instantaneous dipoles formed by random electron motion.

An instantaneous dipole induces a dipole in a neighbouring molecule, producing attraction.

Present in all molecules (only force in non-polar substances)

Strength increases with molecular size, number of electrons, and surface area

Straight-chain molecules show stronger forces than branched ones

van der Waals forces decide physical behaviour.

Standard examples:

Noble gases: He < Ne < Ar < Kr < Xe (boiling points increase)

Halogens: F , Cl (gases),Br (liquid) , I (solid)

DIPOLE–DIPOLE INTERACTIONS

They occur between polar molecules with permanent dipole moments.

The positive end of one molecule attracts the negative end of another.

Directional in nature

Stronger than dispersion forces for similar-sized molecules

Weaker than hydrogen bonding

only polar molecules show dipole–dipole interactions

Examples: HCl, CH Cl, acetone.

Relative strength: Van der Waals forces < Dipole–dipole < Hydrogen bonding

QUESTION BANK

LONG ANSWER QUESTIONS 10 MARKS

1. Explain the free electron theory and band theory of metals.

2. Describe different types of hydrogen bonding with suitable examples and discuss their significance in physical properties of molecules

SHORT ANSWER QUESTIONS 5 MARKS

1. What are Van der Waals forces?

2. What are semiconductors and insulators

3. Define metallic bond and mention its characteristics.

4. . Differentiate between intra- and intermolecular hydrogen bonding, giving examples

MAJOR-1: GENERAL CHEMISTRY

UNIT-V: NUCLEAR CHEMISTRY (9 Hrs)

Definition, Isotopes, n/p ratio, binding energy, types of radioactivity, Soddy-Fajan's displacement law, Law of Radioactivity, Radioactive decay series, Nuclear Reactions- Fission and Fusion, Applications of radioactivity in agriculture and medicine.

Definition, n/p ratio, binding energy, types of radioactivity : It is that branch of chemistry in which we study about the nucleus of atom.

Isotopes :When two or more atoms have same atomic number but different mass number they are called as isotopes. Iso = Same, Topes = Position

Examples: $^{6}C_{12}$,$^{6}C_{13}$, $^{6}C_{14}$ $^{1}H_{1}$ Hydrogen , $^{1}H_{2}$ Deuterium, $^{1}H_{3}$ Tritium Uranium-234, Uranium-235, Uranium-238

Types of Isotopes:

(1) Non-Radioactive Isotopes or Stable Isotopes:

The isotopes which have stable nuclei and do not decompose spontaneously.

For example Carbon has three isotopes: $^{6}C_{12}$,$^{6}C_{13}$ and $^{6}C_{14}$ and $^{6}C_{12}$,$^{6}C_{13}$ are nonradioactive isotopes and $^{6}C_{14}$ is a radioactive isotope.

(2) Radioactive Isotopes:

The isotopes which have unstable nuclei, and these nuclei decompose spontaneously.

For example: $^{6}C_{14}$ and $^{1}H_{3}$ isotopes of carbon and hydrogen respectively, are the radioactive isotopes.

Properties of Isotopes

1. The atomic number of all isotopes of an element is same because no. of protons in their nuclei is same.
2. Number of protons is same but number of neutrons is different in all the isotopes of an element.
3. Chemical properties of all the isotopes of an element are same because electronic configuration of isotopes is same.
4. The isotopes of an element have different physical properties because they have different atomic masses.
5. Radioactive properties of isotopes of an element are different because they have different nuclear structures
6. All the isotopes of an element are placed in one place in periodic table because their atomic numbers are same.

n/p ratio