Chemical Bonding-V

Ionic or Electrovalent Bond :

It is cleared from the Kossel and Lewis approach that the formation of an ionic compound would primarily depends upon :

* The ease of formation of the positive and negative ions from the respective neutral atoms.

* The arrangement of the positive and negative ions in the solid, that is the lattice of the crystalline compound.

Conditions for the formation of ionic compounds :

(i) Electronegativity difference between two combining elements must be larger.

(ii) Ionization enthalpy ($M(g) \rightarrow M^+(g) + e^-$) of electropositive element must be low.

(iii) Negative value of electron gain enthalpy ($X(g) + e^- \rightarrow X^-(g)$) of electronegative element should be high.

(iv) Lattice enthalpy ($M^+(g) + X^-(g) \rightarrow MX(s)$) of an ionic solid must be high.

Lattice Enthalpy :

The lattice enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions.

General properties of ionic compounds :

(a) **Physical state :** At room temperature ionic compounds exist either in solid state or in solution phase but not in gaseous state.

(b) **Isomorphism :** Simple ionic compounds do not show isomerism but isomorphism is their important characteristic. Crystals of different ionic compounds having similar crystal structures are known to be isomorphs to each other and the phenomenon is known as isomorphism.

e.g., $FeSO_4 . 7H_2O$ | $MgSO_4 . 7H_2O$

Conditions for isomorphism

(i) The two compounds must have the same formula type e.g., $MgSO_4$ & $ZnSO_4$; $BaSO_4$ & $KMnO_4$ are isomorphous because they have same formula type. All alums are isomorphous because they have same general formula :

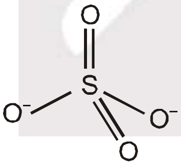
$$M_2SO_4.M_2'(SO_4)_3.24H_2O$$

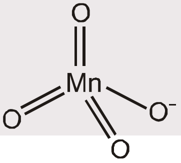
M = monovalent ; M′ = trivalent

(ii) The respective structural units, atoms or ions need not necessarily be of same size in the two compounds but their relative size should be little different.

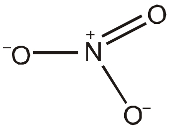
(iii) The cations of both compound should be of similar shape or structure (isostructural). Similarly anions of both compounds should be isostructural.

(a) SO_4^{2-} and MnO_4^- have same shape i.e. tetrahedral, so isomorphous.

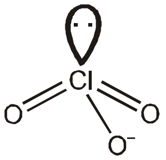




(b) $NaNO_3$ & $NaClO_3$ they have same formula type yet they are not isomorphous because NO_3^- is trigonal planar but ClO_3^- pyramidal.



NO_3^- (sp^2)



ClO_3^- (sp^3)

(iv) The respective structural units should have same polarisation property.

(c) **Electrical conductivity :** Ionic solids are almost non-conductors. However they conduct a very little amount of current due to crystal defects. All ionic solids are good conductors in molten state as well as in their aqueous solutions because their ions are free to move.

(d) **Solubility of ionic compounds :** Soluble in polar solvents like water which have high dielectric constant.

Solved Examples

Ex-1. Arrange in order of increasing ionic radii in water and their mobility : Be^{2+} , Mg^{2+}, Ca^{2+}, Sr^{2+}.

Sol. (i) Size $\propto$ 1/degree of hydration (i.e. with increase in size, number of water molecules around central metal ions decrease). So order of increasing radii is $Sr^{2+} < Ca^{2+} < Mg^{2+} < Be^{2+}$.

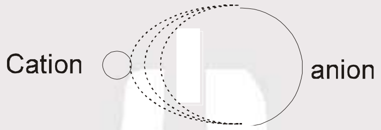
(ii) Heavily hydrated ions move slowly so the order of increasing mobility is

$Be^{2+} < Mg^{2+} < Ca^{2+} < Sr^{2+}$.

Section (A) : Fajan's Rule and its applications

Covalent character in ionic compounds (Fajan's rule) :

When anion and cation approach each other, the valence shell of anion is pulled towards cation nucleus and thus shape of anion is deformed. This phenomenon of deformation of anion by a cation is known as polarisation and the ability of cation to polarize a near by anion is called as polarizing power of cation.



Fajan's pointed out that greater is the polarization of anion in a molecule, more is covalent character in it.

More distortion of anion, more will be polarisation then covalent character increases.

Fajan's gives some rules which govern the covalent character in the ionic compounds, which are as follows:

(i) **Size of cation :** Smaller is the cation more is its polarizing power and thus more will be the polarisation of anion. Hence more will be covalent character in compound.

Size of cation α 1 / polarisation.

e.g. $BeCl_2$ $MgCl_2$ $CaCl_2$ $SrCl_2$ $BaCl_2$

$\longrightarrow$

Size of cation increases Polarisation decreases Covalent character decreases

(ii) **Size of anion :** Larger is the anion, greater is its polarisability and, therefore, more will be the polarisation. Thus more will be covalent character in compound.

Size of anion α polarisation

e.g., LiF LiCl LiBr LiI

$\longrightarrow$

– Size of anion increases
– Polarisation increases
– Covalent character increases

(iii) **Charge on cation :** Higher is the oxidation state of cation, more will be the deformation of anion and thus, more will be covalent character in compound.

Charge on cation α polarisation.

e.g., NaCl $MgCl_2$ $AlCl_3$
Na^+ Mg^{2+} Al^{3+}

$\longrightarrow$

– Charge of cation increases
– Polarisation increases
– Covalent character increases

(iv) **Charge on anion :** Higher is the charge on anion more will be the polarisation of anion and thus more will be covalent character in the compound.

Charge on anion α polarisation.

e.g., AlF_3 Al_2O_3 AlN
F^- , O^{2-} , N^{3-}

$\longrightarrow$

– Charge on anion increases
– Polarisation increases
– Covalent character increases

(v) **Pseudo inert gas configuration of cation :** Cation having pseudo inert gas configuration has more polarizing power than the cation that has inert gas configuration. Thus NaCl having inert gas configuration will be more ionic whereas CuCl having pseudo inert gas configuration will be more covalent in nature.

Cu^+ =	$[Ne]\ 3s^2\ p^6\ d^{10}$	$Na^+ = 1s^2\ 2s^2\ p^6$
	$18e^-$	$8e^-$
	Pseudo inert gas configuration	Inert gas configuration
	(poor shielding of d-electrons)	(more shielding of s and p electrons)

Application & Exceptions of Fajan's Rules :

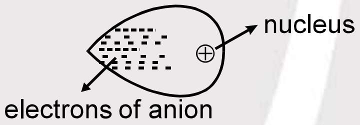
(i) Ag_2S is less soluble than Ag_2O in H_2O because Ag_2S is more covalent due to bigger S^{2-} ion.

(ii) $Fe(OH)_3$ is less soluble than $Fe(OH)_2$ in water because Fe^{3+} is smaller than Fe^{2+} and thus charge is more.
Therefore, $Fe(OH)_3$ is more covalent than $Fe(OH)_2$.

(iii) The colour of some compounds can be explained on the basis of polarisation of their bigger negative ions.

For example :

AgCl is white AgBr, AgI, Ag_2CO_3 are yellow. Similarly, $SnCl_2$ is white but SnI_2 is black. $PbCl_2$ is white but PbI_2 is yellow.
The bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.



Figure

(iv) **Variation of melting point [melting point of covalent compound < melting point of ionic compound] :**

$BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$
————————>————————————>–

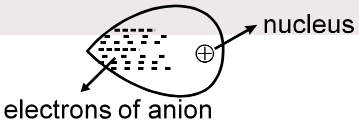
Ionic character increases, melting point increases ; since size of cation increases & size of anions is constant.

CaF_2, $CaCl_2$, $CaBr_2$, CaI_2
————————>——————————>–

Covalent character increase, melting point decrease ; since size of anions increase & size of cations is constant.

Solved Examples

Ex-2. AgCl is colourless whereas AgI is yellow, because of :
(A) Ag^+ have 18 electron shell to screen the nuclear charge.
(B) Ag^+ shows pseudo inert gas configuration.
(C) distortion of I^- is more pronounced than Cl^- ion.
(D) existence of d–d transition.



Sol. (C), the bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.

Section (B) : Dipole moment.

Polarity of bonds :

In reality no bond or a compound is either completely covalent or ionic. Even in case of covalent bond between two hydrogen atoms, there is some ionic character.
When a covalent bond is formed between two similar atoms, for example in H_2, O_2, Cl_2, N_2 or F_2 the shared pair of electrons is equally attracted by the atoms. As a result electron pair is situated exactly between the two identical nuclei. The bond so formed is called nonpolar covalent bond. Contrary to this in case of a heteronuclear 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. The resultant covalent bond is a polar covalent bond.

As a result of polarisation, the molecule possesses the **dipole moment** which can be defined as the product of magnitude of the partial charge (δ^+ or δ^-) developed on any of the covalently bonded atoms and the distance between two atoms.

Dipole moment (μ) = Magnitude of charge (q) × distance of separation (d)

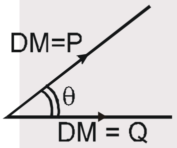
Dipole moment is usually expressed in Debye units (D). The conversion factors are

- 1 D = 3.33564×10^{-30} Cm, where C is coulomb and m is meter.
- 1 Debye = 10^{-18} e.s.u. cm.

Further dipole moment is a vector quantity and is depicted by a small arrow with tail on the positive centre and head pointing towards the negative centre. For example the dipole moment of HF may be represented as

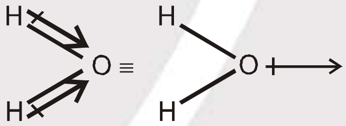
The shift in electron density is represented by crossed arrow (+⟶) above the Lewis structure to indicate the direction of the shift.

In case of polyatomic molecules the dipole moment not only depend upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such case, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. i.e. a molecule will have a dipole moment if the summation of all of the individual moment vector is non-zero.



$R = \sqrt{P^2 + Q^2 + 2PQ\cos\theta}$, where R is resultant dipole moment.

For example of H_2O molecule, which has a bent structure, the two O—H bonds are oriented at an angle of 104.5º. Net dipole moment of 6.17×10^{-30} Cm (1D = 3.33564×10^{-30} Cm) is the resultant of the dipole moments of two O—H bonds.



Net Dipole moment, $\mu = 1.85\ D = 1.85 \times 3.33564 \times 10^{-30}\ Cm = 6.17 \times 10^{-30}\ Cm$.

- **Following compounds have zero dipole moment :**

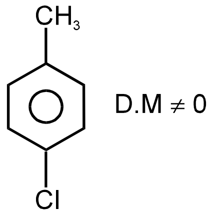
  BF_3, CO_2, SO_3, CF_4, $PF_5(g)$, SF_6, XeF_2, CS_2, CCl_4, $PCl_5(g)$, XeF_4

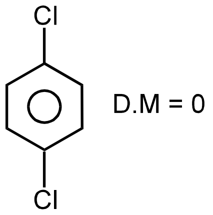
- **Some important orders**

HF >	HCl >	HBr >	HI
1.92 D	1.08	0.78	0.38
CH_3Cl >	CH_2Cl_2 >	$CHCl_3$ >	CCl_4
1.86	1.6	1.0	0

- Usually for disubstituted Benzene order is o > m > p

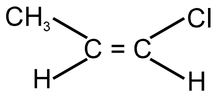
  But it all depends on the substituents



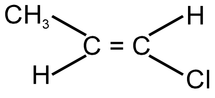


Note : For geometrical isomers usually the dipole moment of cis is more than trans but again there can be exceptions.

For example :

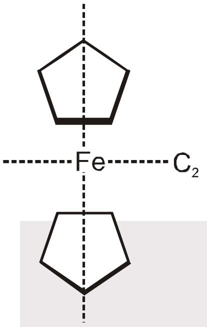


cis - form (low dipole moment)

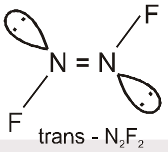


trans - form (high dipole moment)

- ❍ The presence of a centre of symmetry, i, requires that the dipole moment be zero, since any charge on one side of the molecule is canceled by an equal charge on the other side of the molecule.
  Thus $[CoF_6]^{3-}$, trans - N_2F_2 and the staggered conformer of ferrocene do not have dipole moments.



staggered-ferrocene (μ = 0)



trans - N_2F_2

Some important points about dipole moment :

- ❍ A polyatomic molecule having polar covalent bonds but zero dipole moment indicates the symmetrical structure of the molecule. e.g. B–F bonds are polar in BF_3 but BF_3 has μ=0 due to its symmetrical geometry.
- ❍ If molecule have μ = 0, then it should be linear or having symmetrical geometry.
  e.g. linear – CO_2, CS_2, $BeCl_2$(g) ; symmetrical geometry – BF_3, CH_4, PCl_5, SF_6, IF_7, XeF_4.
- ❍ If molecule has $\mu \neq 0$ then it should be angular or having unsymmetrical geometry.
  $SnCl_2$, $PbCl_2$, SO_2 , angular molecular geometry.
  NH_3, H_2O, NF_3, SF_4, H_2S, unsymmetrical molecular geometry.
- ❍ % Ionic character = $\dfrac{\mu_{\text{Experimental}}}{\mu_{\text{Theoretical}}} \times 100 = \dfrac{\mu_{\text{(Observed)}}}{\mu_{\text{(100\% Ionic compound)}}} \times 100$

Solved Examples

Ex-3. The resultant dipole moment of water is 1.85 D ignoring the effects of lone pair. Calculate, the dipole moment of each OH bond (given that bond angle in H_2O = 104°, cos 104° = – 0.25).

Sol. $R^2 = P^2 + Q^2 + 2PQ\cos\theta$

$$(1.85)^2 = x^2 + x^2 + 2x^2\left(-\frac{1}{4}\right)$$

$$(1.85)^2 = 2x^2 - \frac{x^2}{2} \quad \Rightarrow \quad \frac{3x^2}{2} \qquad \therefore \qquad x = 1.51\text{ D}$$

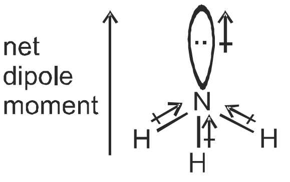
Ex-4. For HCl molecule observed dipole moment is 1.03 D and bond length is 1.275 Å. Calculate % ionic character.

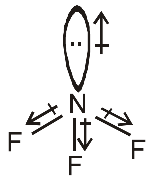
Sol. Dipole moment = $4.8 \times 10^{-18} \times 1.275 \times 10^{-8} = 4.8 \times 1.275$

$$\text{\% ionic character} = \frac{1.03 \times 100}{1.275 \times 4.8} \approx 17\%$$

Ex-5. Why NH_3 is having more dipole moment than NF_3.

Sol. In $\ddot{N}H_3$ molecule Nitrogen is more electronegative than Hydrogen. So the net dipole moment is towards. Nitrogen atom but in NF_3 molecule.
Fluorine is more electronegative than. Nitrogen so the net dipole moment is towards fluorine atoms. In NH_3 the bond pair moments and lone pair moments are in the same direction while in NF_3 the lone pair moment and bond pair moments are in opposite direction.





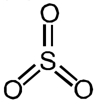
Ex-6. The geometry of SO_3 and its dipole moment are :

(A) pyramidal and non-zero. (B) trigonal planar and non-zero.

(C) trigonal planar and zero. (D) T-shaped and zero.

Ans. (C)

Sol.



The steric number of sulphur = 3; so hybridisation is sp^2. There is no lone pair on sulphur atom, therefore, according to VSEPR theory, the repulsions between the bond pairs of electrons will be similar. Hence the molecule will be symmetrical (trigonal planar) with zero dipole moment.

Section (C) : Acidic and basic character

Types of Oxides and acidic / basic nature of oxyacids and hydra acid :

(a) Acidic oxides

(a) Solution in water will be acidic in nature (b) will react with base but not with an acid

Ex. $SO_2 \xrightarrow{H_2O} H_2SO_3$ Sulphurous acid ⇒ $SO_3 \xrightarrow{H_2O} H_2SO_4$ sulphuric acid

$CO_2 \xrightarrow{H_2O} H_2CO_3$ Carbonic acid

Generally non-metallic oxides are acidic oxides

(b) Basic oxides

(a) Solution in water will be basic in nature (b) will react with an acid but not with a base

Ex. $Na_2O \xrightarrow{H_2O} 2NaOH$ $CaO \xrightarrow{H_2O} Ca(OH)_2$

Generally, metallic oxides are basic oxides

(c) Amphoteric oxides

Can react with an acid as well as with a base.

Ex Generally, metalloids or elements close to metalloids can form amphoteric oxides.

BeO ⇒ $BeO + 2HCl \longrightarrow BeCl_2 + H_2O$, $BeO + 2NaOH \longrightarrow NaAlO_2$ (Sodium meta aluminate)

ZnO ⇒ $ZnO + HCl \longrightarrow ZnCl_2$, $ZnO + NaOH \longrightarrow Na_2ZnO_2$ (sodium zincate)

SnO ⇒ (stannous oxide)

$SnO + HCl \longrightarrow SuCl_2$, $SnO + NaOH \longrightarrow Na_2SnO_2$ (sodium stanite)

SnO_2 ⇒ (stannic oxide)

$SnO_2 + 4HCl \longrightarrow SnCl_4$ $SnO_2 + NaOH \longrightarrow Na_2SnO_3$ (sodium stanate)

(d) Neutral oxides : will not react with acids or bases

CO, N_2O, NO, OF_2

(e) Amphiprotic oxide : which can accept and release H^+ ions

Ex. ⇒ H_2O

Periodicity in nature of oxides

(a) L → R, metallic character ↓ and non-metallic character ↑. So, basic character of oxides ↓ and acidic character ↑

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
strongly basic	basic	Amph	weakly acidic	acidic	strongly acidic	strongly acidic

(b) T → B, metallic character↑ so, basic character of oxide will ↑

LiOH LI_2O , NaOH Na_2O, K O H K_2O

RbOH Rb_2O, CsOH Cs_2O

Basic character increases down the group

(c) If the same element is forming oxides in diff oxidation states, then greater the oxidation no greater will be acidic nature

$$\underset{\text{more basic}}{\overset{+2}{Mn}O} < \underset{\text{basic}}{\overset{+3}{Mn_2}O_3} < \underset{\text{neutral}}{\overset{+4}{Mn}O_2} < \underset{\text{acidic}}{\overset{+6}{Mn}O_3} < \underset{\text{more acidic}}{\overset{+7}{Mn_2}O_7}$$

oxides are anhydrides of oxyacid or hydroxides

$\overset{+4}{H_2SO_3} \xrightarrow{-H_2O} \overset{+4}{SO_2}$, $\overset{+6}{H_2SO_4} \xrightarrow{-H_2O} \overset{+5}{SO_3}$, $H_2CO_3 \xrightarrow{-H_2O} CO_2$

$\overset{+5}{H_3PO_4} \longrightarrow \overset{+5}{P_2O_5}(P_4O_{10})$, $H_3PO_3 \longrightarrow P_2O_3\ (P_4O_6)$

$HNO_3 \longrightarrow N_2O_5$, $HNO_2 \longrightarrow N_2O_3$, $HClO_4 \longrightarrow Cl_2O_7$, $HClO_3 \longrightarrow Cl_2O_5$
$HClO_2 \longrightarrow Cl_2O_3$, $HClO \longrightarrow Cl_2O$, $NaOH \longrightarrow Na_2O$, $Ca(OH)_2 \longrightarrow CaO$

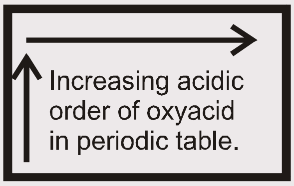
Mixed anhydrides. $\overset{+4}{ClO_2} \xrightarrow{H_2O} \overset{+5}{HClO_3} + \overset{+3}{HClO_2}$

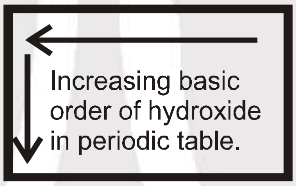
For oxy acids

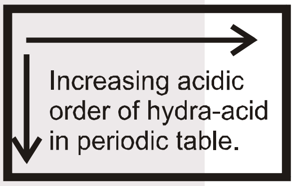
(a) On moving **L** → **R** non-metallic character ↑ acidic strength↑
$H_3BO_3 < H_2CO_3 < HNO_3$ $H_2SiO_3 < H_3PO_4 < H_2SO_4 < HClO_4$

(b) On moving **T** → **B**, non-metallic character ↓ acidic strength ↓
$HNO_3 > H_3PO_4 > H_3AsO_4$ $HClO_4 > HBrO_4 > HIO_4$

(c) If same element is forming oxycids in different oxidation states then, Greater the oxidation no. of the element greater will be the acidic strength
$HNO_3 > HNO_2 > H_2N_2O_2$ $HClO_4 > HClO_3 > HClO_2 > HClO$







MISCELLANEOUS SOLVED PROBLEMS (MSPS)

Ex-1. Classify the following bonds as ionic, polar covalent or covalent and give your reasons :
(a) SiSi bond in $Cl_3SiSiCl_3$ (b) SiCl bond in $Cl_3SiSiCl_3$
(c) CaF bond in CaF_2 (d) NH bond in NH_3

Sol. (a) Covalent, due to identical electronegativity.
(b) Polar covalent, due to less electronegativity difference.
(c) Ionic, due to more electronegativity difference.
(d) Polar covalent, due to different electronegativity.

Ex-2. (a) Which one has highest and lowest melting point and why?
NaCl KCl RbCl CsCl
(b) Why melting points of cesium halide (CsX) decrease in the order given below ?
CsF > CsCl > CsBr > CsI.

Sol. (a) NaCl will have highest lattice energy on account of the smaller Na^+ while CsCl has lowest lattice energy on account of the larger Cs^+. Hence NaCl has highest melting point and CsCl has lowest melting point .
(b) As size of anions increase their polarisability increases thus their covalent character increases and melting point decrease.

Ex-3. Which of the compounds $MgCO_3$ and $ZnCO_3$ is thermally more stable ? Explain.

Sol. Mg^{+2} has less polarising power due to inert gas configuration while Zn^{+2} has higher polarising power due to pseudo inert gas configuration. A cation i.e. Zn^{2+} with a greater, polarising power exercise a strong pull on the electron cloud of the neighbouring O-atom of the CO_3^{2-} ion and as such the metal carbonate ($ZnCO_3$) gets readily decomposed into CO_2 and the oxide of the metal, ZnO. Thus $ZnCO_3$ is less stable than $MgCO_3$.

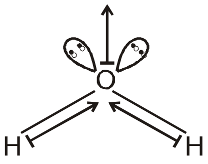
Ex-4. Why is anhydrous HCl predominantly covalent in the gaseous state but is ionic in aqueous solution?

Sol. It exists as HCl (bond formed by equal sharing of electrons) but in aqueous solution ionises as H^+ (or H_3O^+) and Cl^- due to polarity of HCl.

Ex-5. Why BeF_2 has zero dipole moment whereas H_2O has some dipole moment ?

Sol. BeF_2 has linear molecule and H_2O has bent molecule.

$\mu = 0$



$\mu \neq 0$

Ex-6. Why crystals of hydrated calcium sulphate are soft and easily cleaved where as anhydrous calcium sulphate are very hard and very difficult to cleave ?

Sol. With in the Ca^{2+} / SO_4^{2-} layer the ions are held together by strong electrovalent bonds but these separated Ca^{2+} / SO_4^{2-} layers are linked by relative weak H–bond. The weak H-bonds link SO_4^{2-} ion in the intermediate region.

Ex-7. A diatomic molecule has a dipole moment of 1.2 D. If its bond distance is equal to 1.0Å then the fraction of an electronic charge on each atom is :

(A) 25% (B) 37% (C) 52% (D) 42%

Ans. (A)

Sol. Assuming complete charge transfer then dipole moment = $(4.8 \times 10^{-10}$ esu$)(10^{-8}$ cm$)$ = 4.8 D

so % ionic character = $\frac{1.2}{4.8} \times 100\ \% = 25\%$

Ex-8. The dipole moment of KCl is 3.336×10^{-29} Coulomb meter. The interionic distance in KCl is 2.6Å. Find the % ionic character in KCl.

Sol. The theoretical dipole moment in KCl = $e \times d = 1.602 \times 10^{-19} \times 2.6 \times 10^{-10} = 4.1652 \times 10^{-29}$ C meter

% ionic character = $\frac{\text{experimental dipole moment}}{\text{theoretical dipole moment}} \times 100 = (3.336 \times 10^{-29}/4.1652 \times 10^{-29}) \times 100$

Ex-9. The gaseous potassium chloride molecule has a measured dipole moment of 10.0 D, which indicates that it is a very polar molecule. The separation between the nuclei in this molecule is 2.67×10^{-8} cm. Calculate the percentage ionic character in KCl molecule.

Sol. Dipole moment of compound would have been completely ionic

= $(4.8 \times 10^{-10}$ esu$)(2.67 \times 10^{-8}$ cm$)$ = 12.8 D

so % ionic character = $\frac{10.0}{12.8} \times 100\% = 78.125\ \% \approx 78\%$ **Ans.**