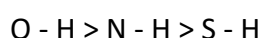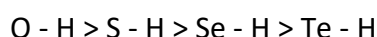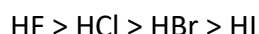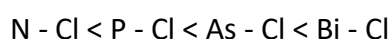## POLARITY - DIPOLE MOMENT:

If covalent bonds are present between same atoms, the electron pairs are equally shared in between them. In such molecules, positive or negative charges are not developed on any atom. Such covalent bonds are called non-polar covalent bonds & the molecules may be called **non-polar molecules. Eg.** H_2, N_2, O_2, F_2, Cl_2, etc.

- If covalent bonds are present between dif. atoms, the bonded e^- pair is unequally shared in between them. More electronegative atom shares more & less electron negative atom shares less As a result, more electronegative develops ⬚⬚negative charge; and less electronegative atom develops ⬚ positive charge. Such covalent bonds are called **Polar covalent bonds** & the molecules are called polar molecules & the phenomenon is called polarity.
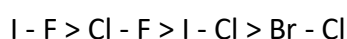
The above polar molecules are called dipoles. Magnitude of polarity will depend on EN difference between bonded atoms.

HF > HCl > HBr > HI

O - H > S - H > Se - H > Te - H

O - H > N - H > S - H

(EN difference decrease s, polarity decreases)

N - Cl < P - Cl < As - Cl < Bi - Cl

(EN difference increases, polarity increases)

I - F > Cl - F > I - Cl > Br - Cl

(EN difference decreases, polarity decreases)

Dipole moment :

The magnitude of polarity in the molecule is expressed in terms of dipole moment value.

Dipole moment is defined as the product of charge & the distance between the charges.

$\mu = e \times d$

$\mu = \delta \times l$

Where $\mu \rightarrow$ dipole moment

$e, \delta \rightarrow$ charge

$d, l \rightarrow$ distance (bond length)

Units of dipole moment : Debyes

1 Debye = 10^{-18} e.s.u cm

1 Debye = 3.33×10^{-30} coloumbmetre

The dipole moment of each bond is called bond - dipole or bond - moment the direction of the bond moment ($\rightarrow$) is from less EN to more EN atom.

- Dipole moment is a vector quantity. $\therefore$ the net dipole moment of molecule is the vector sum of bond dipoles, but it is not simply the sum of bond - dipoles
- The net dipole moment of the molecule depends on

1) Polarity of bonds

2) Shapes of the molecules.

- If only bond - pairs are present the molecule has regular shape & its dipole moment will be zero due to mutual cancellation of the bond moments.

    Eg : All linear molecules are non polar, $\mu = 0$

       $BeCl_2$, BeF_2, CO_2

    All trigonal molecules are non - polar, $\mu = 0$

    Eg : BF_3, PCl_3, BBr_3, SO_3, BI_3, etc

- All regular tetrahedral molecules are non - polar, $\mu = 0$

    Eg : CCl_4, CF_4, $SiCl_4$, SiF_4, CH_4, $SnCl_4$

- The molecule in which central atom contains one or more lone pairs will have irregular geometry & such molecules are polar & they have net dipole moment value.

    Eg : H_2O, H_2S, SO_2, $SnCl_2$

    These are angular & $\mu \neq 0$

- SCl_4, SF_4, $SeCl_4$, are distorted tetrahedral $\mu \neq 0$ and are polar.

- Thus, the molecule with polar bonds may be polar or non-polar as discussed above.

- Among the ortho, meta, para Isomers of a given compound μ ortho > μ meta > μ para

- In cis & trans Isomers of a compound $\mu_{cis} > \mu_{trans}$

- The shape of AB_4 molecule for which observed $\mu = 0$ is tetrahedral.

APPLICATIONS OF DIPOLE MOMENT:

1) The shape of the molecule & hybridisation of central atom can be predicted.

    $\mu_{CO_2} = 0$ linear (sp)

    $\mu_{SO_3} = 0$ trigonal planar (sp^2)

    $\mu_{CCl_4} = 0$ tetrahedral (sp^3)

    $\mu_{SO_2} \neq 0$ Angular (sp^2)

    $\mu_{H_2O} \neq 0$ Angular (sp^3)

    $\mu_{SnCl_2} \neq 0$ Angular(sp^2)

    $\mu_{NH_3} \neq 0$ Pyramidal(sp^3)

2) Cis & trans Isomers of a compound can be distinguished.

    $\mu_{cis} > \mu_{trans}$

3) Ortho, meta, para Isomeras of a compound can be distinguished

$\mu_{ortho} > \mu_{meta} > \mu_{para}$

4) % Ionic character can be calculated. Greater the EN difference, greater is the dipole moment value & greater is the ionic character.

% Ionic Character = $\frac{\mu_{obs}}{\mu_{cal}} \times 100$

Examples:

1. The dipole moment of HCl is 1.03 debyes. If the bond length is $1.28A^0$

    Calculate % Ionic character.

    $\mu_{cal} = e \times d$

    $= 4.8 \times 10^{-10} \times 1.28 \times 10^{-8}$

    $= 4.8 \times 1.28 \times 10^{-18}$

    $= 4.8 \times 1.28$ Debyes

    % Ionic character $= \frac{1.03 \times 100}{4.8 \times 1.285} = 16.8\%$

2. Dipole moment of. HF is 1.92 Debyes If bond length of HF is $0.9A^0$. Calculate its Ionic character.

    $\mu_{cal} = 4.8 \times 10^{-18} \times 0.9\ A^0 = 4.8 \times 0.9$ debyes

    % Ionic character $= \frac{1.92}{4.8 \times 0.9} \times \frac{10^{-18} \times 100}{10^{-18}}$

    $= \frac{192}{48 \times 9} \times 100 = 44\%$

    $\boxed{\mu_{obs} = 2 \times \text{bond moment} \times \cos\frac{\theta}{2}}$

3. The dipole moment of H_2S molecule is 0.95 debyes. If the bond angle is 92^0. Calculate the bond moment of S - H bond

    $(\cos 46^0 = 0.65)$

    $\mu_{obs} = 2 \times \text{bond moment} \times \cos\frac{\theta}{2}$

    $0.95 = 2 \times x \times \cos 46$

    $0.95 = 2 \times x \times 0.65$
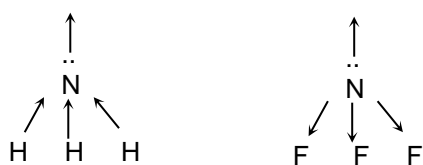
    $2x = \frac{95}{65} = \frac{19}{13}$

    $2x = 1.46$

    $x = 0.73$

Though EN difference between N & F is greater than that of between N & H Even though, both NH_3 & NF_3 are pyramidal $\mu_{NH_3} > \mu_{NF_3}$

In NH_3, the lone pair contributes in the same direction as those of bond dipoles where as in NF_3 lone pair contributes in opposite direction as those of bond – dipoles

In case of AB_2 type tri - atomic molecules μ value increases with decrease in the bond angle

METALLIC BOND:

The force of attraction that binds the metal atoms in metallic crystal is called metallic bond. The nature of metallic bonding is explained by following three theories.

    1) Free e^- theory

    2) Valence bond theory

    3) Molecular orbital theory.

Free electron theory:

(Electron pool theory or electron gas theory)

- This was proposed by Orude & Lorance.
- All metal atoms loose their valence e^- in metallic crystal.
- All these valence electrons together will form an electron pool or electron gas.
- The force of attraction between positively charged metal ions and negative electron pool is called metallic bond.
- These deloclised e^-s move freely into the vacant orbitals of all positively charged ions. Thus, metal is imagined to be positively charged ions immersed in a sea of mobile electrons.

The strength of metallic bond will depend on (1) size of the atom   (2) number of participating e^-s

- Smaller atoms with more number of valence e^-s will form stronger metallic bonds.
- In case of stronger metallic bonds, metals are hard with high melting & boiling points.
- Metallic bond is non-directional as it involves delocalised electrons.
- Though this theory could explain conductivity, metallic luster & some other properties, it fails to explain the differences in properties between various metals.

VALENCE BOND THEORY:

This was proposed by pauling.

- Acc. to this theory, metallic bond is similar to that of covalent bond.
- A metal atom is bonded to its neighbouring atoms by the sharing of e^- pairs. But, these shared pairs are not localised because they move freely into vacant orbitals of metal atoms.
- In metallic crystal, each metal atom is surrounded by numerous metal atoms. The central atom can form a bond with any one of metal atom & it results in various resonance structures.

- Because of resonance, the metallic crystal is stable & metallic bonds are stronger (metal atom).
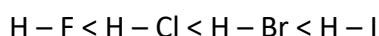
BOND PARAMETERS:

Covalent bond is characterised by the following:

1) bond length   2) bond angle   3) bond energy

Bond length:- It is the average distance between two bonded atoms it is expressed in Angstrom units (A^0).

Bond length depends on

i)   Size of atom: with increase in size of bonded atom, bond-length increases.

   $H - F < H - Cl < H - Br < H - I$

ii)   Bond order: The number of bonds between two atoms is called bond order with increase in bond-order, bond length value decreases

$$\underset{B.O.:}{\underset{1.54A^0}{\overset{1}{C-C}} \quad \underset{1.34A^0}{\overset{2}{C=C}} \quad \underset{1.2A^0}{\overset{3}{C\equiv C}}}$$
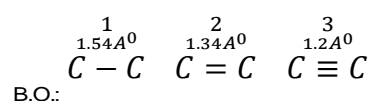
iii)   **S-character:-** With increase in S-character size of orbital decreases and bond length decreases.

$$\underset{S-sp^2}{H - \overset{|}{\underset{S-sp^3}{C}}} > \underset{S-sp^2}{H - \overset{|}{C}} => \underset{S-sp}{H - C \equiv}$$
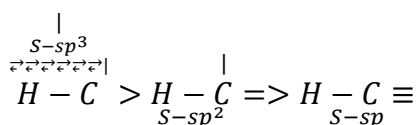
iv)   With increase in polarity, bond length decreases.
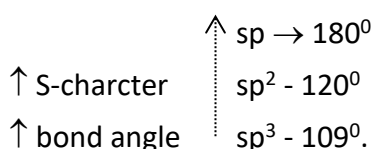
   H - F < H - Cl < H - Br < H - I
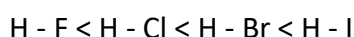
v)   **Resonance:** Because of resonance, the bond lengths of different bonds will become identical. Generally, the bond length will be in between that of single bond length value & double bond length value.

   Eg.: In O_3, bond length between two oxygens is 1.28 A^0 which is in between $\overset{1.48A^0}{O \to O}$ & $\overset{1.2A^0}{O = O}$.
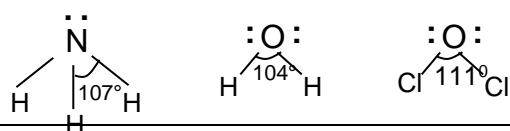
BOND ANGLE:-

   It is the angle between the two adj. bonded atoms. Bond angle depends on

i)   Nature of hybridisation sp - 180^0, sp^2 - 120^0, sp^3 - 109^0.

ii)   S-character: with increase in S-character bond angle increases.

   ↑ S-charcter   sp → 180^0

   ↑ bond angle sp^2 - 120^0

                   sp^3 - 109^0.

iii)   Repulsions in between the electron pairs:- Due to repulsions in between lone pairs, bond angle decreases. If the repulsions between bond pairs are more, bond angle increases.
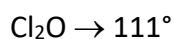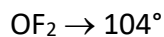
iv) Electrongegativity:- With decrease in EN of central atom, the bond angle decreases.

EN $\downarrow$ H_2O 104° NH_3 107°

          H_2S 92° PH_3 93°

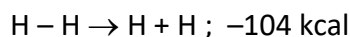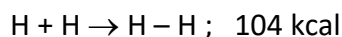BA $\downarrow$s H_2Se 91° ASH_3 91° 30'

          H_2Te 90° SbH_3 91°

If the EN of bonded atoms decreases, bond angle increases

$OF_2 \rightarrow 104°$

$Cl_2O \rightarrow 111°$

BOND ENERGY:-

The amount of energy released when one mole of bonds are formed (or) The amount of energy absorbed to break one mole of bond.

Bond energy usually refers to bond dissociation energy.

     $H + H \rightarrow H - H$;   104 kcal

     $H - H \rightarrow H + H$;   −104 kcal

In case of polyatomic molecule, the bond energy of particular bond is the average of sum of all bond energies.

$CH_4 \rightarrow CH_3 + H$; x_1

$CH_3 \rightarrow CH_2 + H$; x_2

$CH_2 \rightarrow CH + H$; x_3

$CH \rightarrow C + H$; x_4
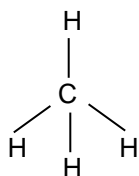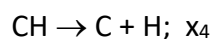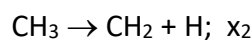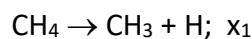
Bond energy of C - H bond = $(x_1 + x_2 + x_3 + x_4) / 4$

1. Bond energy of CH_4 is 360 k.cal/mole & that of C_2H_6 is 620 k.cal/mole. Calculate the bond dissociation energy of C − C bond

   Bond energy of C - H bond = 360 / 4 = 90 k.cal
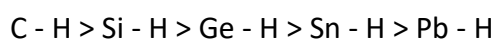
   In Ethane there are six C - H bonds & one C - C bonds. $620 = 6 \times 90 - x$
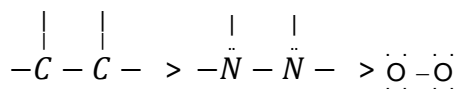
   x = 80 k.cal

Factors influencing bond energy :

1) **Size of bonded atom:**

   with increase in size of bonded atom, bond energy decreases.

   C - H > Si - H > Ge - H > Sn - H > Pb - H
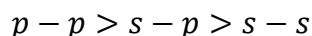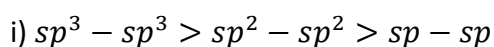
   C-C > Si - Si > Ge - Ge > Sn - Sn > Pb-Pb

2) **Bond order:** With increase in the bond order, bond energy increases.

3) **Presence of lone pairs:** With increase in the number of lone pairs, bond energy decreases.

$$-\overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - \quad > \quad -\overset{|}{\underset{\cdot\cdot}{N}} - \overset{|}{\underset{\cdot\cdot}{N}} - \quad > \quad \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} - \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}$$

4) **P-character:** With increase in the P-character of orbital, the extent of overlapping increases & bond energy increases.

i) $sp^3 - sp^3 > sp^2 - sp^2 > sp - sp$
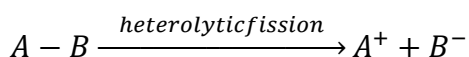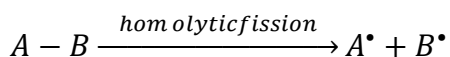
$p - p > s - p > s - s$

5) **Polarity:** With increase in polarity, bond energy increases.

H - F > H - Cl > H - Br > H - I
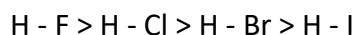
6) **Resonance:** Resonance leads to the stability of bonds & increases the bond energy.

7) **Type of bond fission:** Bond can be fissioned by homolytic or heterolytic way. Energy required for homolytic fission is less than heterolytic fission.

$$A - B \xrightarrow{\;hom\,olytic fission\;} A^{\bullet} + B^{\bullet}$$

$$A - B \xrightarrow{\;heterolytic fission\;} A^{+} + B^{-}$$

If the bond energy is more, the molecule is more stable & reactivity is less.

Even though EN of nitrogen is more N_2 is less reactive due to greater bond energy.

Predicting the type of bonds:-

The bond between two electronegative atoms is covalent bond.

The bond between two electropositive elements is metallic bond.

The bond between electropositive & electronegative element is ionic bond.

	Ionic	Covalent	Co-ordinate covalent
NaCl	✓		
HCl		✓	
NaOH	✓	✓	
NaCN	✓	✓	
HCN		✓	
$CH_3 - NH_3$		✓	
NH_3		✓	
NH_4^+		✓	✓
H_2O		✓	
H_3O^+		✓	✓

NH$_4$Cl	✓	✓	✓
SO$_2$		✓	✓
SO$_3$		✓	✓
SO$_4^{2-}$	✓	✓	✓
CuSO$_4$	✓	✓	✓
CuSO$_4$.5H$_2$O	✓	✓	✓
Ni(CO)$_4$		✓	✓
Fe(CO)$_5$		✓	✓
K$_4$[Fe(CN)$_6$]	✓	✓	✓

Number of sigma bonds = Atomicity - 1

Atomicity → number of atoms in a compound

Eg.:

CO$_2$	$\sigma = 3 - 1$	$= 2$	$\pi = 2$
CH$_4$	$\sigma = 5 - 1$	$= 4$	$\pi = 0$
C$_2$H$_6$	$\sigma = 8 - 1$	$= 7$	$\pi = 0$
C$_2$H$_4$	$\sigma = 6 - 1$	$= 5$	$\pi = 1$
C$_2$H$_2$	$\sigma = 4 - 1$	$= 3$	$\pi = 2$
HCN	$\sigma = 3 - 1$	$= 2$	$\pi = 2$