

Topic on Chemistry

CHEMICAL BONDING

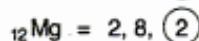
Atoms, except those of inert gases, do not have free existence. They readily combine together to form stable clusters or aggregates of atoms. Such aggregates are called molecules and the attraction operating between atoms within the molecule is called **Chemical-Bond**.

The process of combination of atoms, called chemical bonding, involves the union of two or more atoms through redistribution of electrons in their outermost shell to acquire the stable electronic configuration of noble gases having a state of minimum energy.

Valency is the general term used to explain the power or potential (Valentia = Power) which atoms possess to combine with one another for forming a stable molecule. In general valency means the number of chemical bonds an atom forms, which is not necessarily the number of other atoms to which it is bonded. The valency of any element depends upon the electrons present in the outermost orbit. That is why that outer most shell or orbit of an atom is termed as **Valency shell** or **Valency orbit**. The electrons of valency shell, which are involved in chemical bond formation are called **Valency electrons**.

Types of Valency

(a) **Probable Valency**—Number of electrons present in outermost orbit of an atom is called probable valency.



Probable valency of Na and Mg is $\textcircled{1}$ and $\textcircled{2}$ respectively.

(b) **Important Valency**— $\text{Probable Valency} - 8$

For example— ${}_{8}\text{O} = 2, \textcircled{6}$, has probable valency $\textcircled{6}$, while, it has $\textcircled{6} - 8 = -2$ important valency.

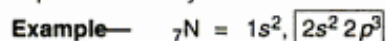
Note

The elements whose atom has only *s*-orbital in outermost shell—the probable valency and important valency are same.

But the elements whose atom has both *s* and *p* orbitals in outermost shell—

Probable Valency = No. of electrons in outermost shell

Important Valency = Probable Valency - 8



Probable valency of N is 5.

Important valency of N is $5 - 8 = -3$

Electronic Theory of Valency

Kossel and **Lewis** (1916) put forth a comprehensive theory of valency, which was completed by **Langmuir**

(1919). Since, it was based on electronic concept of the atom, it was named as **Electronic Theory of Valency**.

Main Characteristics—The main characteristics of electronic theory of valency are as follows—

(1) All atoms except (H, Li and Be), try to achieve noble (inert) gases configuration, i.e., 8 electrons in their outermost orbit.

Such as, ${}_{10}\text{Ne} = 2, 8$

${}_{18}\text{Ar} = 2, 8, 8$

${}_{36}\text{Kr} = 2, 8, 18, 8 \dots \text{etc} \dots$

While, H, Li, Be achieve, configuration of He = 2.

Atoms of elements depending on their configuration try to achieve, the above configuration either by losing or gaining or by sharing one or more electrons.

This theory is also known as **Octet Theory**.

(2) The tendency of atoms to acquire stable noble gas electronic configuration is the fundamental cause of combination of the atoms.

A chemical bond is an attractive force which holds two or more atoms together in chemical species.

(3) The number of electrons that an atom of an element loses, gains or shares in order to acquire stable noble gas configuration represents the **Valency** of that element.

Basis of Rule of Eight (Octet Rule)

(a) Noble gases have outer electronic configuration $ns^2 np^6$ (except $1s^2$ for helium)

(b) This arrangement of electrons imparts unique stability to the atoms of noble gases.

(c) Atoms of all other elements possess less than eight electrons in their outermost shell or valency shell hence, they take part in chemical bond formation.

(d) These elements according to their electronic configuration in valency shell have tendency to either lose or gain or share sufficient electrons to achieve the outer configuration (i.e. eight) of noble gas atoms.

This is expressed as **Octet Rule**.

Note

Some molecules like PCl_5 , SF_6 , IF_7 etc. are exceptions of octet rule. Sidgwick explained these molecules on the basis of single linkage.

Types of Linkages / Valencies / Bonds

Valency is classified mainly into—

(a) **Electrovalency**

(b) **Covalency**

(c) **Co-ordinate valency**

That is combination of the atoms may take place in the following three ways—

(a) By transferring one or more electrons from one atom to the other atom (**Electrovalency**).

(b) By sharing of electrons by one atom with electrons of other atom (both atom contributing equal number of electrons) (**Covalency**).

(c) By sharing of electrons between two atoms in such a way that the shared electrons are contributed by one atom only (**Co-ordinate valency**).

Electrovalent or Ionic or Polar Bond

"This bond formed by complete transfer of one or more electrons from one atom to another atom and in such transfer a noble gas configuration is attained" by both combining atoms.

Conditions for the Formation of Ionic Bond

(i) Ionisation energy of electropositive atom should be low.

(ii) Electron affinity of electronegative atom should be high.

(iii) Lattice energy of the ionic crystal should be high.

Energy consideration of Electrovalent Bond

Following energy steps are responsible for the formation of **Electrovalent Bond**.

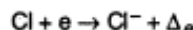
(i) **Sublimation Energy**—When solid metal element is converted into gaseous state, the energy required for this purpose is known as sublimation energy or the **energy for atomization**. It is denoted as Δ_s .

(ii) **Ionization Energy**—The amount of energy needed to separate valency electrons from gaseous atom of the element is called ionization energy. It is denoted by Δ_i .

(iii) **Dissociation Energy**—The energy required to dissociate a non-metallic molecule into constituent atoms is called dissociation energy, denoted as Δ_d .



(iv) **Electron Affinity**—The amount of energy released when an electron is added to non-metallic neutral atom, is known as electron affinity. It is denoted by Δ_e .



(v) **Lattice Energy**—Amount of energy released when cation and anion are brought closer (equilibrium distance) from infinity in a crystal lattice to form one mole of an ionic compound. It is denoted as U.

$$\text{Lattice energy (U)} = \frac{NAe^2Z_+Z_-}{r} \left(1 - \frac{1}{n}\right)$$

(Born-Lande equation)

Where,

- N = Avogadro's number
- e = Charge on the electron
- Z_+ and Z_- = Charges on the positive and negative ions
- r = Inter ionic distance
- A = Madelung constant
- n = Born exponent

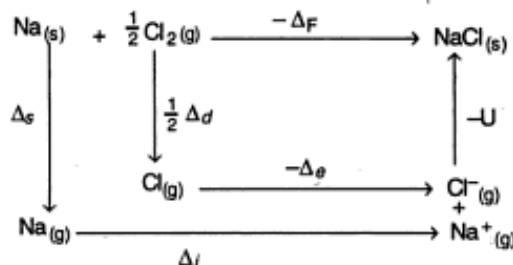
Lattice energies of alkali metal halides are recorded in the following table (kJ per mole).

Table

| Alkali metals ions → | Li ⁺ | Na ⁺ | K ⁺ | Rb ⁺ | Cs ⁺ |
|----------------------|-----------------|-----------------|----------------|-----------------|-----------------|
| Halide ions ↓ | | | | | |
| F ⁻ | -994.5 | -894.5 | -790.2 | -756.7 | -719.0 |
| Cl ⁻ | -802.6 | -758.7 | -681.4 | -660.6 | -618.7 |
| Br ⁻ | -760.8 | -714.8 | -656.3 | -631.3 | -593.6 |
| I ⁻ | -770.6 | -668.8 | -618.7 | -597.7 | -564.3 |

Born-Haber Cycle

A cyclic process devised by Born-Haber to correlate the lattice energy with other thermal quantities is known as Born-Haber Cycle.



The heat of formation of NaCl (Δ_f)

$$= \Delta_s + \frac{1}{2} \Delta_d + \Delta_i + \Delta_e + U$$

Salient Points Regarding Electrovalent / Ionic / Polar Bond

(a) Propounded by **Kossel** (1916)

(b) Atoms of metals which lose electrons are converted into positively charged ions (cations) and those of non-metals which gain electrons become negatively charged ions (anions).

(c) These oppositely charged ions are held together by electrostatic attraction accompanied by release of energy.

(d) Metallic atoms (having low ionization energy) and non-metallic atoms (having high electron affinity) combine to form ionic bond most often.

(e) An ionic bond is favoured when cation is large and the anion is small. The small charges on both cation and anion favour ionic bond.

Examples—NaCl, KBr, MgO, CaBr₂, BaO, CaCl₂, K₂S etc.

Characteristics of Electrovalent Compounds

(1) They are usually soluble in polar solvents like water but insoluble in non-polar organic solvents.

The electrovalent compounds dissolve in a solvent, if
Solvation Energy > Lattice Energy

As, when NaCl is dissolved in water, the ions are solvated by solvent molecules.

(2) Their M.P. and B.P. are high, because a considerable amount of energy is required to overcome the electrostatic force of attraction between oppositely charged ions.

(3) They conduct electricity when dissolved in water or even in molten state, because in both these conditions, the movement of ions is possible.

(4) They are hard crystalline solids.

(5) They do not show space isomerism, because the bond is non-rigid and non-directional.

(6) In solution, ionic compounds react rapidly. The properties of an ionic compound are those of its ions.

Example— CuSO_4 solution in water will respond to the reactions of Cu^{2+} and SO_4^{2-} ions.

Variable Electrovalency

The electrovalency of an element is equal to the number of electrons lost or gained by its atom during the formation of ionic bond. The *s*-block elements do not show variable valency, however, *p*-block elements (with higher atomic number), transition and inner transition elements show variable valency.

There are two main reasons for showing variable valency—

(1) Inert pair effect in *p*-block elements.

(2) Small energy difference between *ns* and $(n-1)d$ sub-shells in transition elements and *ns* and $(n-2)f$ sub-shells in inner transition elements.

(i) **Inert-Pair Effect**—The electronic configurations of III A and IV A group elements are as—

| | | | | |
|----|---------------|-------|---|---------------------------------|
| | | III A | | |
| B | } $ns^2 np^1$ | ↓ | ↑ | Stability of +3 Oxidation State |
| Al | | | | |
| Ga | | | | |
| In | | | | |
| Tl | | | | |
| | | IV A | | |
| C | } $ns^2 np^2$ | ↓ | ↑ | Stability of +2 Oxidation State |
| Si | | | | |
| Ge | | | | |
| Sn | | | | |
| Pb | | | | |

The elements of III A group show +3 oxidation state mainly. But as we go down the group the oxidation state +1 becomes more and more pronounced. Similarly the elements of IV A group show +4 oxidation state in general, but as we go down the group the +2 state becomes more and more pronounced.

The two *s* electrons (ns^2) in the valency shell tend to remain inert and do not participate in formation of bonds. This is called **inert-pair effect**. Thus the inert-pair effect is the main cause of variable valency in *p*-block elements.

(2) In transition elements the variation in oxidation state is due to involvement of incomplete *d*-orbitals in addition to electrons of *ns*-orbital. So the electrons from both the energy levels can be used for bonding.

Similarly inner transition elements show variable valency due to incomplete filling of *f*-orbitals. So in addition to *ns* electrons, the electrons from *f*-orbitals may be used for chemical bond formation.

Covalent Bond

(a) Concept of covalent bond was developed by Lewis (1916).

(b) The covalent bond results from equal sharing of one or more electron pairs of electrons, so that combining atoms acquire noble gas configuration.

(c) No complete transfer of electrons takes place.

(d) Energy is released in the process, known as bond energy.

Examples—

(i) Almost all organic compounds.

(ii) Molecular non-metals (H_2 , O_2 , halogens, P_4 , S_8)

(iii) Compounds made up of non-metals.

Ex.—(CO_2 , NH_3 , HNO_2 , CS_2 , N_2H_4 etc.)

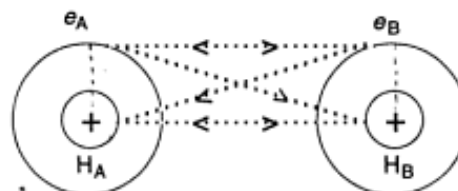
(iv) Giant molecules (Graphite, diamond, silica (SiO_2) etc.

Energy Consideration of Covalent Bond

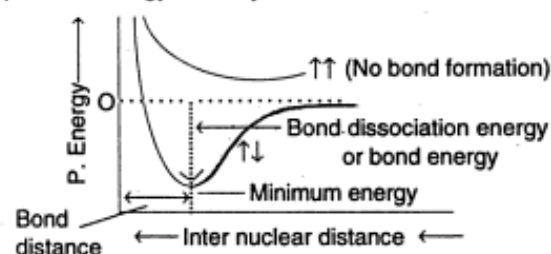
When two hydrogen atoms H_A and H_B with respective electrons e_A and e_B approach each other, following attractive and repulsive forces start operating—

(A) Attractive forces between electrons of atom H_A e_A and nucleus of atom H_B e_B and electron of atom H_B e_B and nucleus of atom H_A e_A .

(B) Repulsive forces between two nuclei and two electrons of two combining atoms.



It is found that during formation of a covalent bond, the magnitude of attractive force is more than repulsive force. Since, the attraction causes decrease in energy, so the potential energy of the system decreases.



The formation of a covalent bond between two hydrogen atoms takes place at a point which corresponds to minimum in the curve. The minimum energy point also corresponds to optimum or equilibrium distance upto which two nuclei can be brought closer, before the force of repulsion between them becomes dominant. This distance corresponds to bond distance or **bond length** of covalent bond. The bond length is defined as distance between nuclei of the two atoms forming a **chemical bond**. For hydrogen molecules

$$\text{Bond distance} = 0.74 \text{ \AA}$$

$$\text{Bond energy} = 458 \text{ kJ mol}^{-1}$$

Types of Covalent Compounds

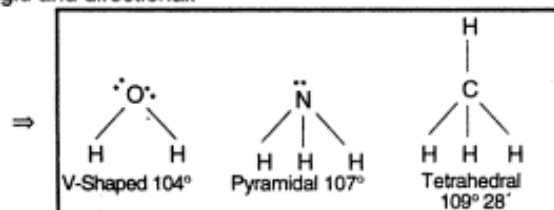
Covalent compounds are of two types—

(i) **Discrete-molecules**—Such as CO₂, N₂, CH₄ etc. Molecules are held together by weak van der Waal's forces of attraction (generally liquid or gases with low M.P. and B.P.)

(ii) **Macro molecules**—Such as diamond, quartz etc. having three dimensional network with high M.P. and B.P. (solids).

Characteristics of Covalent Compounds

(1) Covalent compounds have definite geometry in space and often show space isomerism because the bond is rigid and directional.



(2) They are insoluble or sparingly soluble in water but soluble in non-polar solvents (organic solvents)

(3) They are bad conductor of electricity, because there are no free ions to carry the current.

(4) The reactions between covalent compounds are often slow. The properties of covalent compounds are due to the bonds present in them.

Fajan's Rules—These rules indicate the conditions necessary for showing ionic or covalent characters in a molecule.

Statement—“Smaller the cation, larger the anion and higher the positive charge, the greater is the tendency towards covalency.”

| Condition | Electrovalency | Covalency |
|-----------------|----------------|-----------|
| Positive charge | Low | High |
| Anion | Small | Large |
| Cation | Large | Small |

Polar Covalent Bond/Dipole Moment

In non-polar bond the combining atoms are of equal electronegativity (H₂, Cl₂). But, in polar bond the combining atoms are of different electronegativity. The atom of higher electronegativity draws the shared electron pair towards itself.

For example—HF is the polar molecule having F atom of higher electronegativity. The shared electron pair is drawn towards F, (H^{+δ} – F^{-δ}), giving a partial -ve charge on F and partial +ve charge on other atom.

The dipole moment (μ) of a polar-molecule is defined as a product of partial charges (δ) and the distance between combining atoms (d).

$$\mu = \delta \times d$$

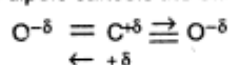
(Dipole-moment is a vector-quantity.)

The unit of dipole moment is **Debye** which is equal to 1×10^{-18} esu.cm.

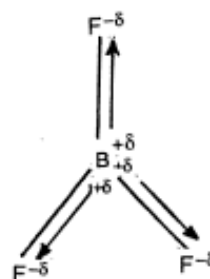
The molecules having polar bonds need not necessarily be polar molecules.

If a molecule possesses a symmetry such that net dipole moment (vector sum of bond moments) is zero, then the molecule will be non-polar.

Examples—C—O bond is polar but net dipole moment of CO₂ molecule is zero, hence, it is a non-polar molecule. Each dipole cancels the effect of other.

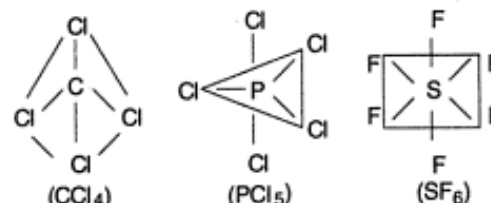


In BF₃ molecule

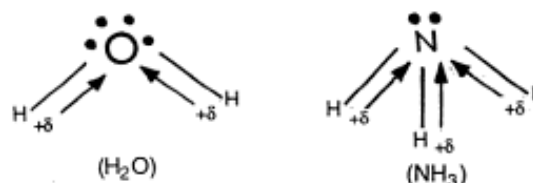


B—F bond is polar with B as positive end and F as negative end, but net dipole-moment is zero.

Hence, the molecules BF₃, CCl₄, PCl₅ and SF₆ are non-polar molecules.



H₂O and NH₃ are polar molecules because net dipole moment (resultant of bond moments) is not zero.



Dipole Moments of Some Common Molecules

| Molecule | Dipole moment | Molecule | Dipole moment |
|--------------------------------|---------------|----------------------------------|---------------|
| H ₂ | 0.0 | CH ₃ OH | 1.69 |
| N ₂ | 0.0 | C ₂ H ₅ OH | 1.67 |
| CCl ₄ | 0.0 | H ₂ O | 1.87 |
| Cl ₂ | 0.0 | HF | 1.91 |
| CO ₂ | 0.0 | HCl | 1.02 |
| C ₂ H ₂ | 0.0 | NH ₃ | 1.44 |
| CH ₂ F ₂ | 1.96 | N ₂ O | 0.17 |
| O ₂ | 0.0 | H ₂ S | 0.92 |
| O ₃ | 0.52 | H ₂ O ₂ | 1.84 |
| C ₂ H ₆ | 0.0 | CHCl ₃ | 1.15 |
| SO ₂ | 1.61 | PH ₃ | 0.58 |
| CO | 1.12 | HCN | 2.93 |
| CsI | 12.1 | SbCl ₃ | 3.9 |
| NaCl | 8.3 | CH ₃ Cl | 1.86 |

Remember

Per cent ionic character of a bond

$$= \frac{\text{Actual dipole moment of the bond}}{\text{Dipole moment of a pure ionic bond}} \times 100$$

For example in HF, the bond distance is 0.92 Å and the dipole moment for the ionic structure H⁺ F⁻, when an electron is supposed to be transferred from H atom to F atom is 4.8 × 10⁻¹⁰ esu × 0.92 × 10⁻⁸ cm = 4.42 Debye. The actual dipole moment is 1.98 Debye.

∴ Per cent ionic character

$$= \frac{1.98 \text{ D} \times 100}{4.42 \text{ D}} = 45\%$$

- **Pauling's** formula for calculating per cent ionic character in covalent bond is as—

Per cent ionic character

$$= 100 \left[1 - e^{-0.25 (X_A - X_B)^2} \right]$$

where X_A and X_B are electronegativities of atoms A and B.

- **Hannay and Smyth Equation—**

Per cent ionic character

$$= 16 (X_A - X_B) + 3.5 (X_A - X_B)^2$$

| | | | | | | |
|---------------------------------|-----|------|-----|-----|------|-----|
| X _A - X _B | 0.6 | 1.0 | 1.4 | 2.0 | 2.4 | 3.0 |
| Per cent ionic character | 9 | 21.9 | 40 | 63 | 75.8 | 89 |

Orbital Concept of Covalency

The orbital concept of covalent bond was put forward by **Heitler & London** and later modified by **Pauling and Slater**. According to this concept **"The presence of one or more unpaired electrons in the valence shell of an atom is mainly responsible for the formation of a chemical-bonding."**

Remember

Noble gases do not take part in formation of a chemical bond because they do not have unpaired electrons.

The combining capacity or covalency of an atom is equal to the number of unpaired electrons present in its ground state or excited state.

Postulates of Orbital Concept of Covalency

- (1) Atomic orbitals of the valence shell of two atoms having unpaired electrons overlap with each other.
- (2) Overlapping of atomic orbitals of two atoms give rise the covalent bond.
- (3) Greater the overlapping of atomic orbitals the stronger is the bond formed.
- (4) Every atom has a tendency to pair up its unpaired electrons with the oppositely spinning electrons of the other atom. Hence, opposite spins of two electrons get neutralised and chemical bond is established.

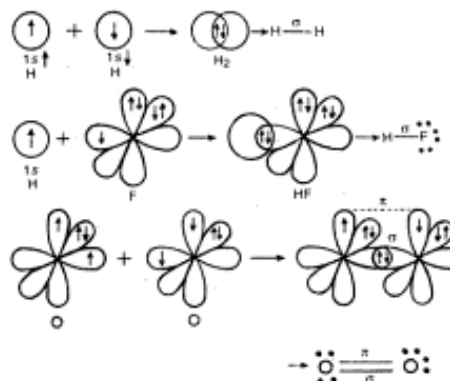
This orbital concept of covalency gives rise the concept of σ and π bonds.

On the basis of nature of orbital overlapping, the formation of covalent bond can be divided into two kinds.

(A) Covalent Bond Formed by Overlapping of Pure Atomic Orbital—

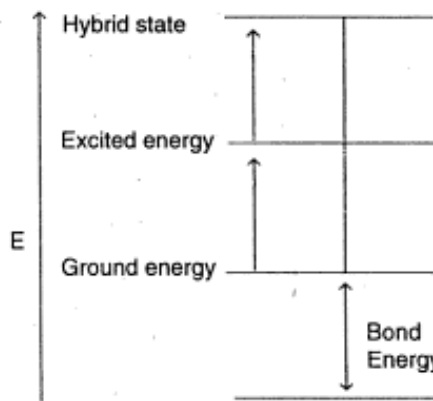
- s-s overlapping
- s-p overlapping
- p-p overlapping

Examples—



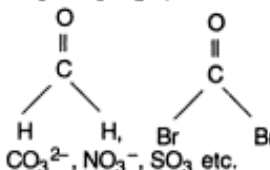
(B) Covalent Bond Formation by Overlapping of Hybridised Atomic Orbitals : Some salient points regarding the hybridisation are summarised as—

- (1) One or more electrons from fully filled valency orbitals of an atom in ground energy state get promoted to next available orbital resulting in a excited state with a number of half-filled orbitals. This process requires input of energy. The orbitals in excited state undergo a process of mixing giving hybrid orbitals of equivalent energy.
- (2) The number of hybrid orbitals formed by an atom is equal to the number of pure atomic orbitals which undergo process of hybridisation.
- (3) Effective hybridisation takes place only when the orbitals undergoing hybridisation are of nearly same energy.
- (4) Hybrid orbitals either form sigma (σ) bond or may contain lone pairs of electrons. They are not involved in the formation of Pi (π) bonds.
- (5) The greater stability of bond formed by the overlapping of hybrid orbitals is due to greater overlapping capacity of such orbitals as compared to overlapping of pure atomic orbitals.



Geometry of molecules containing only bond pairs of electrons

| Type of hybridisation | Shape of molecule | Bond Angle | Examples |
|-----------------------|-------------------|------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| sp | Linear | 180° | BeH ₂ , BeF ₂ , BeCl ₂ , HgCl ₂ , C ₂ H ₂ , HCN, CO ₂ , CS ₂ , N ₂ O, Hg ₂ Cl ₂ etc. |

| | | | |
|------------------------|-------------------------------------|----------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| sp^2 | Trigonal plane or Triangular planar | 120° | $BF_3, BCl_3, C_2H_4,$  CO_3^{2-}, NO_3^-, SO_3 etc. |
| sp^3 | Tetra hedral | $109-28^\circ$ | $CH_4, SiH_4, SnCl_4, PbCl_4,$ $TiBr_4, CCl_4, SiF_4, [BeF_4]^{2-},$ $[BH_4]^- , [BF_4]^- , [NH_4]^+ ,$ $[AlCl_4]^- , [PH_4]^+ , [H_2PO_2]^- ,$ $[HPO_3]^{2-} , [PO_4]^{3-} , POCl_3,$ $[SO_4]^{2-} , [ClO_4]^- , [Ni(CO)_4],$ $[Cu(CN)_4]^{3-} , [Zn(CN)_4]^{2-} ,$ $[AsO_4]^{3-} , [SeO_4]^{2-} , [IO_4]^- ,$ XeO_4 |
| dsp^2 | Square planar | 90° | $[Ni(CN)_4]^{2-} , [PdCl_4]^{2-},$ $[Pt-(NH_3)_4]^{2+} , [AuCl_4]^-$ |
| sp^3d | Trigonal bipyramidal | 120° and 90° | $PCl_5, PF_5, AsF_5, SbCl_5,$ XeO_3F_2 |
| sp^3d^2 or d^2sp^3 | Octahedral | 90° | $SF_6, [BiCl_6]^- , [PF_6]^- ,$ $[PCl_6]^- , [AsF_6]^- , SeF_6,$ $MoF_6, [SbCl_6]^- , TeF_6,$ $WCl_6, UF_6, XeO_2F_4.$ All six co-ordinated metal complexes. |
| sp^3d^3 | Pentagonal bipyramidal | 90° and 72° | $IF_7, [ZrF_7]^{3-} , [UF_7]^{3-},$ $[UO_2F_5]^{3-}$ |

| Remember | |
|----------------------|--------------------------------------------------------------|
| $[Mo(CN)_6]^{4-}$ | is dodecahedral molecule |
| $[TaF_6]^{3-}$ | is square antiprismatic molecule |
| $(C_5H_5)Fe(C_5H_5)$ | is sandwich structure. (This compound is known as Ferrocene) |

Geometry of molecules containing both Bond pairs and Lone pairs of electrons.

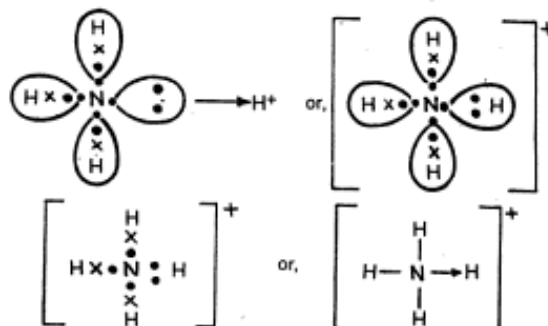
| Type of hybridisation | No. of Bond pairs | No. of Lone pairs | Shape of molecule | Examples |
|-----------------------|-------------------|-------------------|---------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------|
| sp^2 | 2 | 1 | V. shaped | $SnCl_2, PbCl_2, SO_2$ |
| sp^3 | 3 | 1 | Trigonal pyramidal | $NH_3, PH_3, NF_3, PF_3,$ $PCl_3, N(CH_3)_3,$ $P(CH_3)_3, (SO_3)^{2-},$ $AsCl_3, SbCl_3, BiCl_3,$ ClO_3^-, XeO_3 |
| sp^3 | 2 | 2 | V-shaped | $H_2O, H_2S, OF_2,$ $OCl_2, H_2Se,$ $(CH_3)O(CH_3)ClO_2^-,$ $ClOF, SCl_2, NH_2^-$ |
| sp^3d | 4 | 1 | Irregular Tetrahedral or Distorted trigonal bipyramidal | $SF_4, SCl_4, TeBr_4,$ $TeCl_4, XeO_2F_2$ |
| sp^3d | 3 | 2 | T-shaped | $ClF_3, BrF_3, ICl_3,$ $IBr_3, XeOF_2$ |

| | | | | |
|-----------|---|---|------------------|------------------------------------------|
| sp^3d | 2 | 3 | Linear | XeF_2, ICl_2^-, KrF_2 |
| sp^3d^2 | 5 | 1 | Square pyramidal | $IF_5, ClF_5, [SbF_5]^{2-},$ $XeOF_4$ |
| sp^3d^2 | 4 | 2 | Square planar | ICl_4^-, ClF_4^-, XeF_4 |

Co-ordinate Covalent Bond/Co-ordinate Bond/Dative Bond/Semi-Polar Bond

- (1) It is a kind of covalent bond.
- (2) It is shown by an arrow (\rightarrow), pointing from donor to acceptor.
- (3) Only one of the two atoms involved in the bonding supplies a pair of electrons. This type of bond was suggested by **Langmuir** and was named as co-ordinate bond by **Sidgwick**.

Examples— $SO_2, H_3O^+, H_2SO_4, NH_4^+, SO_3$ etc.

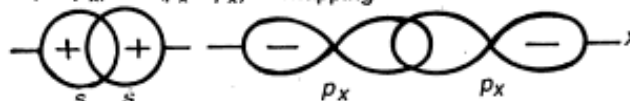


Characteristics of co-ordinate bond

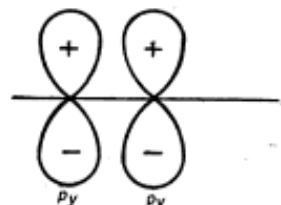
- The electrons in co-ordinate covalent bond are held firmly by the nuclei of atoms, therefore, they do not ionise in water.
- Co-ordinate compounds are sparingly soluble in water. Most of them are soluble in organic solvents.
- Co-ordinate covalent bond is rigid and directional and therefore, the molecules having co-ordinate bond show geometrical isomerism just like covalent compounds.
- A co-ordinate covalent bond results in semipolarity in the molecule. Thus the co-ordinate compounds lie between electrovalent and covalent compounds in their volatility, melting points, and boiling points.

Sigma (σ) and Pi (π) Covalent Bonds

(a) Sigma (σ) Bond—This type of bond is formed by the head on (end to end) overlapping of atomic orbitals along the internuclear axis. It is a strong bond as the extent of overlapping is maximum. It is given by ($s-s$), ($s-p_x$) and (p_x-p_x) overlapping



(b) Pi (π) Bond—This type of bond is formed by the sideways or lateral overlapping of atomic orbitals in a



direction perpendicular to the internuclear axis. It is a weak bond as the extent of overlapping of atomic orbital is very small. It is given by $(P_y - P_y)$ and $(P_z - P_z)$ overlapping.

Differences Between σ and π -Bonds

| Sigma (σ) Bond | Pi (π) Bond |
|----------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1. It results from the end to end overlapping of two s -orbitals or p -orbitals or one s -and one p orbital. | 1. It results from the sideways (lateral) overlapping of two p -orbitals. |
| 2. Its bond consists of a single electron cloud symmetrical about internuclear axis. | 2. Its bond consists of two electron clouds, one above and other below the plane of participating atoms. |
| 3. Since the overlapping is along the combining axes, it is maximum and hence, the bond formed is | 3. The overlapping of orbitals is along the sideways, it is only partial and hence, the bond formed is weak. |
| | 4. The σ -electrons are referred to as localized. |
| | 5. Sigma bonds are less reactive. |
| | 6. The shape of the molecule is determined by the σ -bonds present in the molecule. |
| | 7. σ -bond can have independent existence. |
| | 4. In π -bond the electrons (π -electrons) are held less firmly and can move easily. They can be polarised (i.e., attracted to either end of the M.O.) by external charge and hence, the π -electrons are referred to as mobile electrons. |
| | 5. π -bonds are more reactive. |
| | 6. π -bond does not affect the shape of the molecule in which it occurs. |
| | 7. π -bond always exists along with a σ -bond. |

OBJECTIVE QUESTIONS

- Element X is strongly electro-positive and element Y is strongly electronegative. Both are univalent. The compound formed would be—
(A) $X^+ Y^-$ (B) $X^- Y^+$
(C) $X - Y$ (D) $X \rightarrow Y$
- The electronic structures of four elements a, b, c and d are—
 $a = 1s^2$; $b = 1s^2, 2s^2 2p^2$;
 $c = 1s^2, 2s^2 2p$; $d = 1s^2, 2s^2 2p^6$
The tendency to form electro-valent bond is greatest in—
(A) a (B) b
(C) c (D) d
- Covalent compounds are soluble in—
(A) Polar solvents
(B) Non-polar solvents
(C) Concentrated acids
(D) All solvents
- Which of the following is purest covalent bond?
(A) H—Cl (B) Cl—Cl
(C) C—Cl (D) Na—Cl
- In a double bond connecting two atoms there is a sharing of—
(A) 2-electrons
(B) 4-electrons
(C) 1-electron
(D) All electrons
- Which of the following bonds is the most ionic?
(A) (Cs—Cl) (B) (Al—Cl)
(C) (C—Cl) (D) (H—Cl)
- Which of the following compounds is non-polar?
(A) HCl (B) CH_2Cl_2
(C) $CHCl_3$ (D) CCl_4
- The compound which contains both ionic and covalent bonds is—
(A) CH_4 (B) H₂
(C) KCN (D) KCl
- Co-ordinate covalent compounds are formed by—
(A) Transfer of electrons
(B) Sharing of electrons
(C) Donation of electrons
(D) None of these process
- Which has covalent bond?
(A) Na_2S (B) $AlCl_3$
(C) NaH (D) $MgCl_2$
- Which of the following combinations is best explained by the co-ordinate covalent bond?
(A) $(H_2 + I_2)$ (B) $(Mg + \frac{1}{2} O_2)$
(C) $(Cl + Cl)$ (D) $(H^+ + H_2O)$
- Highest covalent character is found in—
(A) CaF_2 (B) $CaCl_2$
(C) $CaBr_2$ (D) CaI_2
- Which of the following is the most polar?
(A) CCl_4 (B) CH_3Cl
(C) CH_3OH (D) $CHCl_3$
- The maximum covalency of an element of the atomic number 7 is—
(A) 2 (B) 3
(C) 4 (D) 5
- An element A ($Z = 13$) and another element B ($Z = 8$) combine together to form a compound. The formula of the compound is—
(A) AB (B) A_2B
(C) AB_2 (D) A_2B_3
- Which of the following will contain both covalent and ionic bonds?
(A) CCl_4 (B) $CaCl_2$
(C) NH_4Cl (D) H_2O
- NH_3 and BF_3 form an adduct readily because they form—
(A) A co-ordinate bond
(B) A covalent bond
(C) An ionic bond
(D) A hydrogen bond
- Which of the following molecules does not obey the octet rule?
(A) SiF_4

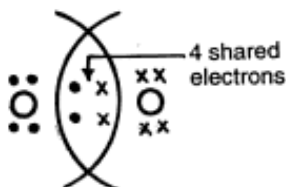
- (B) GeCl_4
 (C) PCl_5
 (D) C_2Cl_6
19. Which of the following molecules involves sp^3d hybridisation?
 (A) SnCl_2 (B) IF_5
- (C) XeF_4 (D) XeF_2
20. Molecule whose geometrical shape is not symmetrical, is—
 (A) PCl_5 (B) SF_6
 (C) PH_3 (D) CCl_4

ANSWERS

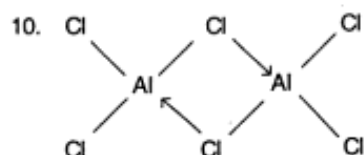
1. (A) 2. (C) 3. (B) 4. (B) 5. (B)
 6. (A) 7. (D) 8. (C) 9. (C) 10. (B)
 11. (D) 12. (D) 13. (B) 14. (C) 15. (D)
 16. (C) 17. (A) 18. (C) 19. (D) 20. (C)

HINTS

5. The correct answer is (B), i.e., 4-electrons.



6. As, in (Cs—Cl), the electronegativity difference is greater between combining atoms. i.e., Cs and chlorine.
 7. As, dipole moment for $\text{CCl}_4 = 0$ on account of symmetrical tetrahedral structure of CCl_4 .
 8. $\text{K}^+ \dots \text{C} \equiv \text{N}^-$

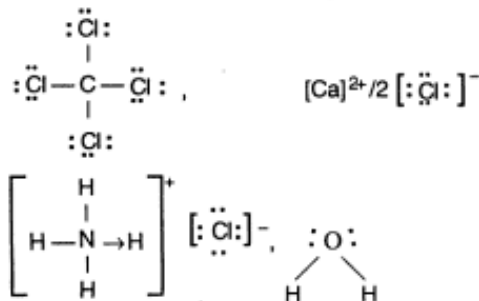


11. $\text{H}_2\ddot{\text{O}} + \text{H}^+ \rightarrow [\text{H}_2\ddot{\text{O}} \rightarrow \text{H}]^+$, Hydronium ion.
 12. As I^- is the biggest of all halide ions, so its electron clouds of valency shell will be the most polarised and hence, have highest covalent character.
 14. As, the electronic configuration is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$.

The valence shell is second principal shell which has only four orbitals. Hence, the element can form a maximum of four bonds. This is also supported by Sidgwick's covalency maxima rule, which states that second period elements can form only four covalent bonds.

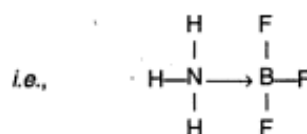
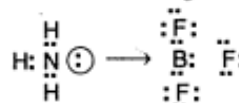
15. As, Electronic configuration of A ($Z = 13$) = 2, 8, 3.
 Electronic configuration of B ($Z = 8$) = 2, 6.
 'A' by losing 3 electrons and 'B' by gaining two electrons achieve the noble gas configurations
 Hence, valency of A is +3 and that of B is -2.
 So, the formula of the compound is A_2B_3 .

16. As, the Lewis structures of these compounds are—



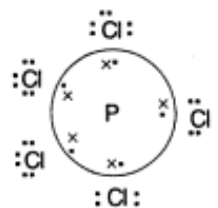
- As, (A) and (D) have only covalent bonds.
 (B) Contains an ionic bond.
 (C) Contains both covalent and ionic bonds.

17. As, the Lewis structures of NH_3 and BF_3 are:



As, the octet of N-atom is complete and B atom is in need of an electron pair to complete its octet. Hence, N-atom donates its lone pair to the B-atom. The bond formed is a co-ordinate bond.

18. PCl_5 does not obey octet rule because the valency shell of P atom has ten electrons.



19. XeF_2 molecule involves sp^3d hybridisation in Xe atom.

