5. CHEMICAL BONDING AND SHAPE OF MOLECULES

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🎯 **Learning outcomes**

After the lesson, learners should be able to:

- Show the structure of atoms and ions by the Lewis dot method.
- Explain the ionic bond and the properties of ionic compounds.
- Explain the covalent bond, the coordinate bond, and the properties of a covalent compound.
- Describe the feature of sigma and Pi-bond
- Describe the coordinate covalent compounds with some examples.
- Write the Lewis dot diagrams of some ionic and covalent compounds (NaCl, $MgCl_2$, NH_4Cl, Oxides of Hydrogen, Nitrogen, and Phosphorus, common mineral acids).
- Write the resonance structure of some covalent species.
- Explain the properties of molecular and metallic solids based on Van der Waals' and metallic bonding.
- Use VSEPR theory to describe the shapes of simple covalent molecules.
- Describe the concept of hybridization in simple covalent molecules.
- Explain the characteristics of a bond in terms of dipole moment, Ionic character, and bond length.
- Describe hydrogen bonding and outline its importance to the physical properties of substances, including ice and water (e.g., boiling and melting points, viscosity, surface tension, and solubility).

Electronic Theory of Valency

Some important terms

1. Valency: Combining capacity of an element or radical measured in terms of the number of H-atoms or equivalent or twice the number of O-atoms or equivalent that it combines with.

e.g.	HCl	$NaCl$	$CaCl_2$	H_2SO_4	HNO_3	CaO	CuS	$BaCl_2$
	1	1	2	2	1	2	2	2

2. Valence shell: The outermost shell of an element or atom is called the valence shell because it determines valency and reactivity.

3. Valence electrons: The electrons present in the valence shell are called valence electrons.

4. Chemical bond: The force of attraction between the atoms of radicals that binds them together in a molecule or crystal of the chemical compound is called a chemical bond.

1. The valency of Mn in MnO_2 and P in PH_3 is, respectively.
   a. 4 and 3 b. 2 and 3 c. 1 and 1 d. 3 and 3

Electronic Theory of Valency (Octet theory)

It was put forth by Lewis and Kossel in 1916 to answer questions like- why are most elements not found in the elemental state? Why a large no of chemical compounds formed from a few elements?

Postulates:

1. The tendency of an atom to take part in a chemical combination is determined by the number of valence electrons. The inner electrons have nothing to do.
2. The element with an octet (8 electrons in the valence shell), e.g., noble gases (Ne, Ar, Kr, Xe, Rn) except He, are found to have very small energies and are stable. So, these do not undergo chemical reaction or bond formation.
3. It is observed that the elements with less than 8 electrons in the valence shell have high energies, hence, are very unstable. So, these undergo chemical reaction or bond formation in an attempt to acquire an octet in the valence shell.
4. A chemical combination or bond formation is always accompanied by a decrease in potential energy.

5. To fulfill their octet, the elements may lose, gain, mutually share, or coordinately share electrons, which form ionic, covalent, or coordinate covalent bonds, respectively. These lead to the formation of ionic, covalent, and coordinate covalent compounds.

Ionic Bonds (compounds)

- The force of attraction between oppositely charged ions that binds them together is called an ionic or electrovalent bond.
- The compounds containing ionic bonds - ionic compounds.
- These are formed by the complete transference of electrons from one atom to another.
- **Generally,** ***ionic bonds are formed between non-metals and metals*** **or** ***elements with high differences in electronegativities*****.**

e.g. $Mg + 2Cl \longrightarrow Cl^- \quad Mg^{++} \quad Cl^-$

Condition for ionic bond:

a. Low Ionization potential of the atom which donates electrons.

b. High electron affinity of the atom which accepts an electron

c. High lattice energy.

- Lattice energy is the amount of energy released when one mole of an ionic compound is formed from its cations and anions.

Characteristics of ionic compounds (Electrovalent compounds)

1. Usually exist in crystalline solid state, which are hard and rigid due to the strong electrostatic force of attraction between the cations and anions.
2. These usually have high melting and boiling points because of the high electrostatic force of attraction between the ions in the crystal lattice.
3. These are soluble in polar compounds like H_2O and insoluble in non-polar solvents, since only polar solvents interact with the ions.
4. These are bad conductors in the crystalline state because the ions occupy a fixed position in the lattice and cannot move. But in solutions and molten states, due to the presence of free movable ions, these compounds conduct electricity.
5. Ionic reactions are faster in solutions.
6. The ionic bonds are non-directional in nature, i.e., the electrostatic force of attraction can operate in any direction.
7. Ionic compounds are brittle, i.e., they break instead of changing their shape when hammered.

Covalent (Bonds) Compounds

The force of attraction that binds atoms of the same or different elements by mutual sharing of electrons is called a covalent bond. The compounds formed in such a way are called covalent compounds. This linkage is non-ionic or non-polar.

Generally, ***non-metals combine*** **with each other** ***in this way*****.**

e.g., H_2, HCl etc.

Condition for covalent bonds:

- High IP of both atoms
- High EA of both atoms

- The electronegativity difference should be generally low (less than 1.8)

Properties of covalent compounds

1. Though covalent bonds are strong bonds, different covalent molecules are not bound together by strong intermolecular forces. They may exist as solids, liquids, and gases, with low melting and boiling points.
2. These compounds are bad conductors of electricity due to the absence of both free electrons and free ions.
3. These are soluble in non-polar solvents and insoluble in polar solvents.
4. These undergo molecular reactions, which are slower than ionic reactions.
5. Covalent bonds have a directional nature. Hence, covalent molecules have particular geometrical shapes. E.g., H_2O is angular, NH_3 is pyramidal, etc.

1. Covalent crystals or atomic crystals or macromolecules

In this type of crystal, the building blocks are atoms, and the force that holds them together is a covalent bond. Diamond and graphite are two typical examples.

In diamond, each carbon atom is covalently linked to four other carbon atoms tetrahedrally, resulting in a 3-D network of carbons. Thus, an entire crystal behaves as a single molecule, which is called a macromolecule.

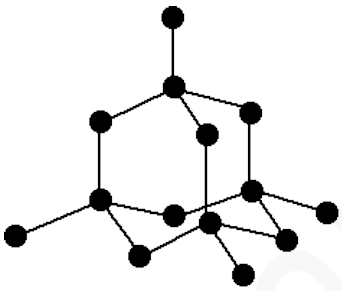


Fig: Structure of Diamond

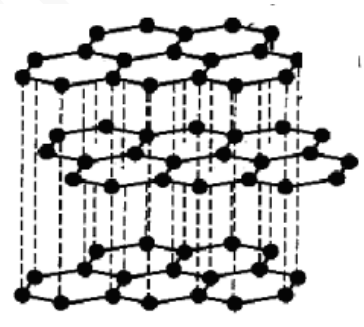


Fig: Structure of Graphite

Coordinate Covalent Bond

The force of attraction between atoms in compounds by mutual sharing of electrons, in which both the shared pair of electrons is contributed by only one of the bonded atoms, is a coordinate covalent bond.

The atom that donates the shared pair of electrons is called the donor, and the one that accepts the shared pair is the acceptor atom.

E.g., $NH_3 + BF_3$

Conditions for a Coordinate Covalent bond:

- The donor atom after the formation of other bonds must be in an octet state and must possess a lone pair of electrons for donation.
- The acceptor atom must acquire two electrons to attain its nearest noble gas configuration.

Properties of coordinate covalent bonds

The coordinate covalent bond is different from the covalent bond only in the mode of formation. Once the bond is formed, there is hardly any difference between a covalent and coordinate covalent bond. Generally, these compounds are slightly more polar than average covalent compounds.

Lewis base: Nucleophiles or chemical species having lone pairs of electrons that can be donated to form coordinate covalent bonds are called Lewis bases. E.g., NH_3, OH^- etc.

Lewis acid: Electrophiles or chemical species having a deficiency of electrons that can accept a lone pair of electrons to form a coordinate covalent bond are called Lewis acids, e.g., BF_3, H^+, $AlCl_3$, etc.

Octet Rule and Exceptions

According to this rule, the atoms tend to adjust the arrangement of their electrons in such a way that they (except H, He, and Li) achieve 8 electrons in their outermost shell.

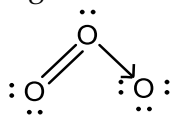
In other words, the tendency of atoms except H and He to have 8 electrons in their outermost energy level is called the octet rule.

The rule is useful for describing bonding in a large number of compounds. But there are a few exceptions to it.

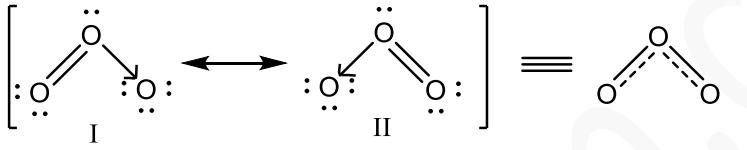
Resonance

There are many molecules in which the actual arrangement of electrons in the molecule cannot be represented by a single Lewis structure.

e.g., the following Lewis structure can be written for O_3.



According to this structure, the two bonds in the ozone molecule should be of unequal bond length. However, the actual bond length in ozone is found to be equal. To account for this O_3 is considered to be a resonance hybrid of two possible structures.



resonating structures Resonance hybrid

So, the actual structure of O_3 is a hybrid of I and II. The actual structure cannot be adequately represented by either structure alone.

Resonating structures can be written following the rules:

1. Each structure should have the same arrangement of atoms.
2. Each structure should have the same number of unpaired electrons if any.
3. The contributing structure should have nearly the same energies.

VSEPR Theory

proposed by Sedgwick and Powell in 1940, developed by Gillespie and Nyholm in 1957

Postulates:

1. The shape of a covalent molecule or ion is determined by the total number of electron pairs present in the valence shell of the central atom in the molecule.
2. The electron pairs in the valence shell of the central atom stay as far apart from each other as possible to minimize the repulsion among them. This gives rise to a certain geometry of the molecules.
   For example,

number of e-pairs in the central atom	ideal shape of the molecule	bond angle	examples
2	linear	180^0	$BeCl_2$, BeF_2
3	trigonal planar	120^0	BF_3, BCl_3
4	tetrahedral	$109^028'$ ~109.5^0	CH_4, CCl_4, NH_4^+
5	trigonal bipyramidal	120^0, 90^0	PCl_5
6	octahedral	90^0	SF_6

7	Pentagonal bipyramidal	90^0, 72^0	IF_7

3. If the central atom has a lone pair of electrons along with bond pairs, the ideal shape is distorted. This is because lone pairs are nearer to the central atom, resulting in more repulsion among the electron pairs. Therefore, the repulsion is in the following order

   lone pair-lone pair > lone pair- bond pair > bond pair- bond pair

Valence bond theory

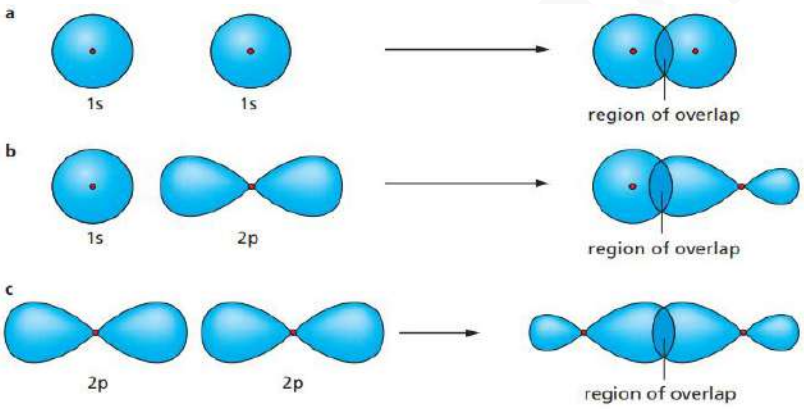
Proposed by Heitler and London in 1927, improved by Linus Pauling.

Postulates:

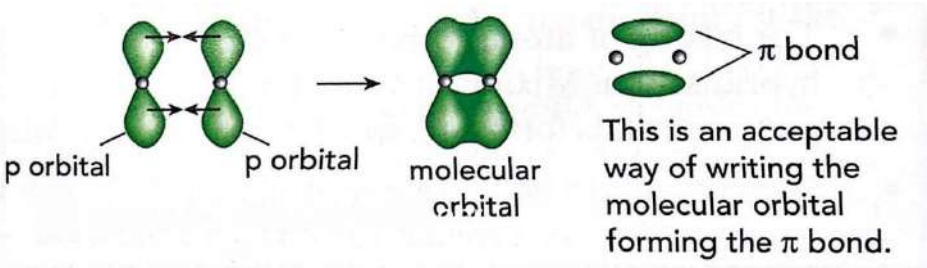
- Half-filled atomic orbitals of one atom overlap with half-filled atomic orbitals of another atom to form a covalent bond.
- The atomic orbitals must be in proper alignment and sufficiently overlap to form the bond.
- The strength of the bond depends upon the extent of overlap; the more overlap, the stronger the bond.
- Such overlapping lowers the energy of the molecule. The energy released is called stabilization energy or **bond energy**. The equilibrium distance between the nuclei of bonding atoms is called the **bond length**.
- The number of unpaired electrons in the ground state or excited state of an atom is called the covalency of the element.

Types of overlapping: the sigma and the pi bond.

1. Head-on overlapping (formation of a σ-bond)
   a. s-s overlapping
   b. s-p overlapping
   c. p-p overlapping



2. Sideways or lateral overlapping (Formation of a π bond)
   a. p- p overlapping.



All the single covalent bonds are sigma bonds. Double and triple bonds consist of 1 and 2 pi bonds, respectively, apart from a sigma bond.

Hybridization

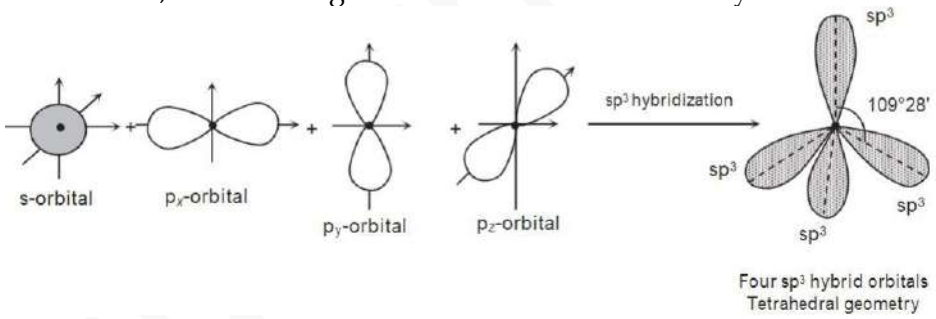
Hybridisation is the process of inter**mixing** the **atomic orbitals** of an atom **having nearly equal energies,** giving rise to an **equal number of hybrid orbitals** having the same shape, size, and energy.

Characteristics of hybridizations

1. The orbitals taking part in the hybridization must have nearly the same energies.
2. Both half-filled and completely filled orbitals can take part in hybridization; empty orbitals do not take part in hybridization.
3. The number of hybrid orbitals produced is equal to the total number of atomic orbitals undergoing hybridization.
4. The hybrid (hybridized) orbitals have different properties than either of the atomic orbitals undergoing hybridization; they have mixed properties.
5. The hybrid orbitals have one lobe larger than the other.
6. The main, bigger lobes of the hybrid orbitals stay as far apart as possible to minimize the repulsion. This gives a particular geometry to the molecule.
7. The hybrid orbitals taking part in bond formation have 1 electron.
8. The hybrid orbitals having a pair of electrons do not take part in bonding. They just hold the lone pair of electrons.
9. Hybrid orbitals do not form π bonds; they only form σ bonds. Unhybridized orbitals may form π bonds.

sp^3 hybridization

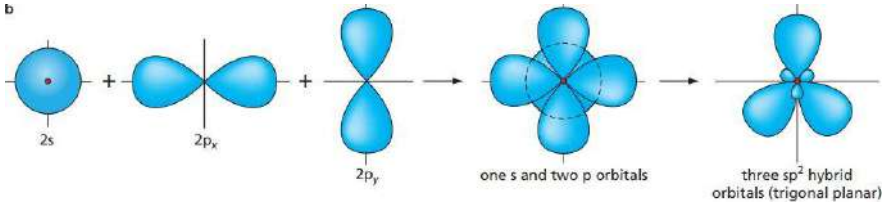
- One s orbital, and three p orbitals undergo intermixing to form 4 sp^3 orbitals.
- Each of the resulting sp^3 orbitals has 25% s character and 75% p character.
- The four sp^3 orbitals are oriented towards the 4 corners of a tetrahedron.
- Hence, the bond angle between the bond formed by these orbitals is $109^0\ 28''$.



Four sp^3 hybrid orbitals
Tetrahedral geometry

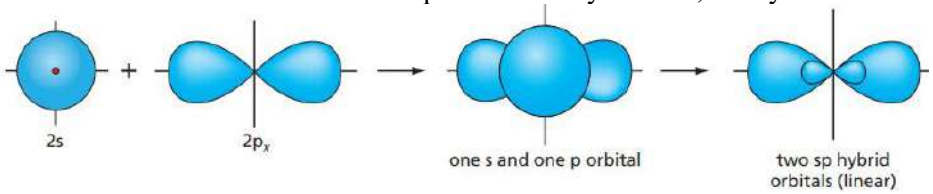
sp^2 hybridization

- One s orbital, and two p orbitals, undergo intermixing to form 3 sp^2 orbitals.
- Each of the resulting sp^2 orbitals has 33.33% s character and 66.67% p character.
- The three sp^2 orbitals are oriented towards the 3 corners of an equilateral triangle.
- Hence, the bond angle between the bond formed by these orbitals is 120^0.
- When one s orbital, and two p orbitals are hybridised, the hybrids are called **sp_2 hybrids**.



sp hybridization

- One s orbital, and one p orbitals undergo intermixing to form 2 sp orbitals.
- Each of the resulting sp orbitals has 50% s character and 50% p character.
- The two sp orbitals are oriented on opposite sides, resulting in a linear shape.
- Hence, the bond angle between the bond formed by these orbitals is 180^0.
- When one s orbital and one p orbital are hybridised, the hybrids are called **sp orbitals**.



Bond characteristics:

Bond length

The distance between the nuclei of two atoms bonded together.

Ionic character of covalent bonds (Polar and non-polar covalent bonds)

A perfect covalent bond is formed by the equal sharing of a pair of electrons. This is formed when two atoms of equal electronegativities get bonded covalently.

But when two atoms of slightly different electronegativities get covalently bonded, the one with higher electronegativity pulls the shared pair of electrons, developing a partial negative charge. An equal positive charge is developed in the other atom. Thus, two poles are developed. Such a covalent bond is said to have a partial ionic character or is termed a polar covalent bond.

E.g., H-Cl

When two atoms of exactly equal electronegativities are bonded, neither of the atoms effectively pulls the shared pair of electrons. Thus, no pole is formed such covalent bond is a non-polar covalent bond.

e.g., H - H I - I O = O

Dipole moment and its application

The charged ends of the polar covalent bond behave as an electric dipole, and the degree of polarity is expressed as dipole moment.

Dipole moment is defined as the product of the magnitude of charge on any one of the atoms and the distance between them.

Mathematically, $\mu = e \times d$

, where e- charge on either atom or the dipole
d - distance

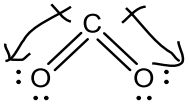
The unit of dipole moment is Debye (D). $1D = 10^{-18}$ esu cm.

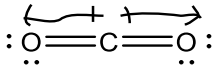
Applications of dipole moment

1. **It is used to find the geometry of molecules.**

e.g., the CO_2 molecule has a net dipole moment of zero.

It can have two possible geometries: linear or bent.



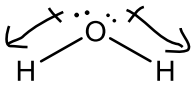


resultant μ = 0

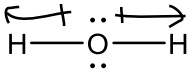
In linear geometry, the two dipole moments cancel each other, and the resultant dipole moment is zero. But in a bent structure, there is a certain resultant dipole moment. Hence, the true geometry of CO_2 is linear.

On the other hand, H_2O has a net dipole moment of 1.84D.

H_2O again can have linear or bent geometries, but the net dipole moment can be non-zero only if H_2O has a non-linear or bent structure.



Resultant μ ≠ 0



Resultant μ = 0

Hence, water is V-shaped.

2. **It can be used to find the % ionic character of a covalent bond** by the formula,

$$\% \text{ ionic character} = \frac{\text{experimental dipole moment}}{\text{theoretical dipole moment}} \text{ X } 100\%$$

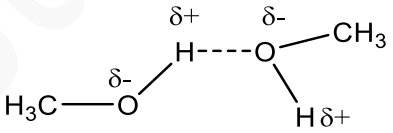
e.g., the exact dipole moment of HCl is found to be 1.03 D. The theoretical dipole moment, which HCl is considered a complete ionic bond, with a regular bond length, is 6.12 D.

$$\% \text{ ionic character of HCl} = \frac{1.03}{6.12} \text{ x } 100\% = 16.83\%$$

H-Bonding

When a hydrogen atom is covalently linked with a highly electronegative atom like fluorine, oxygen, or Nitrogen, the bond pair of electrons is largely attracted towards the electronegative atom and a partial positive charge is developed in the H atom. Such an H atom exerts an electrostatic force of attraction with another such electronegative atom; this force of attraction is called a hydrogen bond.

A hydrogen bond is an attractive force that prevails between the hydrogen atom bonded to a highly electronegative atom, such as F, O, or N, and an electronegative atom of the same or a different molecule. It can be remembered as the FON bond.



e.g., A hydrogen bond between two Methanol molecules

<u>Condition for Hydrogen bond formation:</u>

For the formation of a hydrogen bond, the *atom attached to the hydrogen* should have *high electronegativity* and should be *small in size*. In fact, it is only fluorine, oxygen, and nitrogen that satisfy this condition.

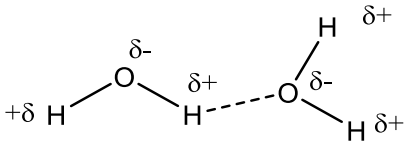
This is the reason why only nitrogen forms a hydrogen bond, though N and Cl both have the same electronegativities.

Types of hydrogen bonds:

There are two types of hydrogen bonds.

i) Intermolecular hydrogen bonds:

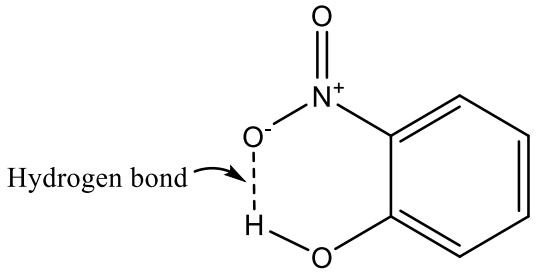
When the hydrogen bond formed is between two atoms of different molecules of the same or different compounds is called an intermolecular H-bond.



e.g., Intermolecular hydrogen bonding between water molecules

i) Intramolecular hydrogen bonds:

The hydrogen bond formed between two atoms of the same molecule is called an intramolecular hydrogen bond.



e.g., o nitrophenol

Effect of Hydrogen Bond on Physical Properties of a Compound

1. Melting point, boiling point, and physical state

Among H_2O, H_2S, H_2Se, and H_2Te, H_2O has the highest boiling and melting points, although it has the lowest molecular mass. This is due to the presence of an H-bond only in H_2O.

Similarly, the boiling points of HF and NH_3 are abnormally high among hydrides of group VA (15) and group VIIA (17) hydrides, respectively.

HI > HBr > HCl > HF: Expected order

HF > HI > HBr > HCl: Actual order

NH_3 > PH_3: Actual order PH_3 > NH_3: Expected order

H_2O exists as a liquid, and H_2S exists as a gas at room temperature, again, due to the presence of an H-bond between H_2O molecules, which is absent in H_2S.

The intermolecular hydrogen bond increases the intermolecular force of attraction between the molecules, increasing the melting and boiling points.

2. Solubility

Generally, ionic compounds are soluble in ionic or polar solvents, and non-polar, covalent compounds are soluble in non-polar solvents.

But organic and covalent compounds that can form a hydrogen bond are soluble in polar solvents such as water.

e.g. -Alcohols are more soluble in water than ethers.

-NH_3 is soluble in H_2O but PH_3 is not.

It is because alcohols and ammonia molecules can form hydrogen bonds with water molecules, while ethers and PH_3 cannot.

Metallic Bonding

GCSE Chemistry - Metallic Bonding #20 (youtube.com)

This is another special kind of bonding found in only pure metals. This is explained by the electron sea model put forward by Lorentz and Drude in 1900.

According to this electron sea or electron gas model of metallic bonding, metals, being electropositive, are unable to hold the outermost valence electrons. So, these electrons get free and roam in the body of the metal. The metal atoms change into positive ions called **kernels**. The force of attraction between these positively charged metallic kernels and free electrons is called the metallic bonding. This bonding is *non-directional* because free electrons are present on all sides of the kernels, which occupy fixed space in the crystal lattice.

Properties of Metal:

1. Electrical conductivity: the free electrons are moving randomly in a body of metal. When an electrical potential is applied, these move towards the positive end at high speed, this lead to electrical conductivity.
2. Thermal conductivity: if one part of a metal is heated, the electrons present there acquire a large amount of kinetic energy. Being free electrons, these move rapidly through the crystal and conduct electricity.
3. Metallic Lustre: When rays of light fall on a freshly cut surface of metal, the electrons absorb energy and then radiate it. This gives metals a metallic luster.
4. Malleability and ductility: When a metal body is hit (hammered) due to the electron sea, it changes shape without breaking.

Van der Waal's Forces

Inert gases like He, Ne, Ar, etc. exist as individual atoms, but these can be liquefied at high pressure and low temperature. Similarly, non-polar gases like Cl_2, CH_4, CO_2, etc. can also be liquefied.

In 1973, J.D. Van der Waals pointed out the existence of weak forces among the nonpolar molecules. Such a force is called the Van der Waals interaction or force.

This force is believed to arise because of the unsymmetrical distribution of the electrons around the nucleus, leading to the formation of an instantaneous dipole.

Thus, the force of attraction between an instantaneous dipole and an induced instantaneous dipole among polar molecules is called Van der Waals' forces.

The molecules that have resonating structures are found to have relatively low energies and high stability.

Molecular crystals

Here, the building blocks are molecules, and the force that binds them together is the Van der Waals' force. Hence, most of these are found in low temperatures. E.g., dry ice, solidified CH_4, I_2, etc.

***This is not a complete note. It is a guide for you. It is recommended to study the prescribed textbooks (*especially the missing topics*) along with this material. ***