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. For example, the lattice enthalpy of NaCl is 788 kJ/mole (and Lattice energy = –788 kJ/mol). This means that 788 kJ of energy is required to separate one mole of solid NaCl into one mole of $Na^+(g)$ and one mole of Cl^- to an infinite distance.

> **Note :** Condition for formation of a stable ionic compound is :
> *Total Ionisation enthalpy + Total Electron Gain Enthalpy – Total Lattice Enthalpy < 0*

Simple Binary Ionic Compounds

Metal	Nonmetal	General Formula	Ions Present	Example
IA	VIIA	MX	$\left(M^{+}, X^{-}\right)$	$LiBr$
IIA	VIIA	MX_2	$\left(M^{2+}, 2X^{-}\right)$	$MgCl_2$
IIIA	VIIA	MX_3	$\left(M^{3+}, 3X^{-}\right)$	GaF_3
IA	VIA	M_2X	$\left(2M^{+}, X^{2-}\right)$	Li_2O
IIA	VIA	MX	$\left(M^{2+}, X^{2-}\right)$	CaO
IIIA	VIA	M_2X_3	$\left(2M^{3+}, 3X^{2-}\right)$	Al_2O_3
IA	VA	M_3X	$\left(3M^{+}, X^{3-}\right)$	Li_3N
IIA	VA	M_3X_2	$\left(3M^{2+}, 2X^{3-}\right)$	Ca_3P_2
IIIA	VA	MX	$\left(M^{3+}, X^{3-}\right)$	AlP

Properties of Ionic Compounds :

(i) The ionic substances are good conductors of heat and electricity in molten state or aqueous medium. In both these states, the lattice is broken and ions are free to conduct electricity and heat.

(ii) Due to stability of lattice, ionic compounds have high melting and boiling points.

(iii) The bond in ionic compounds is non-directional. In these compounds, each ion (cation or anion) has a uniformly distributed electric field, so one can not predict whether a particular ion is bonded to this or that ion.

(iv) These are soluble in polar solvents like water, which acts as a dielectric (*dielectric is a material which weakens the electric field*). When the electric field is weakened, the ions are relatively free to go in water.

COVALENT BONDING — Section - 3

Certain elements which have high ionisation energies are incapable of transferring electrons and other having low electron affinities, fail to take up electrons. The atoms of such elements share their electrons with the atoms of other elements (and sometimes among themselves) in such a manner that both the atoms form complete outer shell. In this manner they achieve stability. Such an association through sharing of electron pairs among atoms of different or of same kinds is known as Covalent Bond. This was proposed by G.N. Lewis.

The covalent bonding can be achieved in two ways :

(i) Sharing electrons between atoms of same kinds, formation of F_2, O_2, Cl_2, etc.

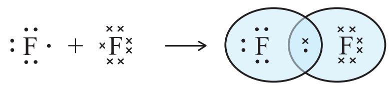
(ii) Sharing of electrons between atoms of different kinds, formation of HCl, CO_2, H_2O, CH_4, etc.

Lewis Symbols : To represent *valence* electrons in an atom, Lewis introduced simple notations called as Lewis symbols. For example, the Lewis symbols for the elements of second period are as under

Li Be ·B· ·C· ·N· :O: :F: :Ne:

The number of dots around the symbol represents the number of valence electrons. This number of valence electrons helps to calculate the common or group valence of an element.

Formation of F_2 and other like molecules : A Fluorine atom has seven electrons in its outermost shell and thus it needs one more electron to complete an octet of electrons and attain a noble gas configuration. A F_2 molecule is thus formed by combination of two F atoms by sharing one electron each. It is represented by Lewis dot structure as follows:



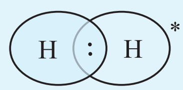
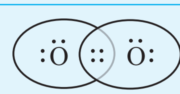
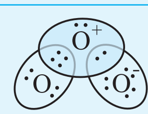
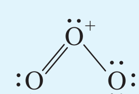
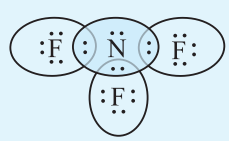
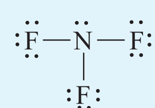
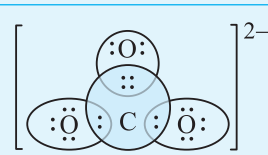
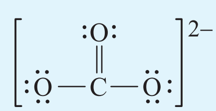
8e⁻ 8e⁻
or F – F

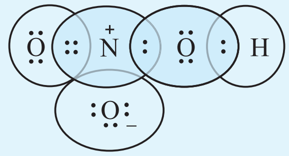
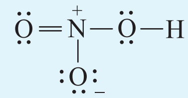
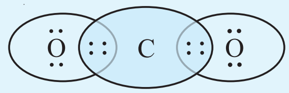
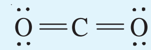
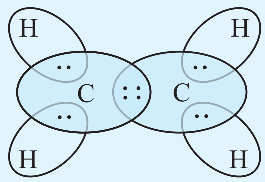
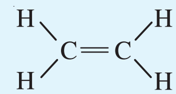
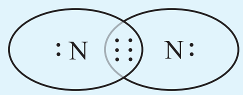
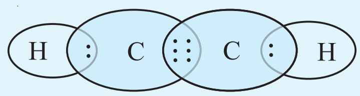
Note that now both of F atoms now have eight (8) electrons each in their outer shell. In a more simple way, electron (Lewis) dot formula can be expressed by using '–' (a dash) instead of • x.

Note :

- Pair of electrons depicted as •• or x x is called as Lone pair (ℓp) and that by x • is called as shared pair or Bond pair (bp). Lone pair is the pair of electrons belonging to one atom only. Thus F_2 has one bp(s) and six ℓp(s).
- When two atoms share one/two/three electron pair(s) they are said to be joined by a *single/double/triple covalent bond* respectively. Eg in the above example of F_2 molecule there is a single bond between the two fluorine atoms.

The Lewis Representation of some molecules is as follows :

H_2		H – H
O_2		:Ö = Ö:
O_3		
NF_3		
CO_3^{2-}		

HNO_3		
CO_2		
C_2H_4		
N_2		$:N \equiv N:$
C_2H_2		$H-C \equiv C-H$

Explanation for O_2 and N_2 :

O_2 : Oxygen (O) has six electrons in valence shell, hence requires 2 more to achieve stability. It can accept two electrons to form ionic bond. It can also share two electrons with another atom of O to form covalent bond as shown in the above table. Here, 2 pairs of electrons are shared, thus double covalent bond is formed between the two oxygen atoms. In simpler way it can be represented by sign '='. So O_2 molecule can be shown as $O = O$.

N_2 : Nitrogen (N) has five electrons in valence shell and requires 3 electrons to achieve stability. It does so by sharing 3 electrons with another N atom to form covalent bond as shown above. Here, 3 pairs of electrons are shared, so there is a triple covalent bond between two nitrogen atoms. In simpler way it can be represented by sign '≡'. So N_2 molecule can be written as $N \equiv N$.

Rules for writing Lewis dot structures :

(i) Add valence electrons of combining atoms of the molecules to get total no. of electrons (T) to be represented in the Lewis structure.

(ii) In case of ions, number of electrons equal to charge on the ion must also be added (for anions) or subtracted (for cations) from T.

(iii) Least electronegative atom occupies the central position in the molecule/ion.

(iv) Draw skeletal structure of the compound/ion using chemical symbols of the combining atom.

(v) Now use pairs of electrons to represent single bonds between bonding atoms of the molecules/ion and represent the rest of the electrons to as lone pairs of atoms or to show multiple bonds between them (in case each of the bonding atom does not have an octet of electrons).

Note : Lewis dot structure, in general, do not represent the actual shapes of the molecules.

Illustration - 1 *Write a Lewis structure for CCl_2F_2, one of the compounds implicated in the depletion of stratospheric ozone.*

SOLUTION :

Step : 1 Place the atoms relative to each other. In CCl_2F_2 carbon has the lowest group number and EN, so it is the central atom. The other atoms surround it but their specific positions are not important.

Cl
F C F
Cl

Step : 2 Determine the total number of valence electrons :

$$\left[1 \times C\left(4e^-\right)\right] + \left[2 \times F\left(7e^-\right)\right] + \left[2 \times Cl\left(7e^-\right)\right] = 32 \text{ valence } e^-$$

Step : 3 Draw single bonds to the central atom and subtract $2e^-$ for each bond : single bonds use $8e^-$, so $32e^- - 8e^-$ leaves $24e^-$ remaining.

Step : 4 Distribute the remaining electrons in pairs, beginning with the surround-atoms, so that each atom has an octet.

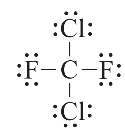


Illustration - 2 *Writing Lewis Structures for Molecules with More than One central atom. Write the Lewis structure for methanol (molecular formula CH_4O), an important industrial alcohol that is being used as a gasoline alternative in car engines.*

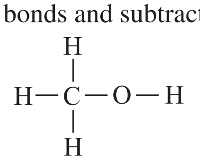
SOLUTION :

Step : 1 Place the atoms relative to each other. The H atoms can have only 1 bond, so C and H must be adjacent to each other. In nearly all their compounds, C has four bonds and has two, so we arrange the H atoms to shown this.

Step : 2 Find sum of valence electrons

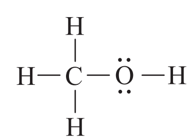
$$\left[1 \times C\left(4e^-\right)\right] + \left[1 \times O\left(6e^-\right)\right] + \left[4 \times H\left(1e^-\right)\right] = 14e^-$$

Step : 3 Add single bonds and subtract $2e^-$ for each bond.



Five bonds use $10e^-$, so $14e^- - 10e^-$ leaves $4e^-$ remaining.

Step : 4 Add remaining electrons in pairs.



Carbon already has an octet, so the four remaining valence e^- form two lone pairs on O and give the Lewis structure for methanol.

Illustration - 3 *Write the Lewis dot structure of CO molecule.*

SOLUTION :

Step : 1 The skeletal structure of CO is written as : CO

Step : 2 Count the total number of outer valence shell electrons of carbon ($2s^2\,2p^2$) and oxygen ($2s^2\,2p^4$) atoms.

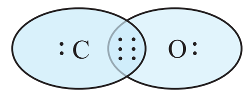
Thus the total number of valence electrons available are $4 + 6 = 10$.

Step : 3 & 4

Draw a single bond (one shared electron pair) between C and O and complete the octet on O, the remaining two electrons will constitute a lone pair on C.

$$:C:\ddot{\underset{..}{O}}: \quad \text{or} \quad :C-\ddot{\underset{..}{O}}:$$

This does not complete the octet on carbon and hence we have to resort to multiple bonding (in this case a triple bond) between C and O atoms. This satisfies the octet rule condition for both atoms.



or $:C^{-}\equiv O^{+}:$

Writing Lewis Structures for Molecules with Multiple Bonds

Illustration - 4 *Write the Lewis structure of the nitrite ion NO_2^-*

SOLUTION :

Step : 1 The skeletal structure of NO_2^- is written as :

O N O

Step : 1 Count the total number of valence electrons of the nitrogen atom, the oxygen atoms and the additional one negative charge (equal to one electron). $N(2s^2\ 2p^3)$, $O(2s^2\ 2p^4)$

$\Rightarrow\ 5 + (2 \times 6) + 1 = 18$ electrons

Step : 3 & 4 Draw a single bond (one shared electron pair) between the nitrogen and each of the oxygen atoms completing the octets on oxygen atoms.

This, however, does not complete the octet on nitrogen if the remaining two electrons constitute lone pair on it.

$$\left[:\ddot{\underset{..}{O}}\ :\ddot{N}:\ \ddot{\underset{..}{O}}:\right]^-$$

Hence we have to resort to multiple bonding between nitrogen and one of the oxygen atoms (in this case a double bond). This leads to the following Lewis dot structures.

$$\left[\ddot{\underset{..}{O}}::\ddot{N}:\ \ddot{\underset{..}{O}}:\right]^- \quad \text{or} \quad \left[\ddot{\underset{..}{O}}=\ddot{N}-\ddot{\underset{..}{O}}:\right]^-$$

$$\text{or} \quad \left[:\ddot{\underset{..}{O}}-\ddot{N}=\ddot{\underset{..}{O}}\right]^-$$

Writing Lewis Structures for Molecules with Multiple Bonds

Illustration - 5 *Write Lewis structures for the following :*

(a) *Ethylene (C_2H_4), the most important reactant in polymer manufacture*

(b) *Nitrogen (N_2), the most abundant atmospheric gas*

Plan : We begin the solution after Steps 1 to 4 : placing the atoms, counting the total valence electrons, making single bonds, and distributing the remaining valence electrons in pairs to attain octets. Then are continue with step 5, if needed.

SOLUTION :

(a) For C_2H_4. After Steps 1 to 4, we have

$$\begin{matrix} H & & & & H \\ & \diagdown C - \ddot{C} \diagup & \\ H & & & & H \end{matrix}$$

Step : 5 Change a lone pair to a bonding pair. The C on the right has an octet, but the C on the left has only $6e^-$, so we convert the lone pair to another bonding pair between the two C atoms.

$$\begin{matrix} H & & & & H \\ & \diagdown C = C \diagup & \\ H & & & & H \end{matrix}$$

(b) For N_2. After steps 1 to 4 : we have $:\ddot{N}-\ddot{N}:$

Step : 6 Neither N has an octet, so we change a lone pair to bonding pair : $:\ddot{N}=N:$

In this case, moving one lone pair to make a double bond still does not give each N an octet, so we move another lone pair to make a triple bond : $:N\equiv N:$

Formal Charge

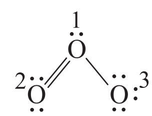
Formal charge is an accounting procedure. It allows chemists to determine the location of charge in a molecule as well as compare how good a Lewis structure might be. The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons and the number of electrons assigned to that atom in the Lewis structure. It is expressed as :

Formal charge (F.C.) on an atom in a Lewis structure	=	[Total number of valence electrons in the free atom]	–	[Total number of non bonding (lone pair) electrons]	–(1/2)	[Total number of bonding (shared) electrons]

Formal charge = number of valence e^- on neutral atom – $(2 \times LP)$ – BP

The counting is based on the assumption that the atom in the molecule owns one electron of each shared pair and both the electrons of a lone pair.

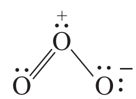
Let us consider the ozone molecule (O_3). The Lewis structure of O_3 may be drawn as :



The atoms have been numbered as 1, 2 and 3. The formal charge on :

- The centre O atom marked 1 $= 6 - 2 - \frac{1}{2}(6) = +1$
- The end O atom marked 2 $= 6 - 4 - \frac{1}{2}(4) = 0$
- The end O atom marked 3 $= 6 - 6 - \frac{1}{2}(2) = -1$

Hence, we represent O_3 along with the formal charges as follows :



If there are more than one possible Lewis structures for a molecule having same number of bonds, the better structure is one which has the least formal charge on each individual atom. It takes energy to get a separation of charge in the molecule (as indicated by the formal charge) so the structure with the least formal charge should be lower in energy and thereby be the better Lewis structure. The non-zero formal charge on any atoms in the molecule are written near the atom.

Formal charge and bond polarity

Formal charge calculations do not indicate how charge is actually distributed in molecules. Remember that most bonds are polar, meaning that the electrons in an bond are skewed toward the more electronegative atom. Formal charges, however, are found by assuming that all bonding electrons are shared equally. As a result, formal charge calculations are extremely useful for assessing whether a valence electron distribution is reasonable, but they do not reliably indicate actual bond polarity or the actual distribution of charge. Some of the following examples illustrate this point.

In chlorine trifluoride, all formal charges are zero. Based on electronegativities, however, each F – Cl bond is significantly polar. The electronegativity of F is 4.0. Indicating that a fluorine atom attracts electrons more strongly than a chlorine atom. In a CIF_3) molecule, each F atom has a small net negative charge (less than one unit), and the Cl atom has a net positive charge of 3 times this amount (also less than one unit). These partial charges are symbolized δ^+ or δ^-.

The ammonium cation illustrates the difference between formal and actual charge even more dramatically. The nitrogen atom of NH_4^+ has a formal charge of 5 – 4 = +1, but electronegativity values indicate that N attracts electrons more strongly than H ($\times$ N = 3.0 = 2.1). Thus the actual electron distribution in an N – H bond is skewed forward nitrogen, leaving each H atom with a partial positive charge and the N atom with a partial negative charge.

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 : $NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$

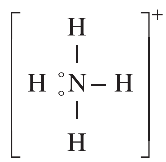
Remember that formal charge are not annual charges. Instead, formal charges are simply a device that helps us determine the most stable distribution of a molecule's valence electron.

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.

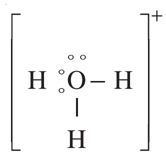
Compounds such as NH_3, having one lone pair readily forms coordinate bonds. It combines with H^+ ion (Hydrogen cation) to from Ammonium ion (NH_4^+) as follows :

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



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

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



Exception to Octet Rule

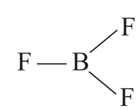
The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. Up to now we have studied the molecules which follow Lewis Octet Rule while forming bonds. It 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)