



### What you already know

- Electron deficient compounds
- Diborane
- Electron deficiency in  $\text{BeCl}_2$ ,  $\text{BeH}_2$ ,  $\text{AlCl}_3$
- Bond parameters
- Bond angle
- Bond length



### What you will learn

- Types of bonds
- Covalent and ionic character of bonds
- Types of covalent bonds
- Polarization
- Dipole moment
- Order of dipole moment
- Dipole moment for diatomic and polyatomic molecules
- Predicting the geometry using dipole moment



BOARDS

### Types of Bonds

The **attractive force** that **holds** various **constituents** (atoms, ions, etc.) **together** in different chemical species is known as a **chemical bond**.

#### Types of bonds

Covalent bonds      Sharing of electrons

Ionic bonds      Transfer of electrons

### Covalent bond

It is a chemical bond that involves the **sharing of electron pairs** between two electronegative atoms. These electron pairs are known as shared pairs or bonding pairs.

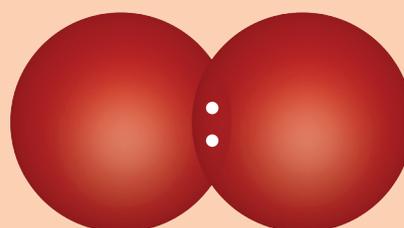


Fig. 1: Covalent bond

## Ionic bond

It is a chemical bond that involves the **complete transfer of valence electron(s)** from an electropositive atom to an electronegative atom. In an ionic bond, the two oppositely charged ions are held together by electrostatic forces of attraction.

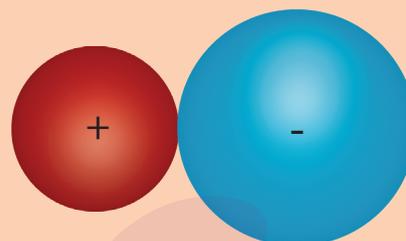


Fig. 2: Ionic bond



## Covalent and Ionic Character of Bonds

The ionic and covalent character of a bond depend upon the atoms attached to form the bond. All the **homonuclear diatomic molecules have purely covalent bonds** and almost every other molecule has some covalent and ionic character depending upon the electronegativity difference of the atoms attached to form the bond.

### Example:

- In case of a **heteronuclear diatomic molecule** like **HF**, the shared electron pair between the two atoms gets displaced more towards fluorine since the electronegativity of fluorine is far greater than that of hydrogen. As a result, a slight positive charge ( $\delta^+$ ) is developed on the H-atom and a slight negative charge ( $\delta^-$ ) is developed on the F-atom. Thus, the resultant **covalent bond has some ionic character**
- In case of a **homonuclear diatomic molecule** like **H<sub>2</sub>**, both the **atoms** involved in bonding are identical with the **same electronegativity values**. Therefore, the shared electron cloud remains in between the two hydrogen atoms. Thus, it is a **pure covalent bond**.
- In **LiBr**, the electron cloud of **Br<sup>-</sup>** is attracted by the nucleus **of the Li<sup>+</sup> ion** and thus, **the tendency of the electron cloud to remain in between the two nuclei gets slightly increased** and therefore, some **covalent character** is developed in **LiBr**.

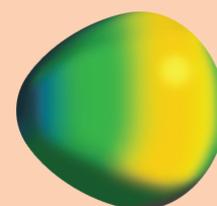


Fig. 3: Heteronuclear molecule

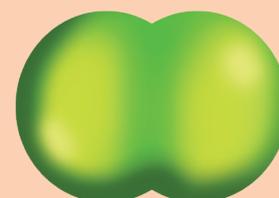


Fig. 4: Homonuclear molecule

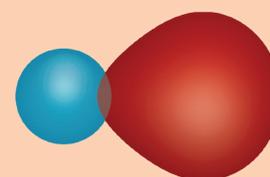


Fig. 5: Covalent character in LiBr



## Types of Covalent Bonds

The covalent bond is mainly of the following two types:

## Covalent bond

### Nonpolar covalent bond

When  $\Delta E.N. \leq 0.4$   
between the  
bonded atoms

### Polar covalent bond

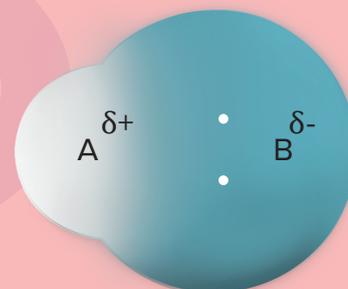
When  $\Delta E.N. > 0.4$   
between the  
bonded atoms

### Polar covalent bond

It is the bond formed **between two dissimilar atoms** having the electronegativity difference of **more than 0.4**.

If the two bonded atoms are dissimilar, having the electronegativity difference of more than 0.4, i.e., like in the **HF** molecule, the **fluorine atom is more electronegative than the hydrogen atom** and the shared pair of electrons are more attracted towards the fluorine atom than to the hydrogen atom. As a result, the **fluorine end** of the molecule acquires a **slight negative charge ( $\delta^-$ )**, while the **hydrogen end** acquires a **slight positive charge ( $\delta^+$ )**, and separation of charges occurs. Thus, the molecule becomes **polar** and the bond between H and F-atoms is known as a polar covalent bond.

Some other examples of molecules having polar covalent bonds are **HCl, HBr, HI**, etc.

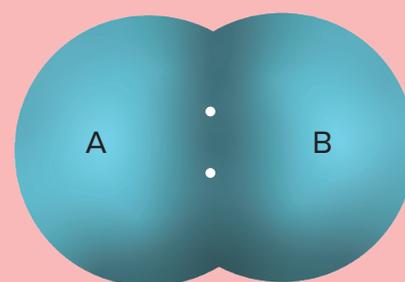


**Fig. 6: Asymmetrical electron cloud in a polar covalent bond**

### Nonpolar covalent bond

It is a bond formed between atoms having the **electronegativity difference that is less than or equal to 0.4**.

**For example**, in the  $\text{CH}_4$  molecule, the electronegativity of a carbon atom is 2.47 and the electronegativity of a hydrogen atom is 2.1. Since the electronegativity difference between the two atoms is less than 0.4, the C–H bond of  $\text{CH}_4$  molecules is considered as a nonpolar covalent bond.



**Fig. 7: Symmetrical electron cloud in a nonpolar covalent bond**



### Note

When the two atoms are identical as in any homodiatom molecule like  $\text{H}_2$  molecule, the **shared pair of electrons** are **attracted equally** by both the nuclei. Thus, it **remains in the centre of the two atoms** and the bond between the two atoms is a pure covalent bond, i.e., no ionic character. Some other examples of the molecules having pure covalent bonds are  $\text{O}_2$ ,  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{N}_2$ , etc.

## BOARDS

### Polarity

Due to asymmetrical electron cloud distribution partially charged ends are developed in the polar covalently bonded molecules and they act as **electric dipoles**.

The presence of this electric dipole leads to the intermolecular attraction and repulsion that determines the various physical and chemical properties of the molecules.

**For example**, most of the molecules such as  $O_2$ ,  $N_2$ , and  $CO_2$  have more molecular mass than water ( $H_2O$ ), and they still exist in the gaseous state and  $H_2O$  exists in the liquid state. This can be explained using the phenomenon of electric dipole.

**Water is a polar molecule** because the electronegativity of the oxygen atom is more as compared to that of the hydrogen atom. Thus, a partial **positive charge develops on the hydrogen atom**, whereas a partial **negative charge develops on the oxygen atom**. Thus, the **molecules of water behave as the electric dipole**. Due to the intermolecular attraction between the electric dipoles, water exists in the form of a liquid.

## BOARDS MAIN

### Dipole Moment

It is the **product of the magnitude of the charge** and the **distance** between the centres of the positive and negative **charges**. It is denoted by the Greek letter  $\mu$ .

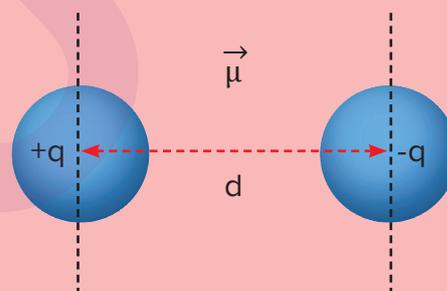


Fig. 8: Representation of a dipole moment

- Mathematically, it is expressed as follows:

$$\text{Dipole moment } (\mu) = \text{Charge } (q) \times \text{Distance of separation } (d)$$

- Dipole moment is usually expressed in **Debye (D)**.
- Magnitude of charge on an electron =  $4.8 \times 10^{-10}$  e.s.u.  
=  $1.6 \times 10^{-19}$  C
- $1 D = 3.33564 \times 10^{-30}$  C m, where C is coulomb and m stands for metre.
- $1 D = 10^{-18}$  e.s.u. cm, where e.s.u. is an electrostatic unit of charge and cm stands for centimetre.

## BOARDS

### Direction and Representation of Dipole Moment

Dipole moment is a **vector quantity**, i.e., it has magnitude as well as direction. It is represented by a crossed arrow ( $\leftrightarrow$ ). **The tail** of the arrow is on the **positive centre** and **the head** of the arrow points towards the **negative centre**, i.e., a dipole moment has the same direction as that of the shift of electron density in the molecule. For example, in the HCl molecule, the chlorine atom is more electronegative than the hydrogen atom. Therefore,



Fig. 9: Direction and representation of a dipole moment in HCl

the electron density will lie towards the Cl-atom resulting in a partial negative charge ( $\delta^-$ ) on the Cl-atom and a partial positive charge ( $\delta^+$ ) on the H-atom. Hence, **in this electric dipole, the tail of the arrow will be on the H-atom and the head of the arrow will be on the Cl-atom.**

## BOARDS

## Dipole Moment for Diatomic and Polyatomic Molecules

## MAIN

## For diatomic molecules

The polar diatomic molecule possesses only one polar bond, so the dipole moment of such molecule depends only upon the dipole moment of this polar bond. The **magnitude of dipole moment depends upon the electronegativity difference between the bonded atoms and the internuclear distance between them.** More the electronegativity difference between the bonded atoms, more is the dipole moment. In homonuclear molecules there is no difference in electronegativity between bonded atoms and hence they have zero dipole moment.

**For example,** the value of the dipole moment for  $O_2$ ,  $F_2$ ,  $Cl_2$ ,  $N_2$ , etc., is zero.

## For polyatomic molecules

In the case of polyatomic molecules, the dipole moment not only depends upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in that molecule. In such a case, **the net dipole moment is the vector sum of the dipole moments of all the bonds.**

Let P and Q be the two individual dipole moments of the bonds in a polyatomic molecule, with the bond angle  $\theta$ , the magnitude of resultant dipole moment (R) can be given by the following equation:

$$R = \sqrt{P^2 + Q^2 + 2PQ\cos\theta}$$

## Examples:

•  $BeCl_2$ 

We know that the hybridization of Be in  $BeCl_2$  (in monomeric form) is  $sp$  and its shape is linear. Since the electronegativity of Cl-atom is more than Be-atom resulting in partial negative charge ( $\delta^-$ ) on the Cl-atom and partial positive charge ( $\delta^+$ ) on the Be-atom, in this electric dipole, the tail of the arrow will be on the Be-atom and the head of the arrow will be on the Cl-atom.

**The dipole moment of two Be-Cl bonds is equal but opposite in direction, so both dipole moment vectors cancel out each other and the net dipole moment for  $BeCl_2$  comes out to be zero.** Thus, the bonds of  $BeCl_2$  are polar but the overall molecule is nonpolar.

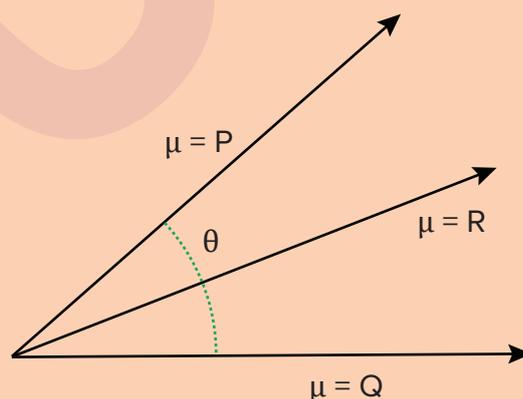


Fig. 10: Dipole moment vectors in a polyatomic molecule

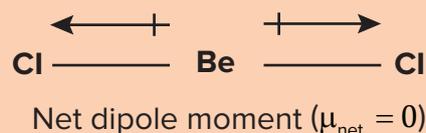


Fig. 11: Dipole moment representation for  $BeCl_2$

### • $\text{BF}_3$

We know that the hybridization of  $\text{BF}_3$  is  $sp^2$  and its shape is **trigonal planar**. Also, the electronegativity of a fluorine atom is more than that of boron. Therefore, the electron density of the bond will lie more towards the F-atom. So, the **direction of the dipole moment will be from B towards the F-atom**. Since the **bond moments** of all the three B–F bonds are equal and are at  $120^\circ$  to each other, they cancel out and the **net dipole moment** for  $\text{BF}_3$  becomes **zero**.

Let  $\mu$  be the dipole moment of each bond. The angle between all the three bond moments is  $120^\circ$ . The bond moment  $\mu$  is resolved into components, i.e., the two components are  $\mu \sin 60^\circ$  and  $\mu \cos 60^\circ$ .

From **Fig. 12**, the calculation can be done as follows:

Comparing vertical components,

$$\mu \sin 60^\circ = \mu \sin 60^\circ$$

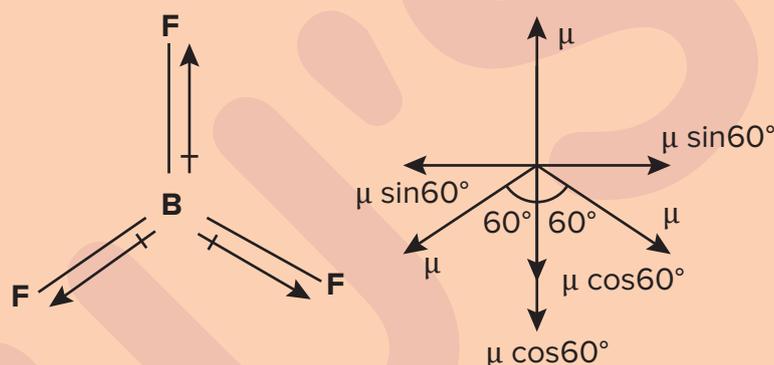
Comparing horizontal components,

$$\mu \cos 60^\circ + \mu \cos 60^\circ = \mu$$

$$2 \times \mu \cos 60^\circ = \mu$$

$$2 \times \mu \times \frac{1}{2} = \mu$$

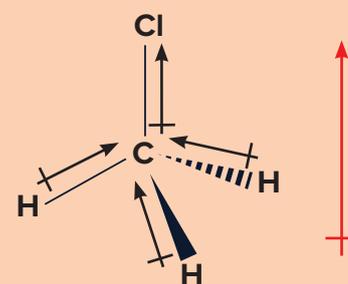
Thus, the net dipole moment is zero.



**Fig. 12: Dipole moment representation of  $\text{BF}_3$**

### • $\text{CH}_3\text{Cl}$

We know that the hybridization of  $\text{CH}_3\text{Cl}$  is  $sp^3$  and its shape is **tetrahedral**. There are three C–H bonds and one C–Cl bond in the molecule. The electronegativity of a chlorine atom is more than the electronegativity of a carbon atom. Therefore, the electron density of the C–Cl bond will lie more towards the Cl-atom and the **direction of bond moment will be towards the Cl-atom**. Similarly, the direction of bond moment for the C–H bond will be towards the central carbon as C is more electronegative than H-atom. **The bond moments of three C–H and one C–Cl bonds add up using vector addition (Fig. 13) to give the resultant non-zero dipole moment for  $\text{CH}_3\text{Cl}$ .**



**Fig. 13: Dipole moment in  $\text{CHCl}_3$  molecule**



We know,

$$\text{Dipole moment } (\mu) = \text{Charge } (q) \times \text{Distance of separation } (d)$$

So, the dipole moment of the bond depends on the electronegativity difference of bonded atoms and the internuclear distance between them. Generally, **out of charge 'q' and internuclear distance 'd', 'q' is the dominating factor on which dipole moment depends.** As the electronegativity difference of the bonded atoms increases, the magnitude of charge increases, hence the dipole moment increases.

## BOARDS

## Order of Dipole Moment in Hydrogen Halides and Alkyl Halides

## MAIN

## Hydrogen halides

We know, **out of charge 'q' and internuclear distance 'd', 'q' is the dominating factor on which dipole moment depends.** Also, the electronegativity of halides decreases down the group. Thus, the electronegativity difference between the hydrogen and the halogen decreases in the same order. Therefore, the order of dipole moment will be as follows:

H-F  
(1.78 D)

&gt;

H-Cl  
(1.07 D)

&gt;

H-Br  
(0.79 D)

&gt;

H-I  
(0.38 D)

We can clearly observe that HF has the highest value of dipole moment, whereas for HI, the value of dipole moment is minimum.

## Alkyl halides

The bond moment of C-H bond is negligible because of the very less electronegativity difference between H and C-atoms. Therefore, it is not considered while comparing the dipole moment of similar alkyl halides. Only the carbon halogen bond moment is considered for the calculation of the dipole moment. The electronegativity of halogens decreases down the group and therefore, the electronegativity difference between the hydrogen and the halogens decreases in the same order. Thus, the dipole moment should be maximum for  $\text{CH}_3\text{F}$  but here, the **bond length of C-Cl dominates as a result, the bond moment of  $\text{CH}_3\text{Cl}$  comes out to be the maximum.** Hence, the order of dipole moment in alkyl halides will be as follows:

$\text{CH}_3 - \text{Cl}$

&gt;

$\text{CH}_3 - \text{F}$

&gt;

$\text{CH}_3 - \text{Br}$

&gt;

$\text{CH}_3 - \text{I}$

Bond length (d) dominates in  $\text{CH}_3\text{Cl}$

## BOARDS

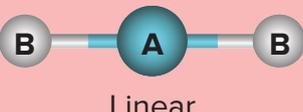
## MAIN

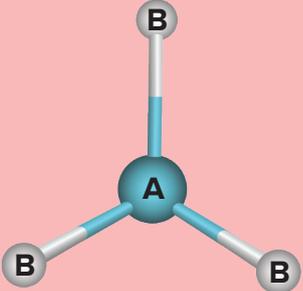
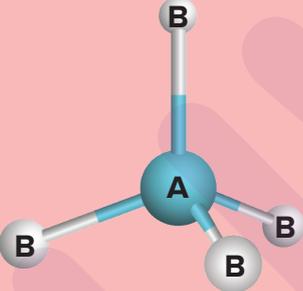
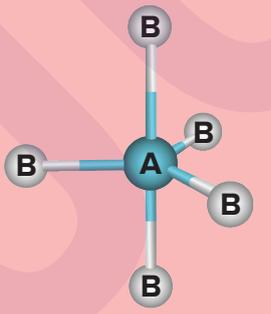
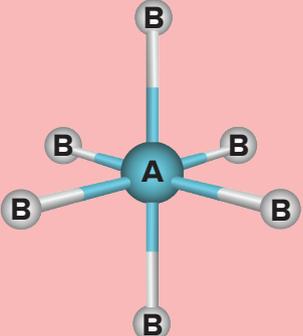
## Dipole Moment in Regular Geometries

## ADVANCED

When the molecule is symmetrical, i.e., when all the atoms attached to the central atom are the same and there are no lone pairs, then the net dipole moment of the molecule will be zero.

**For example:  $\text{BeCl}_2$ ,  $\text{CO}_2$ ,  $\text{CCl}_4$ , etc.**

Molecule type	Steric number (lp + bp)	Hybridization	Shape	Net dipole moment	Examples
$\text{AB}_2$	$0 + 2 = 2$	sp	 <p>Linear</p>	Zero	$\text{BeCl}_2$

$AB_3$	$0 + 3 = 3$	$sp^2$	 <p>Trigonal planar</p>	Zero	$BF_3$
$AB_4$	$0 + 4 = 4$	$sp^3$	 <p>Tetrahedral</p>	Zero	$CH_4$
$AB_5$	$0 + 5 = 5$	$sp^3d$	 <p>Trigonal bipyramidal</p>	Zero	$PCl_5$
$AB_6$	$0 + 6 = 6$	$sp^3d^2$	 <p>Square bipyramidal</p>	Zero	$SF_6$

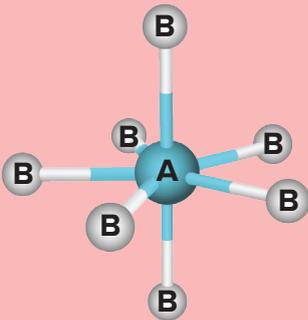
$AB_7$	$0 + 7 = 7$	$sp^3d^3$	 <p>Pentagonal bipyramidal</p>	Zero	$IF_7$
--------	-------------	-----------	--	------	--------

Table 1: Dipole moment of various molecules

When the molecule is **asymmetrical**, i.e., when **all the atoms attached to the central atom are not the same or there are lone pairs distorting the molecule shape**, the **net dipole moment** of the molecule may or may not be equal to **zero**.

Examples:  $CHCl_3$ ,  $XeF_2Cl_2$ , etc.

In  $CHCl_3$ , all the atoms attached to the central atom are not the same in this tetrahedral molecule. Thus, the **net dipole moment** of the molecule is **not equal to zero**.

In  $trans\text{-XeF}_2Cl_2$ , all the atoms attached to the central atom are not the same in this square planar molecule. The bond moments of the  $Xe\text{-F}$  and  $Xe\text{-Cl}$  bonds are equal and opposite to the bond moments of the other two  $Xe\text{-F}$  and  $Xe\text{-Cl}$  bonds. Thus, the **net dipole moment** of the molecule is equal to **zero**.

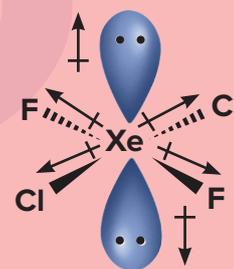


Fig. 14: Dipole moment in  $trans\text{-XeF}_2Cl_2$

**Does a lone pair contribute in the dipole moment?**

Yes, lone pairs on the central atom contribute to the dipole moment. However, its contribution cannot be quantified, as the size of lone pairs is not known. However, the effect of the lone pair on the net dipole moment ( $\mu_{net}$ ) has to be considered.

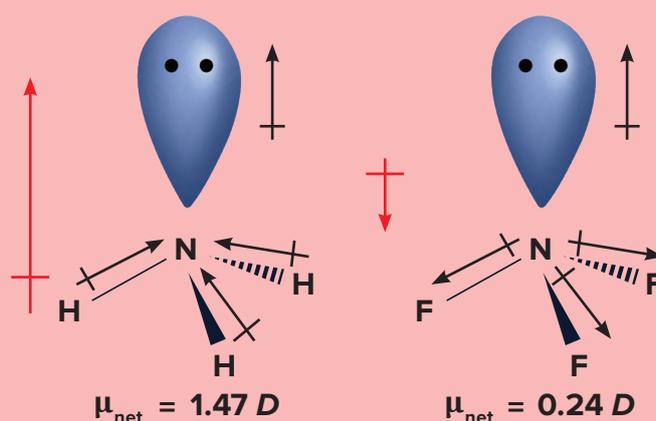


Fig. 15: Lone pair contribution to the dipole moment



### Based on lone pair contribution to the dipole moment

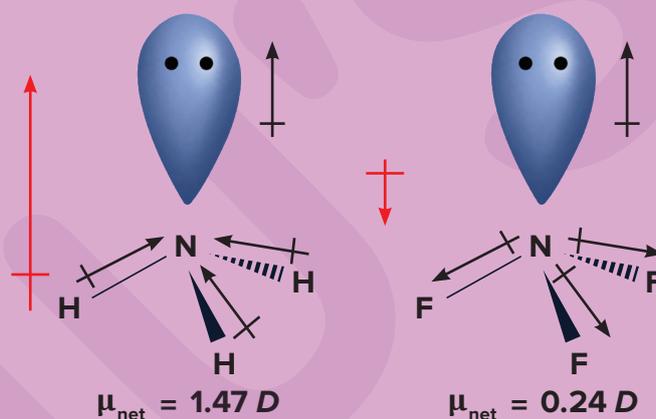
Why does  $NH_3$  have a **higher dipole moment** than  $NF_3$ ?

### Solution

The electronegativity values of nitrogen (N), hydrogen (H), and fluorine atoms are approximately 3.0, 2.1, and 4.0, respectively. So, the electronegativity difference between **N and H is 0.9** and **N and F is 1.0**. In  $\text{NH}_3$  molecules, N is more electronegative than H, so the direction of the bond moment will be from H to N, whereas in  $\text{NF}_3$  molecules, F is more electronegative, so in this case, the direction will be from N to F. Hence, the **direction of the bond moments will be opposite in the two molecules**. Since the electronegativity difference between both the bonds is nearly the same, the value of the dipole moment should also be the same. However, this is not the case.

### Contribution of a lone pair in a dipole moment

- The dipole moment vector of the lone pair will be away from N in both the molecules.
- In case of  $\text{NH}_3$ , two vectors (lone pair dipole moment and sum of dipole moment vectors through bonds) will add up, whereas in case of  $\text{NF}_3$ , these two vectors will be against each other where net magnitude reduces.



Thus,  $\text{NH}_3$  has a higher dipole moment than  $\text{NF}_3$ .



### Based on dipole moment calculations

The **resultant dipole moment** of **water** is **1.85 D**, ignoring the effects of the lone pair. Calculate the **dipole moment of each OH bond**.

(Given that bond angle in  $\text{H}_2\text{O} = 104^\circ$ ,  $\cos 104^\circ = -0.25$ ).

### Solution

The dipole moment of a molecule is the vector sum of the dipole moment of the various bonds. In an  $\text{H}_2\text{O}$  molecule that has a bent structure, two bonds are oriented at an **angle of  $104^\circ$**  and the individual dipole moment of the two bonds is equal, i.e.,  $\mu_1 = \mu_2$ .

Let  $\mu_1$  and  $\mu_2$  be the individual dipole moment of the two bonds. Resultant dipole moment can be written as follows:

$$\mu_{\text{H}_2\text{O}} = [\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta]^{1/2}, \text{ where } \theta \text{ is the bond angle.}$$

$$\text{Since } \mu_1 = \mu_2 = \mu_{\text{OH}},$$

Therefore,

$$\mu_{\text{H}_2\text{O}} = [2\mu_{\text{OH}}^2 + 2\mu_{\text{OH}}^2\cos\theta]^{1/2}$$

$$\mu_{\text{H}_2\text{O}} = [2\mu_{\text{OH}}^2(1 + \cos\theta)]^{1/2}$$

Given, ( $\cos 104^\circ = -0.25$ )

$$1.85 \text{ D} = [2\mu_{\text{OH}}^2(1 + \cos 104^\circ)]^{1/2}$$

$$1.85 \text{ D} = [2\mu_{\text{OH}}^2(1 - 0.25)]^{1/2}$$

$$\mu_{\text{OH}}^2 = \frac{1.85 D \times 1.85 D}{2 \times 0.75}$$

$$\mu_{\text{OH}} = \sqrt{\frac{1.85 D \times 1.85 D}{2 \times 0.75}}$$

$$\mu_{\text{OH}} = 1.5105 D$$

Thus, the dipole moment of each OH bond ( $\mu_{\text{OH}}$ ) = 1.5105 D



### Based on polarity and shape of compound

Consider the following compounds and calculate the value of  $\frac{(P^2 - Q^2)}{(R + S)}$ , where

**P:** Total number of **polar** compounds

**Q:** Total number of **planar** compounds

**R:** Total number of **nonpolar** compounds

**S:** Total number of **non-planar** compounds

(a) BrF

(b) ICl

(c) BrF<sub>3</sub>

(d) BrF<sub>5</sub>

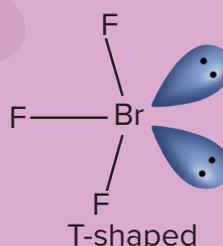
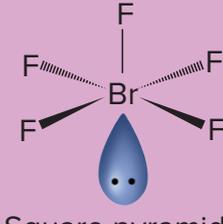
(e) ICl<sub>3</sub>

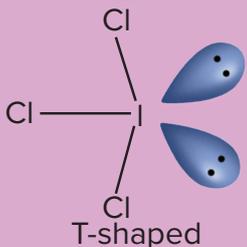
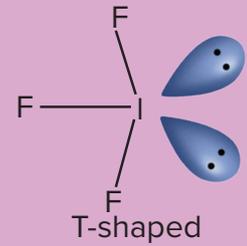
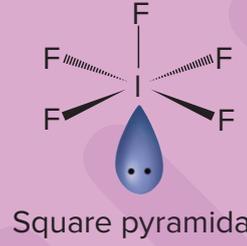
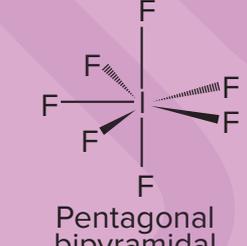
(f) IF<sub>3</sub>

(g) IF<sub>5</sub>

(h) IF<sub>7</sub>

### Solution

Compound	Steric number (lp+bp)	Hybridization	Shape	Dipole moment	Planar or non-planar	Polarity
BrF	0 + 1 = 1	-	Br — F Linear	Non-zero	Planar	Polar
ICl	0 + 1 = 1	-	I — Cl Linear	Non-zero	Planar	Polar
BrF <sub>3</sub>	2 + 3 = 5	sp <sup>3</sup> d	 T-shaped	Non-zero	Planar	Polar
BrF <sub>5</sub>	1 + 5 = 6	sp <sup>3</sup> d <sup>2</sup>	 Square pyramidal	Non-zero	Non-planar	Polar

$\text{ICl}_3$	$2 + 3 = 5$	$\text{sp}^3\text{d}$	 <p>T-shaped</p>	Non-zero	Planar	Polar
$\text{IF}_3$	$2 + 3 = 5$	$\text{sp}^3\text{d}$	 <p>T-shaped</p>	Non-zero	Planar	Polar
$\text{IF}_5$	$1 + 5 = 6$	$\text{sp}^3\text{d}^2$	 <p>Square pyramidal</p>	Non-zero	Non-planar	Polar
$\text{IF}_7$	$0 + 7 = 7$	$\text{sp}^3\text{d}^3$	 <p>Pentagonal bipyramidal</p>	Zero	Non-planar	Nonpolar

Therefore, we have,  $P = 7$ ,  $Q = 5$ ,  $R = 1$ , and  $S = 3$

Putting these values into the equation  $\frac{(P^2 - Q^2)}{(R + S)}$ , we get,

$$= \frac{(7^2 - 5^2)}{(1 + 3)} = 6$$

### BOARDS

## Predicting the Geometry Using Dipole Moment

### MAIN

### Case 1

When the molecule is purely **symmetrical**, i.e., all the atoms attached to the central atom are identical and there are no lone pairs distorting the structure, the **net dipole moment** of the molecule will be **zero**.

### Examples:

- $\text{CCl}_4$

We know that  $\text{CCl}_4$  is an  $\text{sp}^3$  hybridized molecule with zero lone pairs on the central atom and therefore, the shape of  $\text{CCl}_4$  is tetrahedral. Also, the electronegativity of a chlorine atom is more than that of a carbon atom. Therefore, the electron density of the bond will lie more towards the

Cl-atom and the direction of the bond moment will also be towards the Cl-atom. **The bond moments of all the four C-Cl bonds are equal and the molecule is symmetrical, so the bond moments will cancel out each other and the net dipole moment for  $\text{CCl}_4$  will become zero.** Similarly, the dipole moment of  $\text{CH}_4$  is zero.

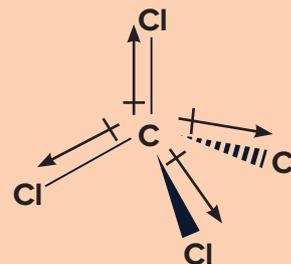


Fig. 16: Dipole moment in  $\text{CCl}_4$  molecule

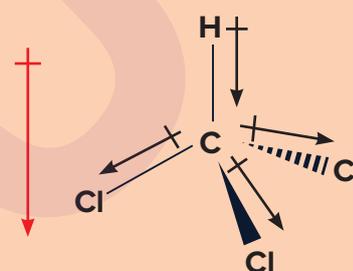
## Case 2

When the molecule is **asymmetrical**, i.e., when all the atoms attached to the central atom are not the same or there are lone pairs affecting the shape, the **net dipole moment** of the molecule **will not be zero**.

### Examples:

- **$\text{CHCl}_3$**

We know that  $\text{CHCl}_3$  is a  $\text{sp}^3$  hybridized molecule with zero lone pairs on the central atom and therefore, the shape of  $\text{CHCl}_3$  is tetrahedral. There are three C-Cl bonds and one C-H bond in the molecule. Also, the electronegativity of the chlorine atom is more than that of a carbon atom. Therefore, the electron density of the C-Cl bond will lie more towards the Cl-atom and the direction of bond moment will be towards the Cl-atom. Similarly, the direction of bond moment for the C-H bond will be towards the C-atom. **All the bond moments of the three C-Cl bonds and one C-H bond add up by using vector addition as shown in Fig. 17 to give the resultant non-zero dipole moment for the molecule.**



$\text{CHCl}_3$

$\mu = 1.04 \text{ D}$

Fig. 17: Dipole moment in  $\text{CHCl}_3$  molecule

### Some important order of dipole moment

- **Dipole moment of  $\text{CD}_3\text{F}$  is more than the dipole moment of  $\text{CH}_3\text{F}$  (Isotopic effect)**

We know that the dipole moment of the bond depends on the electronegativity difference of bonded atoms and the internuclear distance between them. Generally, **out of charge 'q' and internuclear distance 'd', 'q' is the dominating factor on which dipole moment depends.** As the electronegativity difference of the bonded atoms increases, the magnitude of charge increases and thus, the dipole moment increases.

The electronegativity difference in the C-D bond is higher than the electronegativity difference in the C-H bond because deuterium has a lower electronegativity value compared to that of hydrogen. So, the C-D bond is more polar than the C-H bond. Therefore, the dipole moment of  $\text{CD}_3\text{F}$  is more than the dipole moment of  $\text{CH}_3\text{F}$ .

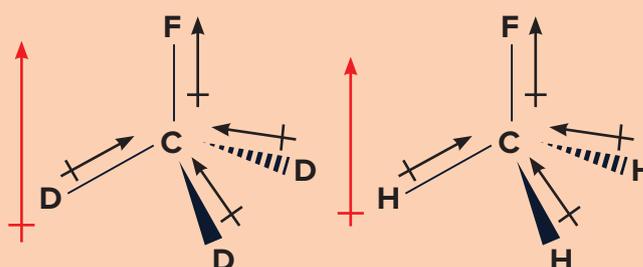


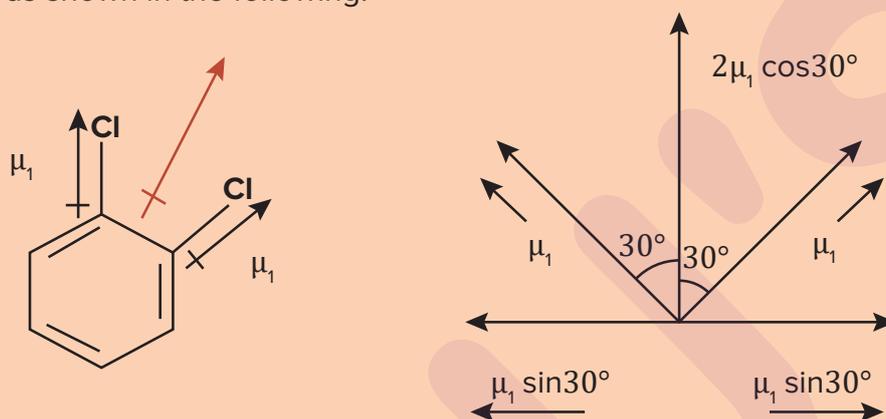
Fig. 18: Dipole moments in  $\text{CD}_3\text{F}$  and  $\text{CH}_3\text{F}$  molecules

## Dipole moments of different isomers of dichlorobenzene

The dipole moment for disubstituted benzene can be calculated by using vector sum as shown:

### • Ortho-dichlorobenzene

Consider  $\mu_1$  to be the bond moment vector of the polar C-Cl bond of ortho-dichlorobenzene, having a  $60^\circ$  angle between them. Net dipole moment can be calculated by resolving  $\mu_1$  into components as shown in the following:



**Fig. 19: Dipole moment in ortho-dichlorobenzene**

$$\mu_1 = \mu_1 \cos 30^\circ + \mu_1 \sin 30^\circ$$

The  $\mu_1 \sin 30^\circ$  components of the two bond moments are equal and opposite to each other. Thus, they cancel out each other and do not contribute to the total dipole moment.

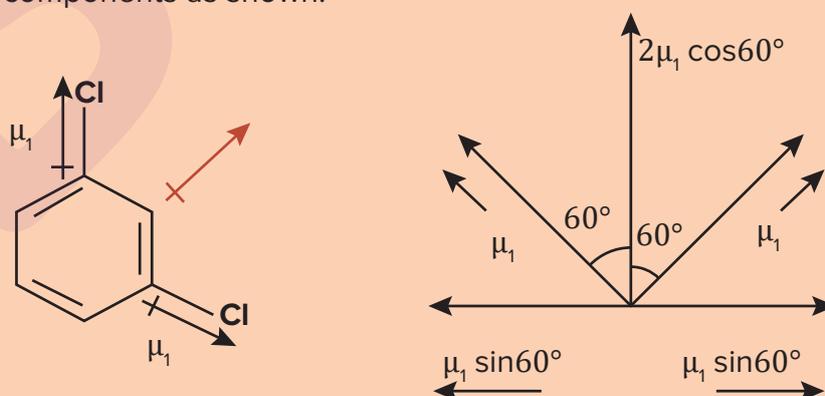
Thus, the total dipole moment =  $2\mu_1 \cos 30^\circ$

$$= 2\mu_1 \times \frac{\sqrt{3}}{2}$$

Thus, the net dipole moment of ortho-dichlorobenzene is  $\sqrt{3} \mu_1$ .

### • Meta-dichlorobenzene

Consider  $\mu_1$  to be the bond moment vector of the polar C-Cl bond of meta-dichlorobenzene, having a  $120^\circ$  angle between them. The calculation for the total dipole moment can be done by resolving  $\mu_1$  into components as shown:



**Fig. 20: Dipole moment in meta-dichlorobenzene**

$$\mu_1 = \mu_1 \cos 60^\circ + \mu_1 \sin 60^\circ$$

The  $\mu_1 \sin 60^\circ$  components of the two bond moments are equal and opposite.

Thus, they cancel out each other.

Thus, the total dipole moment =  $2 \times \mu_1 \cos 60^\circ$

$$= 2 \times \mu_1 \times \frac{1}{2}$$

Thus, the net dipole moment of meta-dichlorobenzene is  $\mu_1$

#### • Para-dichlorobenzene

Consider  $\mu_1$  to be the bond moment vector of the polar C–Cl bond of para-dichlorobenzene, having a  $180^\circ$  angle between them. The bond moment vectors are equal and opposite. Thus, they cancel out each other and the total dipole moment comes out to be zero.



Fig. 21: Dipole moment in para-dichlorobenzene

Thus, order of the dipole moment can be written as follows:

**Ortho-dichlorobenzene > Meta-dichlorobenzene > Para-dichlorobenzene**

★ BOARDS

★ MAIN

### Dipole Moments in Geometrical Isomers

Geometrical isomers are two or more compounds with the same molecular formula and connectivity of atoms but atoms are locked into different spatial positions with respect to one another due to a double bond or a ring structure. This type of isomerism is mainly observed in cyclic rings, alkenes, and allene systems.

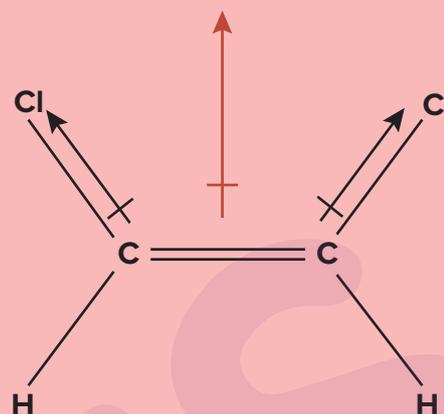
**For example,** cis and trans isomers are the types of geometrical isomers.

#### Cis isomerism

When identical groups are present on the same side of double bond or cyclic ring.

### Dipole moment in the cis isomer of dichloroethene

In the cis isomer of dichloroethene, the two bond moments of the polar bonds, C–Cl are in the same direction. Thus, the net dipole moment is non-zero and the molecule is polar. The total dipole moment along with the bond moments is shown in **Fig. 22**.



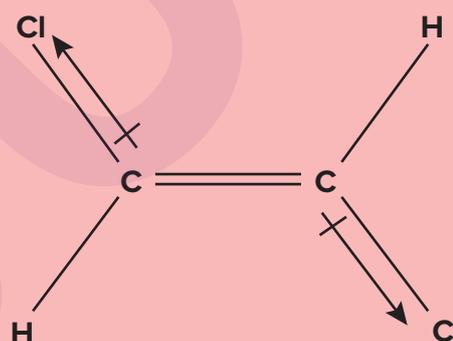
**Fig. 22:** Dipole moment in a cis isomer

### Trans isomerism

When identical groups are present on the opposite side of the double bond or cyclic ring

### Dipole moment in the trans isomer of dichloroethene

In the trans isomer of dichloroethene, the two bond moments of the polar bonds, C–Cl are equal and in the opposite directions. Thus, the net dipole moment is zero and the molecule is nonpolar. The total dipole moment along with the bond moments is shown in **Fig. 23**.



**Fig. 23:** Dipole moment in a trans isomer

### Effect of dipole moment on boiling point

When the dipole moment of a compound is more, more is the intermolecular force of attraction, which results in low vapour pressure. Thus, the boiling point of liquid is more for such liquids. Thus, in the above case, the boiling point of the cis isomer of the compound, is more than that of the trans isomer.



### Note

Vapour pressure is a measure of the tendency of a material to change into the gaseous or vapour state.



## Dipole Moment and Percentage Ionic Character

**Percentage ionic character:** Percentage ionic character is the measure of a compound's ionic character. To determine a bond's percentage ionic character, the dipole moment and electronegativity values can be used.

**Percentage ionic character in a bond can be calculated by the following methods:**

- **From the data of the dipole moment**

$$\% \text{ Ionic character} = \frac{\mu_{\text{Observed}}}{\mu_{\text{Theoretical}}} \times 100$$

$\mu_{\text{Observed}}$  = Experimental value of dipole moment

$\mu_{\text{Theoretical}}$  = Value of dipole moment when the compound is assumed as purely ionic

- **Hannay-Smith equation**

$$\% \text{ Ionic character of compound} = 16 (\Delta E.N.) + 3.5 (\Delta E.N.)^2$$

Where,  $\Delta E.N.$  is the electronegativity difference between the two bonded atoms.



### Percentage ionic character calculation

For an **HCl molecule**,  $\mu_{\text{exp}} = 1.03 \text{ D}$  and **bond length** =  $1.275 \text{ \AA}$ . Calculate **percentage ionic character**.

#### Solution

Observed dipole moment of HCl =  $1.03 \text{ D}$

Bond length of HCl =  $1.275 \text{ \AA}$

Let  $q$  be the magnitude of charge on the H or Cl-atom in HCl molecule and  $e$  be the charge on the H or Cl-atom when the molecule is assumed to be purely ionic. Therefore,

$$\% \text{ Ionic character} = \frac{q}{e} \times 100$$

Multiplying the numerator and denominator of the above equation by  $d$ , i.e., bond length of HCl molecule.

$$\text{Thus, the percentage ionic character} = \frac{q \times d}{e \times d} \times 100$$

Where,  $q \times d$  (Observed dipole moment of HCl) =  $1.03 \text{ D}$

$d$  (Bond length of HCl molecule) =  $1.275 \text{ \AA}$

$e = 1.6 \times 10^{-19} \text{ C}$

On putting all these values in the above equation, we get,

$$\text{Percentage ionic character} = \frac{1.03 D}{1.6 \times 10^{-19} C \times 1.275 \text{ \AA}} \times 100$$

Since,  $1 D = 3.33 \times 10^{-30} Cm$  and  $1 \text{ \AA} = 10^{-10} m$

$$\text{Percentage ionic character} = \frac{1.03 \times 3.33 \times 10^{-30} Cm}{1.6 \times 10^{-19} C \times 1.275 \times 10^{-10} m} \times 100$$

Percentage ionic character = 16.81%



### Polarity of compound

Which of the following compounds are **polar**?

(a)  $\text{NO}_2$

(b)  $\text{B}_2\text{H}_6$

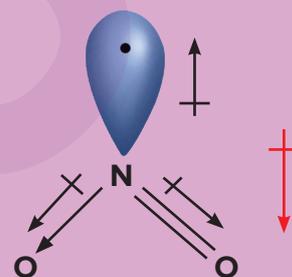
(c)  $\text{PF}_3\text{Cl}_2$

(d)  $\text{C}_6\text{H}_6$

### Solution

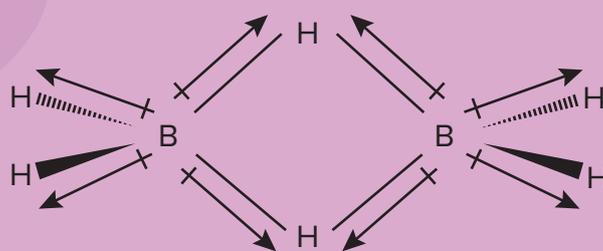
(a)  $\text{NO}_2$

The hybridization of N in  $\text{NO}_2$  is  $sp^2$  and its shape is angular. The **bond moments of the bonds are equal but not anti to each other. So they do not cancel out each other.** Thus, the **net dipole moment** becomes **non-zero** and the molecule is **polar**.



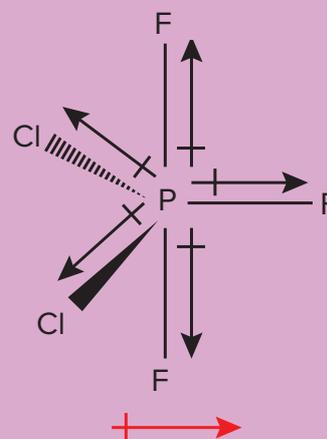
(b)  $\text{B}_2\text{H}_6$

The hybridization of B-atoms in  $\text{B}_2\text{H}_6$  is  $sp^3$  and it is a symmetrical molecule. Thus, the **net dipole moment** becomes **zero** and the molecule is **nonpolar**.



(c)  $\text{PF}_3\text{Cl}_2$

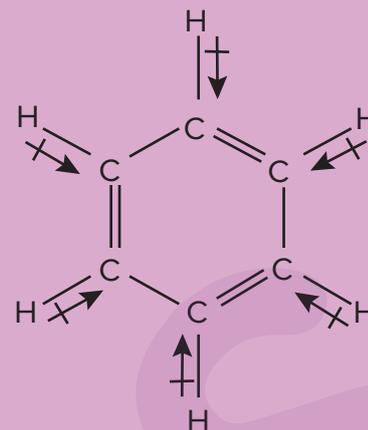
The hybridization of P in  $\text{PF}_3\text{Cl}_2$  is  $sp^3d$  and it is an asymmetrical molecule. Thus, the **net dipole moment** becomes **non-zero** and the molecule is **polar**.



(d)  $C_6H_6$ 

The hybridization of C in  $C_6H_6$  is  $sp^2$  and it is a purely symmetrical molecule. Thus, the **net dipole moment** becomes **zero** and the molecule is **nonpolar**.

Thus, the correct answer is  $NO_2$  and  $PF_3Cl_2$ .



### Dipole moment

There are two compounds, namely,  $PX_2Y_3$  and  $PX_3Y_2$  (where P = Phosphorus atom and X, Y = Monovalent atoms). If all the 'X' atoms are replaced by 'Z' atoms and the electronegativity order is  $X > Y > Z$ , then what is/are the incorrect statement(s)?

- The dipole moment of the product obtained from  $PX_2Y_3$  is non-zero.
- The dipole moment of the product obtained from  $PX_2Y_3$  is zero.
- The dipole moment of the product obtained from  $PX_3Y_2$  is zero.
- The dipole moment of the product obtained from  $PX_3Y_2$  is non-zero.

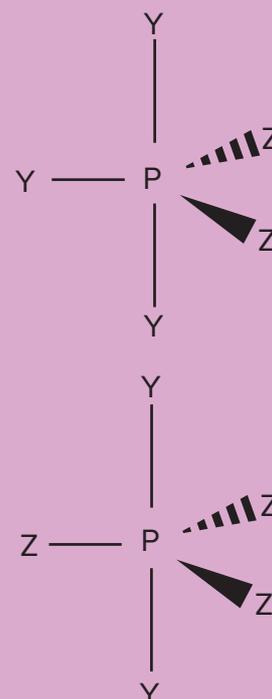
### Solution

The geometry of all the structures is **trigonal bipyramidal** and the hybridization is  **$sp^3d$** . The product obtained after replacing all the X-atoms in  $PX_2Y_3$  with Z-atom is  $PZ_2Y_3$ .

The two Z-atoms are present equatorially as they have low electronegativity, two out of the three atoms of Y are present axially, and one is present equatorially. Thus, the bond moments of all the polar bonds do not cancel out completely and the resultant dipole moment is non-zero.

The product obtained after replacing all the X-atoms in  $PX_3Y_2$  with Z-atom is  $PZ_3Y_2$ . The two Y-atoms are present axially due to higher electronegativity and the three atoms of Z are present equatorially. Thus, the bond moments of all the polar bonds cancel out completely and the resultant dipole moment of the molecule is zero.

Thus, options (b) and (d) are incorrect.





## Comparison between $\text{NH}_3$ and $\text{NF}_3$

Select the **correct order** between following compounds:

- (a)  $\text{NH}_3 > \text{NF}_3$  : Bond angle  
 (b)  $\text{NH}_3 > \text{NF}_3$  : Dipole moment  
 (c)  $\text{NH}_3 > \text{NF}_3$  : % s-character of lone pair  
 (d)  $\text{NH}_3 > \text{NF}_3$  : Reactivity towards Lewis acid

### Solution

#### (a) Bond angle

The interelectronic repulsions between the bonds in  $\text{NF}_3$  is less due to the more electronegativity of F. As a result, the bond angle is less in  $\text{NF}_3$  as compared to that in  $\text{NH}_3$ .

#### (b) Dipole moment

Again, it's the high electronegativity of fluorine that is responsible. As F is more electronegative than N, the bond moments (dipoles) are directed in the opposite sense to the lone pair so that the dipole moment of  $\text{NF}_3$  is  $0.24 D$ , whereas the value for ammonia is  $1.47 D$ . In ammonia, the hydrogens are less electronegative than nitrogen, so the bond dipoles are polarized in the same sense as the lone pair. This reduced polarity evidently makes  $\text{NF}_3$  a poorer (potential) ligand. Another way of looking at it is that the electronegative fluorines withdraw electron density from the nitrogen, making it less electron rich.



#### (c) % s-character of lone pair

Both the molecules are  $sp^3$  hybridized. However, the bond angle in  $\text{NF}_3$  is less than the bond angle in  $\text{NH}_3$ . Thus, the s-character in the bonds of  $\text{NF}_3$  is less than in  $\text{NH}_3$ , resulting in an increased s-character in the lone pair of N-atom of  $\text{NF}_3$  than  $\text{NH}_3$ .

#### (d) Reactivity towards Lewis acid

The reactivity of both the molecules towards the Lewis acid depends upon the electron donating tendency. The tendency to donate electron pair is less in  $\text{NF}_3$  than in  $\text{NH}_3$ , due to more electronegativity of the F-atom attached.

**Thus, the correct options are (a), (b), and (d).**



## Summary

- Covalent bond:** It is a chemical bond that involves the **sharing of electron pairs** between two electronegative atoms. These electron pairs are known as shared pairs or bonding pairs.
- Ionic bond:** It is a chemical bond that involves the **complete transfer of valence electron(s)** from an electropositive atom to an electronegative atom. In an ionic bond, the two oppositely charged ions are held together by electrostatic forces of attraction.
- Polar covalent bond:** It is the bond formed **between the two dissimilar atoms** having electronegativity difference **more than 0.4**.
- Nonpolar covalent bond:** It is the bond formed **between atoms having** electronegativity difference **equal to or less than 0.4**.
- Due to asymmetrical electron cloud distribution partially charged ends are developed in the polar covalently bonded molecules and they act as **electric dipoles**.
- Dipole moment is the **product of the magnitude of the charge** and the **distance** between the centres of the positive and negative **charges**.
  - Mathematically, it is expressed as follows:

$$\text{Dipole moment } (\mu) = \text{Charge } (q) \times \text{Distance of separation } (d)$$

- Dipole moment is a **vector quantity**, i.e., it has magnitude as well as direction. It is represented by a crossed arrow ( $\rightarrow$ ). Dipole moment is usually expressed in **Debye unit (D)**.
- Order of the dipole moment for some molecules,
    - H-F (1.78 D) > H-Cl (1.07 D) > H-Br (0.79 D) > H-I (0.38 D)**
    - CH<sub>3</sub>-Cl > CH<sub>3</sub>-F > CH<sub>3</sub>-Br > CH<sub>3</sub>-I**
  - For a **nonpolar** molecule,  $\mu_{\text{net}} = 0$
  - For a **polar** molecule,  $\mu_{\text{net}} \neq 0$
  - Cis isomer:** Similar groups on same side; so  $\mu_{\text{net}} \neq 0$
  - Trans isomer:** Similar groups on opposite sides; so  $\mu_{\text{net}} = 0$
  - Percentage ionic character:** Percentage ionic character is the measure of a compound's ionic character. To determine a bond's percentage ionic character, the dipole moment and electronegativity values can be used.

$$\% \text{ Ionic character} = \frac{\mu_{\text{Observed}}}{\mu_{\text{Theoretical}}} \times 100$$

$\mu_{\text{Observed}}$  = Experimental value of  $\mu$

$\mu_{\text{Theoretical}}$  = Assuming 100% ionic compound

## 14. Hannay-Smith equation

$$\% \text{ Ionic character} = 16 (\Delta E.N.) + 3.5 (\Delta E.N.)^2$$