Inorganic Chemistry

M.S.C. / First Semester

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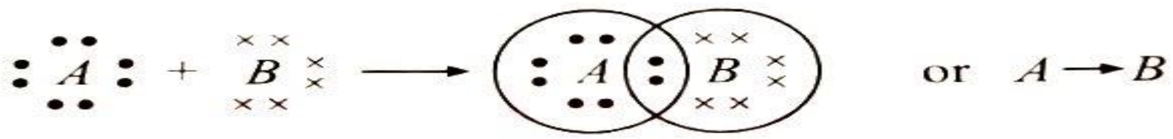
<u>Coordinate Bond:-</u>

It is a special type of covalent bond in which both the shared electrons are contributed by one atom only. It may be defined as "**a covalent bond in which both electrons of the shared pair are contributed by one of the two atoms**". Such a bond is also called as dative bond. A coordinate or a dative bond is established between two such atoms, one of which has a complete octet and possesses a pair of valency electrons while the other is short of a pair of electrons.



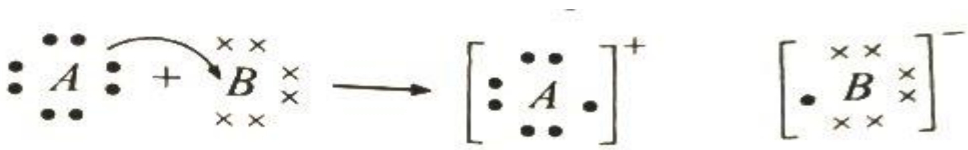
This bond is represented by an arrow (⟶)

The atom which contributes electron pair is called the donor while the atom which accepts it is called acceptor.

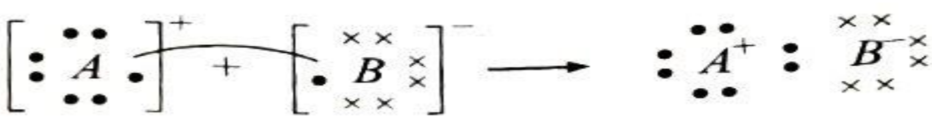
Note : Coordinate bond after formation is indistinguishable from a covalent bond.

The formation of a coordinate bond can be looked upon as a combination of electrovalent and covalent bonds. The formation may be assumed to have taken place in two steps:

(i) The donor atom loses one electron and transferred to acceptor atom. As a result donor atom acquires a positive charge and the acceptor atom acquires a negative charge



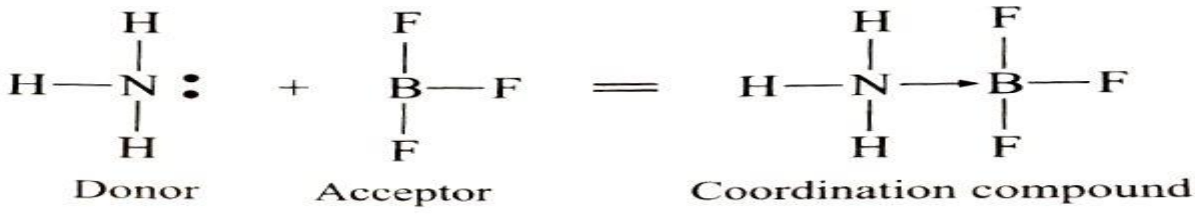
(ii) These two charged particles now contribute one electron each and this pair is shared by both the atoms,



As the coordinate bond is a combination of one electrovalent bond and one covalent bond, it is also termed as semi polar bond.

The compound consisting of the coordinate bond is termed coordinate compound. Some examples of coordinate bond formation are given below

(i) Combination of ammonia and boron trifluoride: Although the nitrogen atom has completed its octet in ammonia, it still has a lone pair of electrons in the valency shell which it can donate. The boron atom in boron trifluoride is short of two electrons which it accepts and completes its octet.



Any atom or ion or molecule which has one unshared electron pair which it can donate is termed as **Lewis base** while those which are capable of accepting the lone pair are termed as **Lewis acids**. In above example ammonia is a Lewis base while boron trifluoride is a Lewis acid.

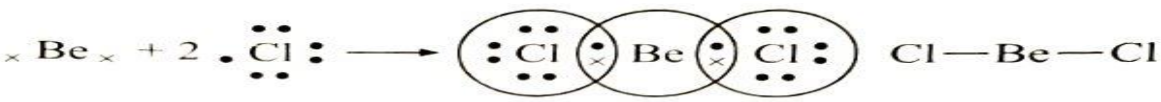
Note : H^+ ion and cations of transition metals such as Cu^{2+},Co^{2+} ,Fe^{2+}, Mn^{2+}, Cr^{2+}, Ni^{2+}, etc., act as Lewis acids. The donors are also called as ligands.

(ii) Formation of ammonium ion : Hydrogen ion (H^+) has no electron and thus accepts a lone pair donated by nitrogen

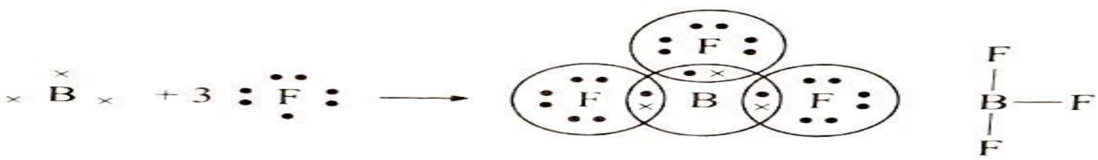
Failure of Octet rule:-

There are several stable molecules known, in which the octet rule is violated, i.e., atoms in these molecules have number of electrons in the valency shell either short of octet or more than octet. Some important examples are:

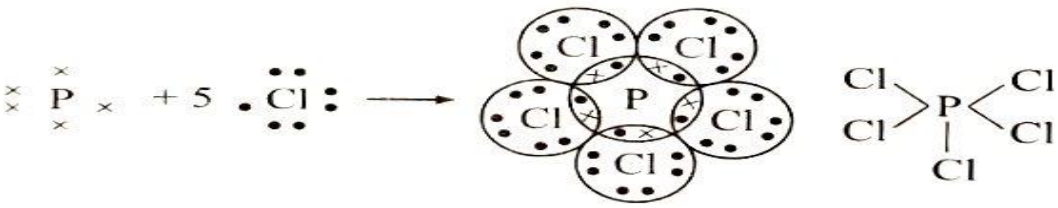
(i) $BeCl_2$ molecule: $BeCl_2$ (beryllium chloride) is a stable molecule. Be atom forms two single covalent bonds with two chlorine atoms, i.e., it attains four electrons in the outer shell.



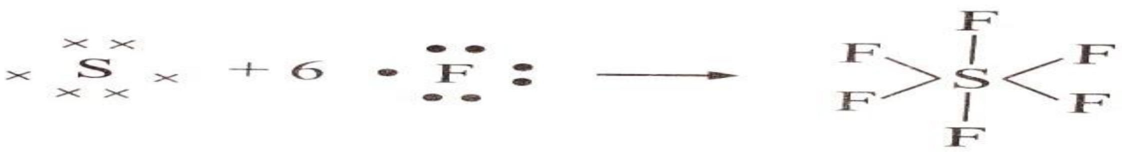
(ii) **BF_3 molecule**: Boron atom forms three single covalent bonds with three fluorine atoms, i.e., it attains six electrons in the outer shell.



(iii) PCl_5 molecule : Phosphorus atom have five electrons in valency shell. It forms five single covalent bonds with five chlorine atoms utilising all the valency electrons and thereby attains 10 electrons in the outer shell.



(iv) SF_6 molecule: Sulphur atom has six electrons in the valency shell. It forms six single covalent bonds with six fluorine atoms utilising all the valency electrons and thereby attains 12 electrons in the outer shell.



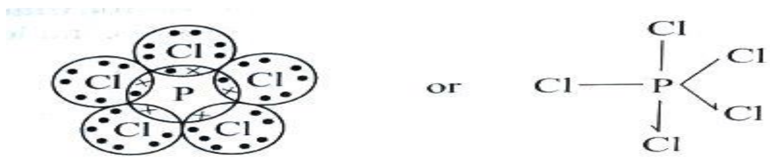
v) IF_7 molecule : Iodine forms seven single covalent bonds with seven fluorine atoms utilising 7 valency electrons. The iodine atom attains 14 electrons in outermost shell.

To explain the above abnormalities, the following two concepts were introduced:

Sugden's concept of singlet linkage :

Sugden introduced the idea of singlet linkage in favour of octet rule. According to this concept the maximum number of electrons in the outermost shell of any atom cannot exceed eight. In the molecules of PCl_5, SF_6, IF_7, etc., the central atom is linked with some of the combining atoms by single- electron bonds, called singlet linkage while the remaining atoms are linked by the normal two electrons bonds. The bond is represented by a half arrow ($\rightharpoondown$) with the head pointing from donor towards the acceptor.

In PCl_5, three chlorine atoms are linked by normal covalent bonds and two chlorine atoms are linked by singlet linkages, thus, phosphorus achieves 8 electrons in the outermost shell.



This structure indicates that the nature of two chlorine atoms is different than the other three as singlet linkage is weaker than normal covalent bond. The above observation is confirmed by the fact that on heating, PCl_5 dissociates into PCl_3 and Cl_2.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Similarly , in SF_6 , four singlet linkages are present while in IF_7 , six singlet linkages are present.

Sidgwick's concept of maximum covalency

This rule states that the covalency of an element may exceet four and octet can be exceeded , The maximum covalency of the elements actualy depends on the period of periodic table to which it belong .The maximum covalency of the elements is tabulated below:

Period	Elements	Maximum covalency	No. of electrons in the outermost orbit
1st	H	2	4
2nd	Li to F	4	8
3rd	Na to Cl	6	12
4th	K to Br	6	12
5th, 6th	Rb onwards and rest of the elements	8	16

This rule explains the formation of PCl_5 and SF_6 This also Explains, why nitrogen does not form NF_5 or NCl_5, because nitrogen belongs to second period and the maximum covalency of nitrogen is four.

Lewis Formulae For Molecules and Polyatomic Ions:-

Lewis electron-dot formula of a molecule or a polyatomic ion shows how atoms are bonded with each other. Bonding electrons are indicated either by two dots or by a dash. For instance, a water molecule can be represented by either of the following two diagrams.

Lewis dot formulae show only the number of valency electrons, the number and kinds of bonds, but do not depict the three dimensional shapes of molecules and polyatomic ions. Lewis formulae are based on the fact that the representative elements achieve a noble gas configuration in most of their compounds, i.e., 8 electrons in their outermost shell (except for H_2, Li^+ and Be^{2+} ions which have 2 electrons).

The following steps are followed in constructing dot formulae for molecules and polyatomic ions :

(i) Write a symmetrical 'skeleton' for the molecules and polyatomic ions.

(a) The least electronegative element is usually taken as the central element except H.

For example : CO_2 has the skeleton OCO.

(b) Oxygen atoms do not bond to each other except in O_2, O_3, the peroxides and superoxides. The phosphate ion (PO_4^{3-}) has the skeleton

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  O
O P O
  O
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(c) Hydrogen actually bonds an oxygen atom and not to the central atom in ternary acids (oxyacids)

For example : Nitrous acid HNO_2 , has the skeleton HONO .However, there are exceptions to this rule , such as for H_3PO_2, the skeleton is

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H P OH
  O
  H
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(d) For polycentred species such as C_2H_4 , the most symmetrical skeleton is used .

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H  H
C  C
H  H
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is the skeleton for C_2H_4

(ii) Calculate the number of electrons available in the valency shell of all the atoms.

For negatively charged ions add to the total number of electrons equal to the charge on the anion and for positively charged ions, subtract the number of electrons equal to the charge on the cations.

The total number of electrons calculated in this way is represented by symbol A.

For example: A for H_2SO_4

A = 2 x 1 (for hydrogen atoms) + 1 x 6 (for S atom) + 4 x 6 (for O atoms)

A = 2 + 6 + 24 = 32 electrons.

A for PO_4^{3-} ion

A = 1x5 (for P atom) + 4 x 6 (for O atoms) + 3 (for charge) = 5 + 24 + 3 = 32 electrons.

A for NH_4^+ ion

A= 1x5 (for N atom) + 4 x 1 (for H atoms) -1 (for positive charge) = 5 + +4 -1 = 8 electrons.

Formal Charge:-

In case of the polyatomic ions, the net charge is possessed by an ion as a whole and not by a particular atom. However, for some purposes each atom in a polyatomic ion or molecule is assigned a **formal charge**. It is defined as the difference between the number of valence electrons in an isolated (i.e., free) atom and the number of electrons assigned to that atom in a Lewis structure. The counting of electrons 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.

Formal charge on an atom = total number of valence in a Lewis structure electrons in the free atom number - total bonding (lone pair) electrons -1/2 total number of bonding (shared) electrons

The concept of formal charge can be explained by nitrous oxide molecule, N_2O. The electron dot structure for N_2O can be written as

Using the given relationship, the formal charges on the three atoms can be calculated as follows :

(a) Terminal nitrogen atom:

Valence electrons = 5

Lone pair = one (two electrons)

Total number of bonding electrons = 6

Formal charge = 5- 2 – 1/2 x 6 =0

(b) Central nitrogen atom:

Valence electrons = 5

Lone pair = nil

Total number of bonding electrons = 8

Formal charge = 5 – 1/2 x 8 = +1

(c) Terminal oxygen atom :

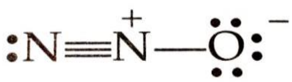
Valence electrons = 6

Lone pair = three (six electrons)

Total number of bonding electrons = 2

Formal charge = 6 - 6 – 1/2x2 = -1

Thus, the structure can be written as follows:



The advantage of calculation of formal charges is that it helps to select the most stable structure of the molecule or ion. **The most stable structure is the one which has the smallest formal charges on the atoms or zero formal charges on the atoms**. Negative formal charges should appear on the most electronegative atoms. Adjacent atoms in the structure should not carry the formal charges of same sign. The total formal charges on the atoms in a Lewis structure must be zero for a neutral molecule and must equal to net charge for apolyatomic ion.