The positively charged environment of the hydrogen atoms is reflected in its chemical behaviour. This ion readily gives up a hydrogen cation to a hydroxide anion : $NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$

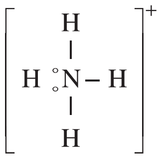
Remember that formal charge are not annual charges. Instead, formal charges are simply a device that helps us determine the most stable distribution of a molecule's valence electron.

CO-ORDINATE COVALENT BONDING Section - 4

The bonding in which one atom furnishes a pair of electrons to the other atom, in such a manner that both of the atoms achieve stability (*i.e.* 8 *electrons in outer shell*), is called as Co-ordinate Covalent or Dative Bonding.

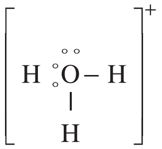
Compounds such as NH_3, having one lone pair readily forms coordinate bonds. It combines with H^+ ion (Hydrogen cation) to from Ammonium ion (NH_4^+) as follows :

$$H^+ + NH_3 \longrightarrow NH_4^+$$



Similarly, H_2O forms Hydronium ion (H_3O^+ ion) by combining with H^+.

$$H^+ + H_2O \longrightarrow H_3O^+$$



Exception to Octet Rule

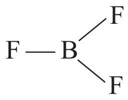
The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. Up to now we have studied the molecules which follow Lewis Octet Rule while forming bonds. It is observed that atoms in some molecules could exist with some other number of electrons in their valence shells, rather than eight electrons without affecting the stability.

There are three types of exceptions to the octet rule :

(i) The incomplete octet of the central atom

In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are LiCl, BeH_2, BCl_3, $AlCl_3$, BF_3 etc. Li, Be and B have 1,2 and 3 valence electrons only.

BF_3 : Boron atom has only six electrons in its outer-shell even after making three single bonds with three F atoms (i.e., it completes only sixet).

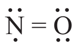


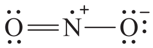
$BeCl_2$: Beryllium has only four electrons in its outershell even after making two single bonds with two Cl atoms.

$$Cl - Be - Cl$$

(ii) Odd-electron molecules

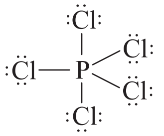
In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, NO_2, the octet rule is not satisfied for all the atoms (as shown below)



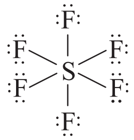


(iii) The expanded octet

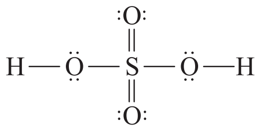
Elements in and beyond the third period of the periodic table have, apart from 3*s* and 3*p* orbitals, 3*d* orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases. Eg : PF_5, SF_6, H_2SO_4 and a number of coordination compounds.



PCl_5
10 electrons around the P atom



SF_6
12 electrons around the S atom



H_2SO_4
12 electrons around the S atom

PCl_5 : Phosphorus after making five single bonds with five Cl atoms has ten electrons in its outershell.

SF_6 : Sulphur makes six single bonds with six F atoms and thus has 12 electrons in its outershell.

H_2SO_4 : Sulphur makes 2 single bonds and 2 double bonds with 4 oxygen atoms and thereby has 12 electrons in its outermost shell

Other drawbacks of the octet theory

- It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2, KrF_2, $XeOF_2$ etc.,
- This theory does not account for the shape of molecules.
- It does not explain the relative stability and energy of the molecules.

Some Terminologies related to a Chemical Bond :

(i) Bond Energetics

The basic rule followed when a chemical bond is formed is that the total energy of the system must be lower in the bonded state than in the non-bonded state (or free atomic state). For both Ionic and Covalent bonding, association can take place only when the combined state achieves the stability, i.e., *a state of minimum energy*.

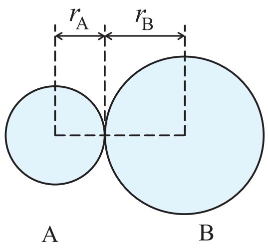
When two atoms combine to form ionic covalent bond, the total energy of the system must be lowered. Therefore energy must be given off when bonding occurs. This evolved energy is known as Bond Energy. It means, whenever *a bond is to be formed the energy will be released* and to break it, *energy must be supplied*. The covalent bonding is understood in terms of electrostatic interactions. The electrons in atoms are negatively charged and protons are positively charged, so it is electrical columbic interactions between these particles that give rise to covalent bonding.

We know that Ionic bonding is formed through electrostatic attractive force. So in both types of bonding the formation of compounds is the result of electrical interactions by columbic forces in some sense or the other.
(*You will study more about electrical forces in Physics*).

(ii) Bond Length

Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule. In the case of a covalent bond, the contribution from each atom is called the covalent radius of that atom. $R = r_A + r_B$

(R is the bond length and r_A and r_B are the covalent radii of atoms A and B respectively

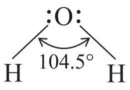


The Bond length in a covalent molecule AB

(iii) Bond Angle

It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion. Bond angle is expressed in degree which can be experimentally determined by spectroscopic methods.

It gives some idea regarding the distribution of orbitals around the central atom in a molecule/complex ion and hence it helps us in determining its shape. For example H – O – H bond angle in water can be represented as under :



Ionic Character in covalent bonds (Polar Covalent Bond) :

Covalent bond when formed between two alike atoms, bonded pair of electrons is equally shared. However when it is formed between two atoms of different kinds (unlike atoms), bonded pair is not equally shared. An atom which has more tendency to attract the shared pair of electrons towards itself (high electronegativity) will pull the bond pair towards itself.

For example: Let us consider a single covalent bond between A and B, i.e., A – B.

Let B be more electronegative than A, then the bond pair will be shifted towards B, i.e., the electron cloud of bond will distort and moves slightly over to B. As a result B acquires a partial negative charge (denoted by $-\delta$). Since the molecule is neutral, A will acquire a partial positive charge (denoted by $+\delta$). Such a state where +ve and –ve charges are separated by a certain distance, is known as *Polarised state* and the process is known as Polarisation, and the covalent bond is known as Polar Covalent Bond.

A molecule with positive and negative charge centres in *equilibrium* is called as dipole and is characterised by possessing a quantity dipole moment (μ) defined as the product of the magnitude of charge (q) and the distance (d) separating the centres of +ve and –ve charges. $\mu = q \times d$, Its unit in CGS system is debye (D). $1\ D = 1 \times 10^{-18}$ esu.cm. The charge q is measured in esu. The distance d is measured in cm and is of order of 1 Å, i.e., 10^{-8} cm. The direction of dipole moment is from +ve end to –ve end. Note : Charge on 1 electron = 1.6×10^{-19} C = 4.8×10^{-10} esu

Here, $A^{\delta+} - B^{\delta-}$ is characterised as dipole and is known as Bond Dipole. The overall dipole moment of a molecule is the vector sum of the dipole moments of all bond dipoles in a molecule. Now covalent molecules having bond dipoles are classified into two categories : **(a)** Polar molecules **(b)** Non-polar molecules

A molecule is said to be *polar* if the net dipole moment of a molecule is not equal to zero. For example : HF, H_2O, NH_3, CH_3OH, etc, are polar as in all of these, the net dipole moment is not equal to zero ($\mu_{net} \neq 0$).

For a molecule to be polar both of the following conditions must be satisfied :

(i) There must be at least one polar bond present.

(ii) The polar bonds, (if there are more than one), and lone pairs must not be so symmetrically arranged that their bond polarities cancel each other.

This means if there are no polar bonds or lone pairs on the central atom, the molecule cannot be polar. And even if these are present, they may be arranged in such a manner that their polarities cancel each other, resulting in a non-polar molecule. So a molecule is non–polar if its net dipole moment is equal to zero. For example : H_2, Cl_2, BF_3, CO_2, $BeCl_2$, etc, are non-polar as $\mu_{net} = 0$. In such molecules, in spite of bond dipoles, the molecules are non-polar.

H – H

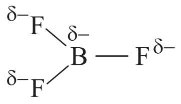
(no bond dipole, $\mu_{net} = 0$)

Cl – Cl

(no bond dipole, $\mu_{net} = 0$)

$^{\delta-}\text{Cl}-\overset{\delta+}{\text{Be}}-\text{Cl}^{\delta-}$

(2 bond dipoles but $\mu_{net} = 0$)



(3 bond dipoles but $\mu_{net} = 0$)

The conclusion is that, the dipole moment of a molecule, (zero or non–zero), depends upon the structure or shape (or on geometry) of the molecule. For example H_2O is polar whereas $HgCl_2$ is non–polar. The difference lies in the shapes of two molecules. H_2O is angular ($\mu \neq 0$) and $HgCl_2$ is linear ($\mu = 0$). Both have polar bonds, O–H bond in water while Hg–Cl bond in mercuric chloride, but due to structure of $HgCl_2$ being linear, the dipole moments of two bond dipoles cancel each other whereas in water, due to angular shape the dipole moments of two bond dipoles do not cancel and give rise to a net dipole moment.

Applications of Dipole Moment

(i) **To decide polarity of the molecule :** Molecules having zero dipole moment μ are said to be non-polar molecules and those having $\mu_R \neq 0$ (resultant dipole moment) are polar in nature.

(ii) **To determine percentage of ionic charcter :** The value of dipole moment can be used for determining the amount of ionic character in a bond.

$$\mu = q \times \text{d}$$

Consier a diatomic molecules say HCl. Suppose this molecule is completely ionic. Under this condition H^+ and Cl^- ions would bear a unit charge equal to 4.8×10^{-10} esu and the bond distance between H and Cl atoms = 1.27 Å.

Thus, theoretical value of $\mu = 4.8 \times 10^{-10} \times 1.27 \times 10^{-8} = 6.09$ D

Dipole moment of HCl is also determined experimentally. Let the experimental value be 1.03 D.

Percentage of ionic character in H — Cl bond in HCl molecule $= \dfrac{\text{Experimental value of } \mu}{\text{Theoretical valueof } \mu} \times 100 = \dfrac{1.03}{6.09} \times 100 = 16.9\ \%$

Thus, $$\boxed{\text{percentage of ionic character} = \dfrac{\text{Experimental value of dipole moment}}{\text{Theoretical value of dipole moment}} \times 100}$$

(iii) **To determine geometry of molecules :** The values of dipole moments provide value information about the structure of molecules.

(a) CO_2, CS_2 molecules are linear as value of their dipole moments are zero.

(b) H_2O is not a linear molecule as it has dipole moment. Actually, it has V-shaped structure and the bond angle is 105°. Similary, SO_2 has a bent structure.

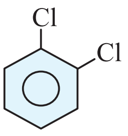
(c) In ammonia, three hydrogen atoms do not lie symmetrically with respect to nitrogen as it has dipole moment. It has pyramidal structure.

Molecular Geometry and Dipole Moment

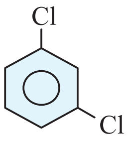
General Formula	Molecular Geometry	Dipole Moment	Example
AX	Linear	May be non zero	HF, HCl
AX_2	Linear Bent or V-shape	Zero Non zero	CO_2, CS_2 H_2O, NO_2
AX_3	Triangular planar Pyramidal T-shape	Zero Non zero Non zero	BF_3 NH_3, PCl_3 ClF_3
AX_4	Tetrahedral Square planar See saw	Zero Zero Non zero	CH_4, CCl_4 XeF_4 SF_4, $TeCl_4$
AX_5	Trigonal bipyramidal Square pyramidal	Zero Non zero	PCl_5 $BrCl_5$
AX_6	Octahedral Distorted octahedral	Zero Non zero	SF_6 XeF_6
AX_7	Pentagonal bipyramidal	Zero	IF_7

(iv) To determine orientation in benzene ring : Dipole moment is useful to ascertain the orientation of substituents. In general, dipole moment follows the order :

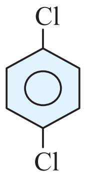
ortho-isomer > meta-isomer > p-isomer



Ortho
μ = 2.54 D



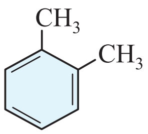
Meta
μ = 1.48 D



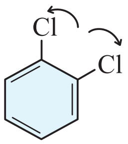
Para
μ = 0

Observe that :
$\mu_o > \mu_m > \mu_p$

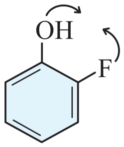
In ortho isomers, experimental value of dipole moment is found different from theoretical value of dipole moment. This difference is due to dipole-dipole interaction of two groups.



$\mu_{exp} = \mu_{theo}$
(No interactions between two group)



$\mu_{exp} < \mu_{theo}$
(Repulsion)
(θ increase, μ decreases)



$\mu_{exp} > \mu_{theo}$
(Attraction due to H-bond)
(θ decreases, μ increases)

(v) **Bond moment :** The contribution of individual bond in the dipole moment of a polyatomic molecule is termed bond moment. The measured dipole moment of water molecule is 1.85 D. This dipole moment is the vectorial sum of the individual bond moments of two O — H bond having bond angle 104.5°.

Thus, $\mu_{obs} = 2\mu_{O-H}\ \cos 52.25$

$$1.85 = 2\mu_{O-H} \times 0.6129$$

$$\mu_{O-H} = 1.51 \text{ D}$$

Illustration - 6 *(a) A diatomic molecule has a dipole moment of 1.2 D. If the bond distance is 1.0 Å, what fraction of an electronic charge, e, exists on each atom ?*

(b) *The dipole moment of LiH is 1.964×10^{-29} Cm and the interatomic distance between Li and H in this molecule is 1.596 Å. What is the per cent ionic character in LiH ?*

SOLUTION :

(a) Partical charge $= \dfrac{\text{Dipole moment}}{\text{Bond distance}}$

$$= \frac{1.2 \times 10^{-18}\ \text{esu cm}}{1.0 \times 10^{-8}\ \text{cm}}$$

$$= 1.2 \times 10^{-10}\ \text{esu}$$

The fraction of an electronic charge

$$= \frac{1.2 \times 10^{-10}}{4.8 \times 10^{-10}} = 0.25 = 25\% \text{ of e.}$$

(b) The dipole moment of 100% ionic molecule (Li^+H^-)

$$= (\text{1 electronic charge})\ (\text{interatomic distance})$$

$$= (1.602 \times 10^{-19}\ \text{C})\ (1.596 \times 10^{-10}\ \text{m})$$

$$= 2.577 \times 10^{-29}\ \text{Cm}$$

Fractional ionic character

$$= \frac{\text{Exp. value of dipole moment}}{\text{Theoretical value of dipole moment}}$$

$$= \frac{1.964 \times 10^{-29}}{2.557 \times 10^{-29}} = 0.768$$

The bond in LiH is 76.8% ionic.

Illustration - 7 *Predict whether each of the following molecules has a dipole moment :*

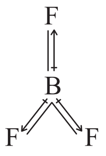
(a) *IBr* **(b)** *BF_3* **(c)** *CH_2Cl_2*

SOLUTION :

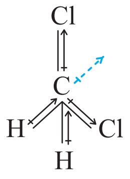
(a) Since IBr molecule is diatomic, it has a linear geometry. Bromine is more electronegative than iodine, hence, IBr is polar with bromine at the negative end. Thus, the molecule does have a dipole moment.

$$\overset{+\!\dashrightarrow}{\text{I}\text{———}\text{Br}}$$

(b) Since fluorine is more electronegative than boron, each B – F bond in BF_3 is polar and three bond moments are equal. However, the symmetry of a trigonal planar shape means that the three bond moments exactly cancel one another.



(c) CH_2Cl_2 is similar to CH_4 (tetrahedral), but it has three different bond angles : HCH, HCCl, and ClCCl, which are close to but not equal to 109.5°. Since Cl is more electronegative than C and which is more electronegative than H, the bond moments do not cancel and the molecule possesses a dipole moment. CH_2Cl is thus a polar molecule.



Resultant dipole moment is indicated by $+\!\dashrightarrow$

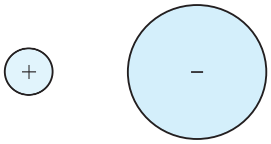
Covalent Character in Ionic bonds :

When a cation is placed near an anion, it distorts the spherical shape of the anionic electron cloud due to its attractive force. Such a distorted anion is said to be polarized.

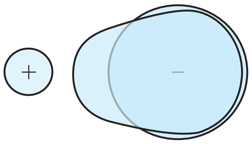
Since the electrons now have a better tendency to stay between the two nuclei rather than entirely on the anion, the ionic compound is said to have acquired a certain covalent character. The tendency of cation to polarize the anion is called its polarizing power.

The tendency of the anion to undergo polarisation is called its polarisability.

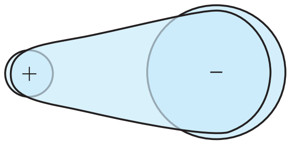
Greater the polarizing power of cation or polarisability of anion, greater is the covalent character of the molecule.



No polarization
Idealized ionic
bond



Anion is polarized.
Cation may be slightly polarized
Some covalent character.



Anion and cation
are both polarized.
Covalent bond.

The covalent character of an ionic compound is favoured by :

(a) **A small cation :** In a small cation the positive charge is concentrated over a small surface area and as a result its effect in polarizing the anion would be large. e.g, the covalent character of the chlorides of the Be group decreases in the order, Be > Mg > Ca > Sr > Ba.

(b) **A large anion :** Large anions have a high polarisability since their outermost orbitals are shielded from the positive nuclear field by a number of completely occupied orbitals and are thus readily polarized by a suitable cation. E.g, the halides of Ca; the covalent character increases in order

$$CaF_2 < CaCl_2 < CaBr_2 < CaI_2. \;\; ; \;\; \text{polarisability is } F^- < Cl^- < Br^- < I^-$$

(c) There should be a high charge on either the cation or the anion or both. It is obvious that the electrostatic forces which cause polarization will be considerably enhanced, if the ions are highly charged. e.g., polarizing power of cations increases in the order $Na^+ < Mg^{2+} < Al^{3+}$ (all the three are isoelectronic).

(d) The cation should possess an electronic configuration which is not that of an "inert" gas. It follows that the noble gas electronic configuration must be the most effective in shielding the nuclear charge of a cation from its surface. Cations without this configuration will have high positive field at their surface and consequently will have high polarizing powers.

The combined influence, of ionic size and charge on the polarizing power of a cation is sometimes expressed in terms of ionic potential. $\phi = \dfrac{\text{cationic charge}}{\text{cation radius}}$

Fazan rule is used to decide relative ionic and covalent character in molecules. According to this rule a molecule is predominant covalent if :

- smaller the size of cation
- larger the size of anion
- greater the charge on cation and anion.
- ion does not have inert gas configuration.

We can also say that these factors favour polarisation.

Note : Greater the covalent nature

- lower the mp/bp
- smaller conducting nature
- lower solubility in polar solvent
- higher solubility in non polar solvent.

(a) LiCl, NaCl, KCl, RbCl, CsCl

Size of cation is the deciding factor (charge of each ion and size of Cl is same)

$$\xrightarrow[\text{size of cation}]{Li^+ < Na^+ < K^+ < Rb^+ < Cs^+}$$

$$\xleftarrow[\text{polarisation}]{}$$

$$\xleftarrow[\text{covalent}]{LiCl > NaCl > KCl > RbCl > CsCl}$$

$$\xrightarrow[\text{mp/bp}]{}$$

$$\xrightarrow[\text{conductivity}]{}$$

$$\xrightarrow[\text{solubility in } H_2O \text{ (polar solvents)}]{}$$

$$\xleftarrow[\text{solubility in non polar solvent}]{}$$

(b) NaF, NaCl, NaBr, NaI

Deciding factor is the size of the anion. Larger size of the anion, greater the polarization hence greater the covalent nature.

$$\xrightarrow[\text{size of anion}]{F^- < Cl^- < Br^- < I^-}$$

$$\xrightarrow[\text{polarisation}]{F^- < Cl^- < Br^- < I^-}$$

$$\xrightarrow[\text{covalent nature}]{NaF < NaCl < NaBr < NaI}$$

(c) $NaCl, MgCl_2, AlCl_3, SiCl_4, PCl_5$

$$\xleftarrow[\text{size of cation}]{Na^+ > Mg^{2+} > Al^{3+} > Si^{4+} > P^{5+}}$$

$$\xrightarrow[\text{charge on cation}]{}$$

Note : Greater the charge, smaller the size then greater the polarisation

$$\xrightarrow[\text{polarisation}]{Na^+ < Mg^{2+} < Al^{3+} < Si^{4+} < P^{5+}}$$

$$\xrightarrow[\text{covalent nature}]{NaCl < MgCl_2 < AlCl_3 < SiCl_4 < PCl_5}$$

(d) NaF, Na_2O, Na_3N

$\xrightarrow{F^- < O^{2-} < N^{3-}}$ size of anion

$\xrightarrow{F^- < O^{2-} < N^{3-}}$ charge on anion

$\xrightarrow{F^- < O^{2-} < N^{3-}}$ polarisation

$\xrightarrow{NaF < Na_2O < Na_3N}$ covalent nature

(e) CuCl and NaCl

$[Cu^+]$ $[Ar]\ 3d^{10}$

$[Na^+]$ $[Ne]$

Cations with 18– electron shells have greater polarising power than the 8-electron shell ions with the same charge and size. This is due to the increased electronegativity of the 18-electron shell ions as the inner electrons have poor shielding effect on the nucleus. Thus CuCl is covalent and NaCl is ionic.

SHAPES OF MOLECULES (VSEPR THEORY) Section - 5

The shapes or geometry of a molecule is quite accurately predicted by VSEPR (Valence Shell Electron Pair Repulsion) theory. According to this theory *all valence shell electron pairs surrounding the central atom arrange themselves in such a manner as to be as far away from each other as possible.* By separating the electrons from each other, the electrostatic repulsion, (that is the cause of higher energy), is minimised. As a result each molecule tends to acquire a state of lowest energy.