to break the crystal lattice in order to separate two positive and negative ions to infinite distance.

During the formation of an ionic compound it can be seen that the processes involved are; (i) The formation of a positive ion by removal of one or more electrons from a neutral atom and (ii) the formation of negative ions by the neutral atoms by acquiring electron. The first process involves the ionization energy and the second process involves the electron affinity of the atoms. The ionization energy required for the formation of positive ion and the energy released during the negative ion formation are opposed to each other. As a general rule, the ionization energy is much greater than the electron affinity. When the difference between the two values for given atoms is small, the chemical combination results in the formation of ionic compound. When the difference is large, the compound produced will be either partly or almost completely covalent.

But the formation of an ionic compound is not only dependent upon the difference between the amounts of ionization energy and electron affinity but also upon the lattice energy of the compound. Thus in chemical reactions leading to ionic compounds the energy required to produce the positive ion must be supplied by the release of energy in another part of the reaction. For instance, the formation of the solid from the ions would provide energy through the action of electrostatic forces, i. e., the lattice energy is available to supply the difference between ionization energy and electron affinity. It may be noted that ionic compounds are not made up of individual molecules. Th crystal lattice is built of a cluster or ion pairs in the form of groups. The number of groups around a central ion (crystal coordination number) is determined by the radii of the respective ions involved. Measurements of lattice energy have been made by means of a cyclic process known as energy cycle, specifically known as Born-Haber Cycle. as given in Fig.3—3 in the case of NaCl :

E = Electron affinity for Cl, I = ionization energy of Na (gas), S = sublimation energy of Na (solid), D = dissociation energy of Cl_2 and U = Lattice energy of the formation of NaCl (solid).

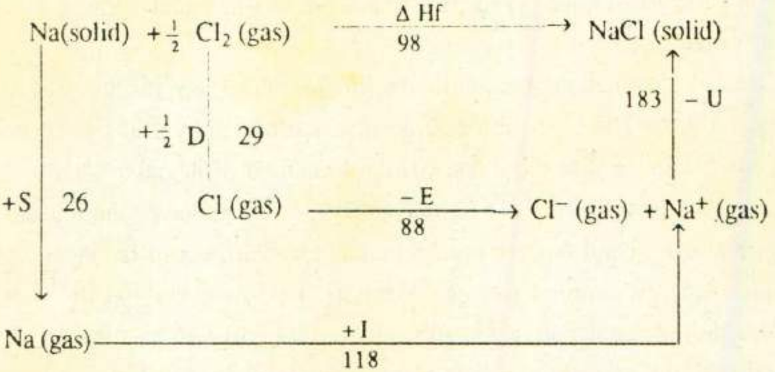


Fig. 3—3. Born-Haber cycle for NaCl

The heat of formation ΔHf of NaCl from Na (solid) and Cl_2 (gas)

$$\Delta Hf \equiv E - I - S - {}^{1}/_{2}\, D + U$$

$$\text{Lattice Energy}\quad U = \frac{-121.4nZ^{+}Z^{-}}{r^{+} + r^{-}}\left(1 - \frac{0.0345}{r^{+} + r^{-}}\right)$$

The Relationship Between Ionic and Covalent Bond

Covalent Character of Ionic Bond : In most cases the distinctions between ionic and covalent bonds are not very sharp. It may be remembered that ionic bond and covalent bond are extreme types of electronic interaction. Many chemical compounds involve a complex blending of both types of bonds. Hence the chemical bond may be considered as partly ionic and partly covalent and the relative degree of each type of bonding varies from compound to compound.

The difference between ionization energy of positive ions and electron affinity of negative ions indicate the nature of bounding between the two atoms. A small difference indicate ionic bond whereas a large difference points to covalent bond.

In a molecule containing two dissimilar atoms, displacement of electric charge takes place. This is much more prominent in the case of atoms of different sizes. Thus when a small positive ion comes very close to a large negative ion, the negative ion may be pulled out of shape or distorted as shown in Fig. 3—4. The distorted ion is not symmetrical but its centres of negative and positive charges have been displaced.

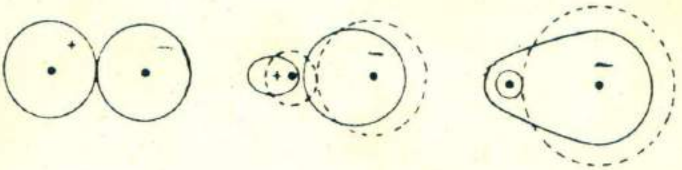


Fig . 3—4. Distortion of electron clouds.

Polarisation : The distortion of the electron cloud of a negative ion by a positive ion in a molecule is known as "polarisation." Molecules containing distroted electron clouds having separate centres of positive and negative electricity are known as polar molecules. The bonds between polarised ions or atoms are known as *polar bonds*. An extreme case of polarity is represented by an ionic compound such as sodium chloride (Na^+ — Cl^-) in which the sodium ion is almost completely positive and chloride ion is almost completely negative, and hence the bond is purely ionic. But if the size of the anion is much larger than that of the cation, the ionic bond has tendency to show covalent character because of polarisation. For instance, AgF is an ionic compound, soluble in water and colourless, whereas AgI is, to a great extent, covalent compound insoluble in water and coloured. In general, the greater the extent of polarisation, the greater is the covalent character of the chemical bond.

Fajans' Rule : Polarisation of ions depends upon a number of factors. According to Fajans' rule, the greatest effect of polarisation is produced in molecules having,

(i) Small size of cation,

(ii) Large size of anion,

(iii) High charge on either cation or anion,

(iv) Cations with electrons in **d** and **f** orbitals.

The overall effect of the above factors produce increased degree of covalent bond in ionic compounds.

Taking melting point as a criterion to distinguish between ionic and covalent bond, the comparison in Table 3.6 gives some idea about the effects of charge and size and distortion in the respective molecules according to the Fajans' rule. It may also be remembered that some covalent substances, such as diamond and silica, have high melting points because they occur as giant molecules.

Table 3.6. Melting points and Fajans' Rule.

Molecules	*m. p. (°C)*	*Bond Type*	*Polarisation due to*
MgF_2	1396	Ionic	—
MgI_2	632	Less ionic	large I^-
$BaCl_2$	962	Ionic	—
$BeCl_2$	440	Almost covalent	Small Be^{+2}
NaCl	801	Ionic	—
$SnCl_2$	247	Less ionic	Sn^{+2}
$SnCl_4$	−30	Covalent	Sn^{+4}
$CuCl_2$	422	Less ionic	Cu^{+2} (with d electron)
KCl	776	Ionic	—
$TiCl_4$	−30	Covalent	Ti^{+4}

Electronegativity

"Electronegativity has been defined as the power of attraction by an atom for electrons in a molecule." The atom which has greater attracting power for the electrons in a molecule is said to be strongly electrophilic or electronegative or it is said to have a high electronegativity. A covalent bond between like atoms may be regarded as a true covalent bond since both the atom exhibit equal power of attraction for the electrons in the molecule.

The polarity of a covalent bond depends primarily on the difference in the electronegativity of the two elements forming the bond. Changes of the polar character of covalent bonds can be observed in the following series of isoelectronic molecules (molecules having the same total number of electrons).

CH_4 NH_3 OH_2 FH

The C— H, N— H, O — H and F — H bonds are increasingly more polarised so that F is more electronegative than O which, in turn is more electronegative than N and C is least electronegative. The electronegativity of these atoms are in the order of

$$F > O > N > C$$

The term electronegativity is connected with a number of properties which may characterize an element and the behaviour of its compounds. Electronegativity of an element is influenced by the size of the atom and by the number of electrons required for it to form a stable ion.

By considering various types of experimental data Pauling has made a quantitative calculations of electronegativity values of various elements. The relative electronegativity values of some of the more common elements are given in Table 3.7. These values are based upon an arbitrary scale. Notice that the non-metals have higher electronegativity values than the metals. Thus, fluorine, the most chemically active non-metal, has highest electronegativity (4.0) and cesium, the most chemically active metal (with the possible exception of francium), has the lowest electronegativity (0.7). Because the metals have relatively low electronegativities and tend to assume a positive charge in compounds, they are generally called electropositive and non-metals are known as electronegative.

Calculation of Electronegativity Values : Two main methods for calculating the electronegativity values of elements are (a) Pauling's method and (b) Mulliken's method.

Table 3.7. Electronegativity of some elements (Pauling Scale).

Li	Be	H	B	C	N	O	F
1.0	1.5	2.1	2.0	2.5	3.0	3.5	4.0
Na	Mg		Al	Si	P	S	Cl
0.9	1.2		1.5	1.8	2.1	2.5	3.0
K	Ca			Ge	As	Se	Br
0.8	1.0			1.8	2.0	2.4	2.8
Rb	Sr			Sn	Sb	Te	I
0.8	1.0			1.8	1.9	2.1	2.5
Cs	Ba			Pb	Bi		
0.7	0.9			1.8	1.9		

(a) *Pauling's method :* This is based on the estimated contribution of the ionic nature A^+B^- of bond between two atoms A and B to the actual bond between A and B (AB).

If the actual bond energy measured experimentally between A and B = ΔH and the bond energy for a truly covalent bond = E_{AB}, then the resonance energy caused by the ionic character of the bond = $\Delta H - E_{AB}$. The value of E_{AB} was obtained from either the arithmatic or geometric mean of the bond energies of the bonds A—A (E_{AA}) and B—B (E_{BB}) respectively so that

$$E_{AB} = \frac{E_{AA} + E_{BB}}{2} \quad \text{or} \quad E_{AB} = \sqrt{E_{AA} \times E_{BB}}$$

The difference between ΔH and E_{AB} is the ionic resonance energy of bond A—B. This ionic resonance energy, designated as Δ, is large for molecules having widely different electronegativities.

If χ_A and χ_B are the electronegativities of element A and B respectively, then these were related to Δ by the relationship :

$$\chi_A - \chi_B = 0.208 \sqrt{\Delta}$$

Pauling arbitrarily fixed χ for H = 2.1 and for F = 4.0 in order to calculate the electronegativity values of other elements.

(b) *Mulliken's method :* According to Mulliken's definition, electronegativity of an atom is equal to the arithmatic mean of its electron affinity and its ionization potential.

Thus the electronegativity χ_A of atom A is given by the relationship :

$$\chi_A = \frac{I_A + E_A}{2}$$

where I_A is the ionization energy and E_A is the electron affinity of atom A.

This method is of limited value since the measurement of electron affinity is difficult, but has been found to be useful in explaining the ionic changes in bond hybridization. Thus the difference in the properties of sp, sp^2 and sp^3 hybridized carbon compounds can be readily explained.

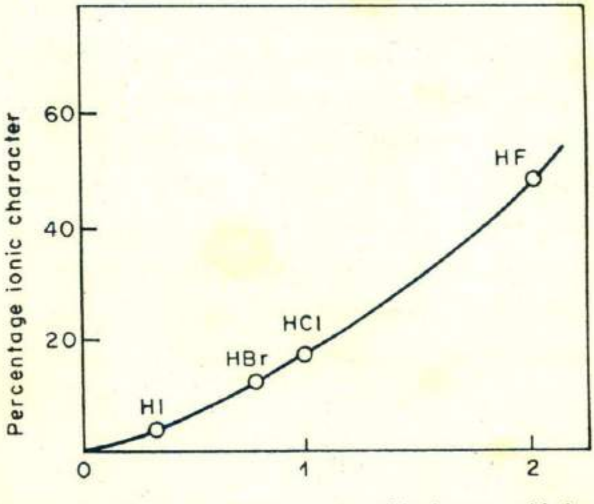
Ionic Character of Covalent Bond

The calculated electronegativity values are in accord with chemical facts when the differences in electronegativity values are used as the basis for comparison. A small difference in the electronegativity values of the two atoms forming the bond indicates almost equal sharing of electrons forming a non-polar type of bond (covalent bond). The larger the electronegativity difference, the more polar is the bond and charge separations between the atoms are greater resulting in pronounced ionic character. The amount of ionic character in the series of hydrogen halides indicates a decrease in the order of HF, HCl, HBr and HI as shown in Fig. 3—5. The charge separation in HF is much greater than that in HI. HCl and HBr are intermediate between HF and HI. H in, say, HCl, has a partial positive charge and Cl, a partial negative charge, represented as δ^+ and δ^- respectively.

$$\overset{\delta^+}{\mathrm{H}}\ \ \overset{\delta^-}{\stackrel{\cdot}{\times}\overset{\circ\circ}{\underset{\circ\circ}{\mathrm{Cl}}}\,\colon}$$

Thus HCl molecule has a strong polar covalent bond.

When a molecule contains a number of bonds, the charge separation is rather complex. Some schematic representations of the molecules showing the displacement of electron pair bond and partial charges are given in Table 3.8.



Difference in electronegativities $\chi_A - \chi_B$ of hydrogen and halogen.

Fig. 3—5. Relationship between ionic character and electronegativity.

Table 3.8. Charge separation in molecules.

Compound	*Electron-pair displacement*	*Partial charge displacement*
HBr	$\mathrm{H} : \overset{\circ\circ}{\underset{\circ\circ}{\mathrm{Br}}} :$	$\overset{\delta^+}{\mathrm{H}} - \overset{\delta^-}{\mathrm{Br}}$
ICl	$: \overset{\circ\circ}{\underset{\circ\circ}{\mathrm{I}}} : \overset{\circ\circ}{\underset{\circ\circ}{\mathrm{O}}} :$	$\overset{\delta^+}{\mathrm{I}} - \overset{\delta^-}{\mathrm{Cl}}$
H_2O	$\mathrm{H} : \underset{\substack{\circ\circ \\ \mathrm{H}}}{\overset{\circ\circ}{\mathrm{O}}} :$	$\overset{\delta^+}{\mathrm{H}} - \underset{\substack{\vert \\ \mathrm{H}^{\delta+}}}{\overset{\delta^{=}}{\mathrm{O}}}$
H_2S	$\mathrm{H} : \underset{\substack{\circ\circ \\ \mathrm{H}}}{\overset{\circ\circ}{\mathrm{S}}} :$	$\overset{\delta^+}{\mathrm{H}} - \underset{\substack{\vert \\ \mathrm{H}^{\delta+}}}{\overset{\delta^{=}}{\mathrm{S}}}$

Dipole Moments : One important physical property which is the result of charge separation in polar covalent compounds is dipole moment or electrical dipole moment. The extent of charge separation between two atoms in a molecule is measured by $\delta = \mu/de$, where δ is the bond length, e is the charge of an electron and μ is dipole moment of the bond. δ is a fraction of an electron charge and its quantity is such if $+\delta$ be placed on one atom and $-\delta$ on the other, the molecule would have the observed dipole moment μ. Distance between A and B = d. δ = fraction of charge on either A or B.

$$\overset{+\delta}{\mathrm{A}} \xleftrightarrow{\ \ d\ \ } \overset{-\delta}{\mathrm{B}}$$

Dipole moment provides an index of the polarity of a molecule; the greater the value of dipole moment, the greater is the polarity. The values of dipole moments for hydrogen halides and the electronegativities of halogens are given below.

Hydrogen halide	*Electronegativity of halogens*	*Dipole moment* μ (Debye Unit)
HF	F = 4.0	1.91
HCl	Cl = 3.0	1.03
HBr	Br = 2.8	0.78
HI	I = 2.5	0.38

Thus from the electronegativity values, HF is the most polar of all hydrogen halides and has a large value for the dipole moment.

Resonance Structures

The polar covalent bond does not indicate the presence of both covalent and ionic bonds in the same molecule. The polar bond has been produced by the combination of different types of electronic interactions in certain proportions. In a molecule of HCl having largely a covalent bond but with some ionic character, the bond may be considered as a blend of covalent bond and ionic bond between H and Cl. Hence the bond is neither purely covalent, nor purely ionic but a blend of the two extreme types with varying proportions. (see Chapter 2 Page 85)

Bond Length, Bond Angle and Bond Energy

Bond Length : The distance between the centres of two nuclei of atoms connected by a chemical bond is known as bond length. The distance between two atoms or bond length in a molecule has been calculated by the use of the sum of covalent radii. The distance involved between two atoms or the bond length is very small and is generally expressed in terms of Angstrom units (1 Å $=10^{-8}$ cm). (See also page 106)

The bond lengths in molecules are measured by various methods, such as X-ray diffraction and spectroscopic methods. The bond lengths between two atoms bonded by a single covalent bond appear to be nearly constant. Thus C—Cl bond length in CH_3Cl, CH_3CH_2Cl, $CHCl_3$ and CCl_4 is almost 1.76 Å. Similarly, C—C single bond in many of the organic compounds is of the order of 1.54 Å.

If R_{AB} is the interatomic distance between two atoms A and B, it has been found that R_{AB} is equal to the mean of the bond lengths A—A and B—B. In other words, if r_A is the covalent radius of A and r_B the covalent radius of B, then

$$R_{AB} = r_A + r_B = \frac{R_{AA} + R_{BB}}{2}$$

Bond lengths between two atoms may also be designated as double or triple bond which are measured in similar manner as the single bond. Hence for atoms we can assign single, double and triple bond covalent radii. Radii of some atoms are given in Table 3.9. (See also Table 3.1)

Table 3.9. Single, double and triple bond covalent radii in Å unit.

Atom	*Single bond covalent radius*	*Double bond covalent radius*	*Triple bond covalent radius*
H	0.30	—	—
B	0.88	0.76	0.68
C	0.77	0.67	0.60
N	0.74	0.62	0.55
O	0.73	0.55	—
P	1.10	1.00	—
S	1.04	0.94	—
Cl	1.00	—	—

But there are factors which influence the bond lengths; for instance, the polarity of a covalent bond has tendency to decrease the bond length and hence the calculated value may be a little too large. Again, the increase in coordination number may increase the bond distance. Bond distance in molecules may also be influenced by resonance and electronic interactions of complex types and also the strength of bond varies for different reasons. Thus CO_2 the structure O—C—O is more appropriate since C uses **sp** hybrid and two π bonds due to overlapping between delocalized **p** orbitals.

Bond Angle : The angle between the directions of two bonds in a molecule is called the "bond angle".

A bonding electron pair is concentrated most strongly in the direction of the line joining the bonded atoms. These bonded atoms may be joined to a central atom and then each electron pair or pairs may form separate bond. The bond angle in molecules depend upon various factors, namely the charge distribution, geometry of the molecules, symmetry, hybridization etc. Some of these are shown below for normal molecules.

Bond hybridization	*Geometry*	*Bond angle*
sp	Linear	180°
sp^2	Triangular	120°
sp^3	Tetrahedral	109° 28′
sp^3d or **dsp^3**	Trigonal bipyramid	Basal — 120° Apical—90°
sp^3d^2 or **d^2sp^3**	Octahedral	90°
dsp^2	Square planar	90°

In most cases regular geometrical shapes are distorted for various reasons giving rise to the variation of bond angles.

Bond angles for some molecules and ions are given in Table 3.10. The geometry of the molecules have been discussed in Chapters 5 and 24.

Table 3.10. Bond angles of some molecules and ions.

Species	*Angle*	*Species*	*Angle*
CH_4	H—C—H 109°	SO_3	O—S—O 120°
NH_4^+	H—N—H 109°	NO_3^-	O—N—O 120°
H_2O	H—O—H 105°	NH_3	H—N—H 107°

Bond Energy : "Bond energy" is defined as the energy required to split the molecule into atoms. This may also be defined as the energy released in the formation of a molecule from atoms by assuming that the total energy is composed of separate contributions from each bond. Bond energy may be determined from the spectrum or by measurement of equilibrium constants for dissociation of the molecules at high temperatures. When there is only one formulation of covalent bond in a molecule, the bond energy calculated by applying summation of Hess' Law agrees well with the experimental determination, for instance, in CH_4, but not in C_6H_6. Bond energy, therefore, gives indication of the type of bonding involved and also points out the existence of single, double or triple bonds in a molecule. The bond strength resulting from a variety of reasons throws much light on the stability of molecules, and are of great practical applications.

For example, Pauling's values of electronegativities of elements have been derived from the experimentally determined values of bond energies. The bond energy of Cl—Cl bond is the energy required to separate the molecule of Cl_2 into two atoms (2Cl), not ions. Similarly, bond energy of H_2 is the energy required to split H_2 into two atoms of H. The bond energy of H—Cl can be calculated as the arithmatic or geometric mean of the two bond energies of Cl—Cl and H—H. In the same way, calculations for bond energies of other molecules can be derived. Bond energies of molecules can also be directly determined experimentally. The difference between the calculated bond energies and the experimentally determined values, Δ, is a measure of the polarity of the bond and is related to the electronegativity. The greater the difference in bond energies, the greater is the polarity and hence greater will be the difference in electronegativity values of the atoms forming the molecule. These facts are illustrated in Table 3.11 with some examples.

Table 3.11. Bond energy and electronegativity difference.

Bond *A—B*	*Calculated mean bond energy Kcal / mole*	*Experimental bond energy Kcal / mole*	*Energy difference* Δ	*Electronegativity difference between A—B*
Si—F	43	128	85	2.2
H—F	67	135	68	1.9
H—O	59	108	49	1.4
H—Cl	79	103	24	0.9
Cl—O	43	49	6	0.5

QUESTIONS AND PROBLEMS

1. Explain how positive and negative ions are formed from neutral elements.
2. What is meant by "ionization potential"? How is it related to the tendency of the elements to form positive or negative ions?
3. Explain the term "electronegativity" of the elements.
4. What is meant by polar molecule ? Give example.
5. How the polarity of bond in a molecule is related to electronegativity differences between the atoms of the molecules?
6. Explain Fajans' Rule with examples.
7. Discuss : (a) The ionic character of covalent bond, (b) The covalent character of ionic bond.
8. What is meant by radius-ratio effect in ionic crystals? How it governs the geometrical shape of the crystalline substances?
9. Define the following :— (a) Crystal lattice (b) Lattice energy, (c) Crystal co-ordination number, (d) Polarisation, (e) Electron affinity, (f) Bond length, (g) Bond angle, (h) Bond energy, (i) Covalent radii, (j) Ionic radii.
10. Which of the following pairs of substances should be more polar than the other? (a) H_2O and H_2S; (b) HI and HF; (c) AlF_3 and $AlCl_3$; (d) KCl and PCl_3; (e) ICl and KI.
11. Discuss the bonding systems and shapes of the following molecules :
    NH_3 ; SF_4; PCl_5; $SiCl_4$
12. The bond lengths of Cl_2 and Br_2 are 1.988 Å and 2·290 Å respectively. Find the length of the Br–Cl bond in bromine monochloride.
13. Given H to H distance in NH_3 is 0.1634 nm and N–H bond distance is 0.101 nm. Calculate the bond angle H–N–H.
14. The electronegativities of F, Cl, Br and I are 4.0, 3.0, 2.8 and 2.5 respectively. Explain why the dipole moments decreases in the sequence HF, HCl, H Br, and HI, even though the bond length and the number of electrons increase.
15. Bond evergies for the following bonds are :

    H—H = 104 Kcal/mole

    O = O = 118 ,,

    O = H = 111 ,,

    Calculate energy change in the reaction :

    $2H_2(g) + O_2(g) = 2H_2O(g)$.
16. Calculate the heat of formation *ΔHf* of crystalline NaF using the following data according to Born-Haber cycle.

    $Na(g) \rightarrow Na(g) = +26.0$ Kcal (S)
    $F_2(g) \rightarrow 2F(g) = +36.6$ Kcal (D)
    $Na(g) \rightarrow Na^+(g) = +120.0$ Kcal (I)
    $F(g) + e^- \rightarrow F^-(g) = -83.5$ Kcal (E)
    $Na^+(g) + F^-(g) \rightarrow Na^+F^-(s) = -216.7$ Kcal (U)

CHAPTER 4

CLASSIFICATION OF THE ELEMENTS

The 105 substances well-known as elements are the foundation of the study of chemistry. Attempts have always been made to discover an arrangement and order in a complex science such as chemistry comprising a vast number of experimental facts about all the 105 elements. In order to facilitate a systematic study of the vast facts we must classify them in a way that lays emphasis on similarities and differences between isolated and unrelated phenomena. The earlier attempts at such a classification have been attributed to many scientists and proved to be very useful in developing the modern system which is based upon the electronic arrangement of atoms. It is, therefore, worthwhile to trace the developments.

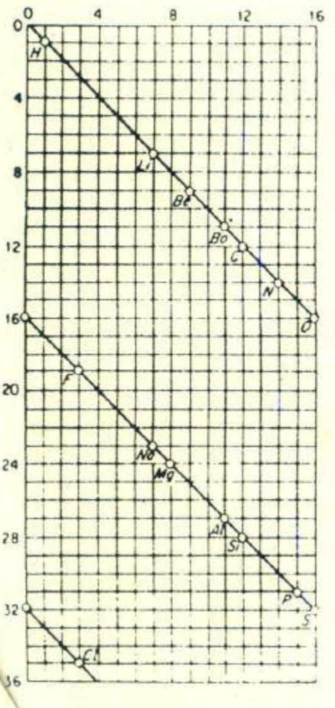
Early Attempts at Classification

1. Noble Metals and Base Metals : In one of the earliest attempts at the classification, the metals were divided into two groups. gold and silver were considered to be noble metals, whereas copper, iron, tin lead etc. were included among the base metals. When elements which are non-metals were discovered, a further classification into metals and non-metals were introduced and made it possible to anticipate the difference in the properties of hitherto unknown elements.

2. Dobereiner's Triads : In 1829, J. W. Dobereiner observed that several of the elements could be grouped together in sets of three, called *triads*, which have closely related properties. The triads are found to have either nearly the same atomic weights or differ by an almost constant difference. Using present-day atomic weights which are more accurate than those used by Dobereiner, the relationships among some triads may be shown as in Table 4.1.

Table 4.1 Dobereiner's Triads.

Triads	*Atomic weights*	*Difference between consecutive elements*
Li	6.940	
Na	22.997	16.057
K	39.100	16.103
Cl	35.457	
Br	79.916	44.459
I	126.91	46.994
Fe	55.85	
Co	58.94	Almost the same at. wts.
Ni	58.71	



4—1. A portion of the Telluric Screw on a flat surface

The triads of Dobereiner represent the first reported attempt at classification of elements on the basis of atomic weights. This observation stimulated further attempts to seek additional and wider numerical relationships. But most of the attempts did not meet with much success, largely because the atomic weights were not evaluated correctly. Mention may be made about Pettenkofer series which suggested that the atomic weights of chemically similar elements can be represented by arithmatic series. Thus oxygen, sulphur, selenium and tellurium could be classed as family of elements represented by the series $l+2n\times8$ where $l=$ at. wt. of O and $n=0, 1, 2, 3,$ A French scientist, de Chancourtois, constructed a vertical cylinder on which he arranged the elements spirally at heights proportional to their atomic weights. It was found that similar elements appeared above one another on the cylinder. This arrangements is known as the Telluric Screw and this proved to be the forerunner of the modern classification of elements. A flat surface of the Telluric Screw is shown in Fig. 4—1.

3. Law of Octaves : In 1864, John Newlands arranged the elements in the increasing order of their atomic weights and observed that every eighth element in the list beginning from any given element showed a repetition of the physical and chemical properties of the first element. Because of its resemblance with the eight notes in musical scale this concept of the classification of elements was known as the Law of Octaves. Unfortunately this basically sound idea was not well received by scientists of Newlands' time. It may be pointed out that the inert gases were not then known and the discovery of the inert gases completely shelved the idea of the Law of Octaves.

Periodic Law :

In 1869, a German chemist, Lother Meyer, and a Russian scientist, Dmitri Mendeleeff, working independently and from different viewpoints, proposed a detailed relationship between the physical and chemical properties of the

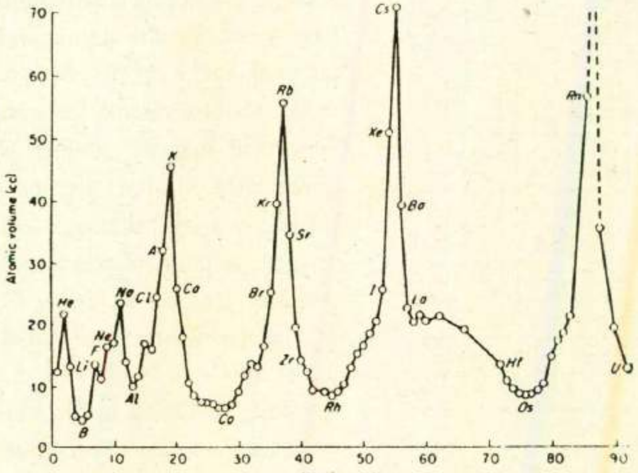


Fig. 4—2. The atomic volume curve of the elements.

elements and their atomic weights. Meyer selected some physical properties related to the atomic weights, namely atomic volume. Taking atomic numbers instead of atomic weights as the basis a graph of atomic volumes (the volume occupied by 1 g. atom of an element or at. wt. divided by the density) against atomic numbers is shown in Fig. 4—2. This graph does reveal a periodic variation of atomic volume when the elements are arranged in the increasing order of atomic weights or atomic numbers. It may be noted that a periodic variation repeats itself more or less at regular intervals or periods with the change of variables. Thus the change of seasons in a year is a periodic phenomenon. Night and day are periodic phenomena. The swing of a pendulum to and fro is a periodic phenomenon.

Mendeleeff gave a more detailed comparison of the physical and chemical properties of the elements and set up a periodic system in which the elements were arranged in horizontal ROWS (series) and vertical COLUMNS (groups) according to increasing atomic weights. This arrangement is the basis of our modern Periodic Table. Mendeleeff observed that when all the 65 elements (known at that time) were arranged according to increasing atomic weights, similarities and differences in their properties would be apparent. This was enunciated in the form of a PERIODIC LAW which stated that the physical and chemical properties of the elements are periodic functions of their atomic weights.

The discovery of rare gases during 1890—1900 did not produce any serious difficulty with regard to Mendeleeff's PERIODIC TABLE. Mendeleeff is usually given the principal credit for establishing the periodic system of the elements.

With the advancement of our knowledge about atomic structure and discovery of new elements, a modification in the definition of periodic law was proposed on the basis of atomic number. The modern statement of the periodic law is:

The physical and the chemical properties of the elements are periodic function of their atomic numbers.

There are various forms of the Periodic Table and a modern long form is given in Table 4.2. based on Aufbau Principle (building up of the atomic lectronic configurations. As the nuclear charge increases, the electronic nfigurations become more complex.

The Modern Periodic Table

The original Periodic Table suggested by Mendeleeff has undergone many modifications, although the basic features have been maintained in all the modified forms.

It is seen that the first short period (horizontal series) contains only two elements—hydrogen and helium. Helium has a complete energy level of two electrons ($1s^2$). The second short period consists of eight elements beginning with lithium and ending with neon. Neon has complete electronic arrangements of $1s^22s^22p^6$ and contains 8 electrons in the outermost level. The third short period again consists of eight elements beginning with sodium and ending with argon. Argon has the electronic configuration of $1s^22s^22p^63s^23p^6$ and the outermost energy level contains 8 electrons.

The fourth period is the first long period containing eighteen elements and this period starts from potassium (atomic number 19). Potassium has electronic configuration $1s^22s^22p^63s^23p^64s^1$ and the next element calcium (atomic number 20) has one more election in 4s level, i. e., $4s^2$ and thereby making it complete. Scandium having atomic number 21 with the electronic arrangements $1s^22s^22p^63s^23p^63d^14s^2$ starts building up the 3d energy level. The process of filling up of 3d level is completed until copper (atomic number 29). In copper the third quantum level contains 18 electrons. Each succeeding element in this period contains one more electron in the fourth quantum level. The fourth period comes to an end with the inert gas krypton (atomic number 36) containing eight electrons in the outermost energy level.

The fifth period begins with rubidium (atomic number 37). The last element is xenon (atomic number 54) and contains again eight electrons in the outermost energy level. The process of filling up of the energy levels follows the same pattern as in the fourth period and, therefore, the fifth period also contains eighteen electrons.

The sixth period consists of thirtytwo elements. This period starts from cesium (atomic number 55) having one electron in the 6s level, i.e., $6s^1$. The next element barium has two electrons in the 6s level. the next fifteen elements starting from lanthanum (atomic number 57) to lutecium (atomic number 71) contains 8 and 2, or 9 and 2 electrons respectively in the two outermost energy levels together with increasing number of electrons in the inner **4f** orbital. The fourteen elements starting from Ce (58) to Lu (71) have almost identical chemical properties and all are placed in the same position in the Periodic Table. They are known as rare earth elements and constitute the lanthanide series named after lanthanum. From cerium to lutecium each succeeding element has one more electron in the **4f** energy level. Lutecium (atomic number 71) and above have a total of 32 electrons in the fourth energy level. The single electron in the **5d** energy level in all the elements from lanthanum to lutecium starts building up with hafnium (atomic number 72) and becomes complete ($5d^{10}$) in gold (atomic number 79). From gold to the end of the period each such succeeding element has one more electron in the **6p** energy level. The period ends with the inert gas radon (atomic number 86) containing 8 electrons in the outermost energy level ($6s^26p^6$). The seventh period is still incomplete. The first element francium (atomic number 87) has one electron in **7s** energy level and after radium (atomic number 88) with $7s^2$ electrons the building up of **6d** level starts but for all the elements upto the present element hahnium (atomic number 105) it remains constant, i.e., consists of only one electron. From actinium (atomic number 89) a new series of elements starts which is known as actinides and may be considered to be complete at the element having atomic number 103 (Lr) placed along with lanthanides below the Periodic Table.

The elements actinium, thornium, protoactinium and uranium are naturally occurring radioactive elements in the actinide series. The eleven elements after uranium, known as transuranium elements, have been made artificially. Because of the filling up of the **5f** energy level and identical electron arrangements in the **6d** and **7s** energy levels, the actinide series of elements have similar chemical properties. Like the lanthanides these are also placed in one position after radium in the Periodic Table. The recently discovered element kurchatovium (atomic number 104) is the beginning of the seventh period which is incomplete and will be considered to be complete at the element of atomic number 118. The next element (atomic number 105) has been named tentatively as hahnium (Ha).

The vertical arrangements of elements in the Periodic Table are called ps. It may be seen that the groups are numbered IA, IIA IIIB, IVB VB, VIB, VIII, IB, IIB, IIIA, IVA, VA, VIA, VIIA and 0. The elements in sub-group A show some similarities to the corresponding elements in the B sub-group of the same number. The sub-grouping of elements was originally empirical, but now it is based on the electronic arrangement of the atoms. The division into the sub-groups A and B is based on the fact that the penultimate energy levels (last but one quantum level) of electron in these groups contain the arrangement s^2p^6 and $s^2p^6d^{10}$ respectively. It may be noticed that the similarities between A and B sub-groups of the same group of elements sometimes are confined only in the oxidation states and some of their compounds. Thus manganese in group VIIB is a metal and chlorine in VIIA is a non-metal and a gas. However, oxidation states of +7 for Mn in $KMnO_4$ and Cl in $KClO_4$ is common for both and these compounds have similar crystalline form, solubility and oxidizing action.

The elements in group VIII have no sub-groups, instead these consist of three elements in one single group of the Periodic Table and occur in the middle of each long period. These have striking horizontal similarities. This group contains iron, cobalt and nickel in the fourth period' ruthenium, rhodium and palladium in the fifth period; and osmium, iridium and platinum in the sixth long period. The group VIII elements may be called bridge elements, because they form bridge between the hard, high melting metals of group VIB and VIIB and the softer metals of group IB and IIB. The inert gases, having elements of completed electronic levels, are placed at the end of the period where they fit excellently and are termed as elements of group 0.

Electronic Structure and the Periodic Law

Types of Elements : According to the electronic configurations, the elements may be divided into four types. Mention has already been made regarding the four types of atoms on the basis of electronic arrangement. The four types of elements are :

(1) The Inert Gases. (Elements of 0 group).

(2) The Representative Elements (s and **p** book elements).

(3) The Transition Elements (**d** block elements).

(4) The Inner Transition Elements (**f** block elements)

The Inert Gases : The zero group elements have been placed at the end of each period in the Periodic Table. It appears that these elements having s^2p^6 electronic arrangements in the outermost level are very stable. Helium has $2s^2$ stable arrangement and all other inert gases have s^2p^6 outer configurations. It may be noted that no atom has a complete energy level except helium and neon. This is one reason that discontinuities in the building up of energy level take place. These elements are colourless gases.

The Representative Elements (s and p block elements) : These elements generally belong to A sub-group of the Periodic Table.These elements have the outermost energy level incomplete just after the complete or stable groupings of s^2p^6. The chemical behaviour of these elements depends upon the valence electrons and these are both metals and non-metals. Thus the alkali metals, alkaline earth metals are **s** block or **s** orbital elements. Group IIIA elements under boron have a single electron in their valence **p** orbitals. The valence electrons of all the elements from boron to halogens (groups IIIA to VIIA vertically) occupy **p** orbitals. Hence these elements are called **p** block or **p** orbital elements. They generally form colourless compounds.

The Transition Elements (d block elements) : These elements are generally heavy metals of sub-group B and contain two incomplete energy levels because of the building up of the inner **d** electrons. The chemical properties of these elements depend upon the electrons from the two outermost levels (s and **d** electrons). These elements generally form coloured compounds.

As the atomic number increases each successive electrons enters the outermost energy level of the atom. But sometimes the additional electron enters one of the inner levels, such as the 3**d** on account of its lower energy than 4**p**, although this is not attained until 4**s** levels is completed. When 4s has got its 2 electrons, the next electron now goes to 3**d** instead of 4**p** and as the atomic number increases, it is the 3**d** level which is being filled up. The 4s continue to have 2 electrons and the properties of the successive elements do not appear to change much. Elements which have normally the same number of electrons in the outermost level but have a progressively greater number of electrons in an inner level (such as **d** level) are called "Transition Elements". In the Periodic

Table 4.2. The Periodic Table of elements(Long form).

Period →
s block elements
Group ↓

d block elements

Transition elements

s electrons

p block elements

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	O
H 1																	He 2
Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12											B 13	C 14	N 15	O 16	F 17	Ne 18
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La 57	Hf 58	Ta 59	W 60	Re 61	Os 62	Ir 63	Pt 64	Au 65	Hg 66	Tl 67	Pb 68	Bi 69	Po 70	At 71	Rn 72
Fr 87	Ra 88	Ac 89	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	(110)	(111)	(112)	(113)	(114)	(115)	(117)	(118)	(119)
(119)	(120)	(121)	(154)	(155)	(156)	(157)	(158)	(159)	(160)	(161)	(162)	(163)	(164)	(165)	(166)	(167)	(168)

Lanthanides	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
Actinides	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103
Superactinides	(122)	(123)	(124)											(153)

Table we come across four such transition series in which the additional electrons enter the 3d, 4d, 5d and 6d orbitals. some of these are shown in Table 4.3.

Besides the transition elements, there are the inner transition elements in which not only the **d** levels but also the 4f or 5f levels are being progressively filled up. These are generally called the Lanthanides (the rare earths) and the Actinides (mainly trans-uranium elements).

Table 4.3. Outer electron levels of the transition metal groups.

21	Sc	$3d^14s^2$	39	Y	$4d^15s^2$	57	La	$5d^16s^2$
22	Ti	$3d^24s^2$	40	Zr	$4d^25s^2$	72	Hf	$5d^26s^2$
23	V	$3d^34s^2$	41	Nb	$4d^45s^1$	73	Ta	$5d^36s^2$
24	Cr	$3d^54s^1$	42	Mo	$4d^55s^1$	74	W	$5d^46s^2$
25	Mn	$3d^54s^2$	43	Tc	$4d^55s^2$	75	Re	$5d^56s^2$
26	Fe	$3d^64s^2$	44	Ru	$4d^75s^1$	76	Os	$5d^66s^2$
27	Co	$3d^74s^2$	45	Rh	$4d^85s^1$	77	Ir	$5d^76s^2$
28	Ni	$3d^84s^2$	46	Pd	$4d^{10}$	78	Pt	$5d^96s^1$
29	Cu	$3d^{10}4s^1$	47	Ag	$4d^{10}5s^1$	79	Au	$5d^{10}6s^1$
30	Zn	$3d^{10}4s^2$	48	Cd	$4d^{10}5s^2$	80	Hg	$5d^{10}6s^2$

The first transition series of elements involving the completion of 3d level start from Sc (21) to Zn (30) which may be discussed as the elements of representative characters. The second series of transition elements start from Y (39) upto Cd (48) involving **4d** energy level. The third group of transition metals starts from La (57) but with a break from Ce (58) to Lu (71) which are classified as inner transition metals and proceed upto Hg (80). Sometimes the metals of group IIB, namely, Zn, Cd, Hg, are not included in the transition metals. But for the sake of systematic study of chemistry they are included as transition metals on the basis of electron arrangement.

The properties of transition elements are summarized in the following points :—

1. All the elements are of high melting points, electropositive and heavy metals.
2. These metals have almost the same atomic and ionic sizes. There is only slight increase in the ionization energy of the formation of M^{+2} ions.
3. All these elements show positive oxidation states of +2 and +3 generally and form mostly ionic compounds. Higher oxidation states are also exhibited in some cases.
4. As a general rule, the transition elements form coloured compounds.
5. These elements are also effective catalytic agents.
6. All these form quite a large number of complex compounds.

These properties are due to the influence of the incomplete inner **d** orbitals in the transition elements. The properties are similar in the case of inner transition elements where **f** orbitals are being completed (see Chapter 18).

The Inner Transition Elements (f block elements) : These elements have three incomplete outer levels. The orbital in which the electron is added on increasing the atomic number is an **f** orbital. The series of 14 elements in which 4**f** level is being build up follows lanthanum (57) and are called Lanthanides. The series of elements in which 5**f** level is being filled follows actimium and is known as Actinides. The inner transition elements (lanthanides and actinides) are all metals and show variable oxidation states. Their compounds are highly coloured (see Chapter 18). Lawrencium (103) is the last element of the actinide series. The recently discovered element now named Rutherfordium (104) is, therefore, the first element of the Transactinide series and should be chemically similar to lanthanum and hafnium. The report of the discovery of element 105 (Hahnium) now named as Dubnium by the Russian scientists and if the synthesis of the new elements continues, it is expected that elements 114 and 126 should possess increased stability. The most suitable means to achieve such a break-through towards the farther reaches of Periodic Table is evidently the bombardment of heavy nuclei. This requires more powerful cyclotrons and possibly a *superactinide* series of elements may be discovered. (see page 138 and 154)

Periodicity of Valence Electrons : When the elements are arranged in order of increasing atomic numbers, elements with similar physical and chemical properties repeat at definite intervals. In regard to atomic structure, it implies a periodicity in the number of valence electrons in the atoms of elements. If the elements containing the same number of valence electrons are grouped together, the elements within each group will be similar in properties. Table 4.4 gives the electron levels for the elements of atomic numbers in the beginning of the Periodic Table showing the periodicity as regards the number of electrons in the outermost energy level.

Table 4.4 Periodicity of valence electrons.

Element	H							He
Electron level	1							2
Element	Li	Be	B	C	N	O	F	Ne
Electron level	2,1	2,2	2,3	2,4	2,5	2,6	2,7	2,8
Element	Na	Mg	Al	Si	P	S	Cl	Ar
Electron level	2,8,1	2,8,2	2,8,3	2,8,4	2,8,5	2,8,6	2,8,7	2,8,8

It is seen that the elements in the vertical columns (groups) have the same number of electrons in the outermost energy level. The similarity in the chemical properties among the elements of the same group can be attributed to the number of electrons in the outermost energy level of an atom. Periodicity as regards valence electrons is reflected in the periodicity of oxidation states (the number of positive or negative charges of the atoms). This feature is shown in Table 4.5.

Table 4.5. Periodicity of Oxidation State.

+1 H							0 He
+1 Li	+2 Be	+3 B	+4,−4 C	+5,−3 N	−2 O	−1 F	0 Ne
+1 Na	+2 Mg	+3 Al	+4,−4 Si	+5,−3 P	−2 S	−1 Cl	0 Ar

Hydrogen, lithium and sodium have one valence electron each, and each shows an oxidation state of +1 when this electron is transferred to another atom in the formation of chemical bonds. Carbon and silicon atoms with four valence electrons may form four polar covalent bonds in which the shared electron pairs are shifted away (+4 oxidation state) or move towards (–4) oxidation state) of the carbon or silicon atom. Fluorine and chlorine atoms, each with seven valence electrons, normally assume completed octets by the addition of one electron giving them–1 oxidation states.

Variation of Properties within Periods and Groups

The physical and chemical properties of the elements are largely determined by their electronic structure. Differences in the properties within groups may be attributed primarily to three characteristics of atomic structures : (i) The nuclear charge and the number of electrons surrounding the nucleus (atomic number). (ii) The total number of electrons—particularly the number of valence electrons. (iii) The size of the atoms, i.e., the volume occupied by the electron in various energy levels.

1. Variation of Metallic Character of the Elements : Generally, it may be noticed that in the Periodic Table the metallic character of the elements decreases from left to right progressing in the series but increases in moving vertically from top to bottom in the groups.The term "metallic character" is a rough and qualitative combination of a number of specific properties, such as electrical and thermal conductivities, metallic lustre, reducing properties etc. Except the transition elements, the trend in the variation of metallic character of elements follows the above generalisation. For instance, the most non-metallic elements, fluorine, chlorine, oxygen, sulphur, nitrogen are found at the upper right of the Periodic Table whereas the most basic matals, the alkali and alkaline earth metals are at the lower left of the Table.

2. Variation in Atomic Size : The atomic size in each succeeding element in a period decreases but the atomic radii of inert gases at the end of the periods, however, are larger than those of the elements of the preceding atomic number. The inert gases have completed outer energy levels, i. e., the **p** sub-level has been filled up with six electrons (p^6). As the nuclear charge increases in a period the electrons may occupy the same or different energy levels. When the succeeding electrons go into the same energy levels they are subject to greater attraction by the increased nuclear charge and hence the elements in a series show gradual decrease in the atomic size. Since the inert gases, such as argon, exhibit very weak binding force to hold the atoms together in a crystal lattice, the interatomic distances and atomic radii of these elements become greater than those of the preceding halogens.

The gradation from highly metallic sodium to highly non-metallic chlorine in the third period shown in Table 4.2 is explainable in terms of the smaller size of each succeeding element in the series. The tendency for each succeeding element to become less metallic results from the fact that the valence electrons are less readily lost as their distance from the nucleus becomes less, and the attraction for additional electrons from other atoms becomes greater.

Vertically in the groups the succeeding elements have increasing atomic radii. Thus, each alkali matal atom has a much greater atomic radius than that of the inert gas just before it. This is due to the fact that the additional electron occupies a new sub-level with a quantum number higher than those of the already filled energy levels. These elements become more metallic, i.e., lose valence electrons more readily as their size increases. This results from the fact that the valence electrons are held less strongly due to the increasing size of the atom.

A similar trend is noticed in the long periods but the gradation is less marked and also shows some exceptions, such as in Rh—1.24Å, Pd—1.28Å, Ag—1.34Å. Within a given group the heavier elements have the larger atomic size.

3. Variation in Ionic Radii : It is obvious that the size of a positive ion will be less than that of the atom from which it is formed. There is considerable decrease in size due to the loss of the outermost electron particularly in the case of alkali metals. In the cases of ions having inert gas electronic configurations, the contraction in size in a given period is well-marked. Thus in the series, Na^{+}, Mg^{+2}, $A1^{+3}$ and Si^{+4}, which are isoelectronic with argon configuration, the decrease in their ionic sizes appears to be considerable as compared to the atomic sizes of the parent atoms. It will be seen that greater the nuclear charge, the smaller is the ionic radius in a series of isoelectronic ions. In a given group of the Periodic Table positive ions of succeeding elements have larger ionic radii.

A simple negative ion formed by the addition of one or more electrons to the outermost energy level of an atom, is expected to be much larger than the parent atom. In a given group the negative ions will have larger radii due to larger number of electron levels. The ionic sizes in a series also follow the same trend as in the case of the positive ions, i.e., the sizes decrease gradually from element to element. The trends are given in the Table 4.6 and Table 4.7.

Table 4.6. Trend in ionic sizes in a series.

Atom	Na	Mg	Al	Si	P	S	Cl	Ar
Radius(Å)	1.86	1.60	1.48	1.17	1.10	1.04	0.99	1.54
Ion	Na^+	Mg^{+2}	Al^{+3}	Si^{+4}	P^{-3}	S^{-2}	Cl^-	Ar
Radius(Å)	0.95	0.78	0.57	0.40	2.12	1.84	1.81	1.54

Table 4.7 : Trends in ionic sizes in a group(Å)

Atom	*Radius*	*Ion*	*Radius*
Li	1.52	Li^+	0.60
Na	1.86	Na^+	0.95
K	2.31	K^+	1.33
Rb	2.44	Rb^+	1.48
Cs	2.62	Cs^+	1.69
F	0.72	F^-	1.36
Cl	0.99	Cl^-	1.81
Br	1.14	Br^-	1.95
I	1.33	I^-	2.16

In the Long Periods, the ionic sizes of transition metals of the same charge (say, M^{+3}) show slight gradation with irregularities. The radii of the rare earth ions (M^{+3}) show regular decrease from lanthanum to lutecium. It is due to the relationship between ionic sizes and chemical properties that the pairs of elements, such as Zr and Hf, Nb and Ta, Mo and W, have almost identical chemical behaviour. These pairs of elements although placed widely apart in the

Periodic Table have almost identical ionic radii due to the trends in the variation of ionic sizes.

4. Variation in the Ionization Potentials : Ionization potential of an atom is the most important fundamental property of an atom and the metallic character is largely determined by its ionization potential, its atomic radius and its ionic radius. These three properties may be interdependent since the ionization potential is defined as the energy required to remove the outermost electron from an atom. In general, the greater the nuclear charge of atoms having the same number of electron orbit, the greater the ionization potential. Thus the elements in the same period have gradually increasing ionization potential. Slight irregularity within a period is due to building up of new sub-level for electrons. Metals generally have small ionization potentials and non-metals have large values. This indicates that metals give positive ions readily by the loss of electron and non-metals have no tendency to form positive ions during chemical reactions. The magnitude of the ionization potential to some extent gives a measure of the chemical activity of an element (particularly of metals). Thus the ionization potential increases in a series and shows decreasing tendency with a group in the periodic classification. In other words, the periodic variations are well-marked (see Fig. 3—1. page 111)

5. Variation in Electron Affinities : Electron affinity, as defined earlier, is a measure of the energy released when an electron is added to an atom to form a negative ion. Metals obviously have small electron affinities and non-metals, on the other hand, have large values of electron affinities and are therefore, good oxidising agents. In general, in a series of elements of a given period of the Periodic Table succeeding elements have higher electron affinities. Within a group having smaller electron affinities the metallic character becomes more prominent.

6. Variation in Electronegativities : The power of attraction that an atom shows for electron in a covalent bond (electronegativity) also shows periodic variations. The most electronegative elements are found towards the end of the periods. Metals having low electronegativities are found at the beginning of the periods. Thus the alkali metals show gradually decreasing electronegativity values within the group. The halogens are most electronegative elements and the values decrease from fluorine to iodine. It follows that elements at the extreme left of the Periodic Table form ionic bonds with, say, halogens. The elements adjacent to one another in a period generally form covalent bonds. The variations of electronegativities with the atomic numbers of elements are given in Fig. 4—3.

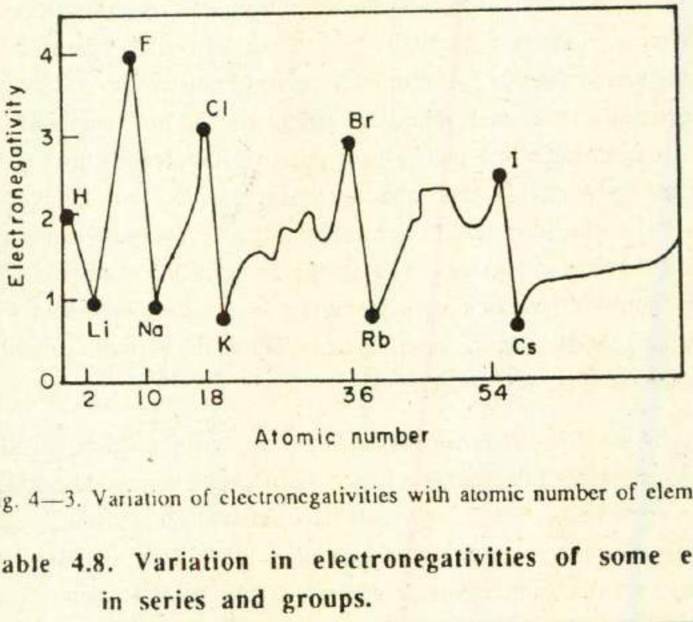


Fig. 4—3. Variation of electronegativities with atomic number of elements.

Table 4.8. Variation in electronegativities of some elements in series and groups.

Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na						Cl
0.9						3.0
K						Br
0.8						2.8
Rb						I
0.8						2.4
Cs						
0.7						

*7. **Variation in the Stability of Oxidation States*** :The transition elements generally exhibit more than one oxidation states. This is due to successive loss of electrons from the inner partially filled d sub-level. Thus, vanadium shows +3, +4 and +5 states and for chromium +2, +3 and +6. Those for manganese are +2, +3, +4, +6 and +7. It may be noted that the higher oxidation states become more stable near the bottom of each transition metal groups in the Periodic Table whereas the stability of +3 state decreases in the opposite order.

Among the families of post-transition metals having completely filled d levels if there are two possible oxidation states, it is found that the lower one is more stable than the higher ones. Thus in the case of tin having the electron configuration :

Sn ... $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2 4d^{10} 5p^2$

Sn^{+4} ... ... $4d^{10}$ ($5s^2$ and $5p^2$ lost)

Sn^{+2} ... ... $5s^2 4d^{10}$ ($5p^2$ lost)

$5s^2$ electrons in Sn occur after $4s^2 4p^6 4d^{10}$ completed levels and are inert in Sn^{+2}.

The inner $5s^2$ electrons are more inert and are referred to as "inert pair" of electrons. Hence Sn^{+2} is more stable than Sn^{+4}.

*8. **Variation in the Oxidising and Reducing Powers*** : Oxidising substances have tendency to accept electrons and are converted into lower oxidation states. The non-metals at the extreme right of the Periodic Table having high ionization potentials, electron affinities and eectronegativities tend to act as oxidising agents in chemical reactions with other substances. Similarly, reducing substances give up electrons and are converted into higher oxidation states during chemical reaction. The reducing power is the highest with the metals at the beginning of the periods, where the ionization potentials, electron affinities and electronegativities are low. Thus, alkali metals have the greatest reducing power. In general, the reducing power of the elements is progressively lower as we pass across the periods and higher, as we go down the groups. Francium should be the strongest reducing agent and fluorine, the strongest oxidising agent of all the elements.

9. Variation in the Basic Properties : The hydroxides of elements at the beginning of the Periodic Table dissociate in water solution giving OH-ions and show basic characters. The large positive ions form hydroxides which are strongly basic. On the other hand, elements of small positive ions at the end of the periods form hydroxides which in water give acidic behaviour. In general, the metals on the left of the Periodic Table form basic oxides and the non-metals on the right form acidic oxides. This accounts for the fact that the positive ions may exist in water solution with hydroxide ions (OH^-) and the negative ions may be found in water solution with a high concentration of hydronium ions (H_3O^+).

When an element exhibits two or more oxidation states, the ion of the element in its lowest state is less electronegative than in the higher state and the lowest state is the more basic than the higher one. Thus stannous ion is more basic than stannic ion.

10. Variation in Physical Properties : Almost any physical property of the elements, when plotted against the atomic numbers, shows periodicity and the curves obtained have remarkable similarity with the atomic volume curve. Thus the densities of the elements in the solid state vary periodically with their atomic numbers. The variation occurs in a regular manner within a period and shows a maximum in the central members.

Similarly, melting points and boilding points show periodic vaiations. The inert gases show minimum melting points and boiling points and occur at the bottom of the melting point curve against atomic number. The elements of groups IV and VI occupy the peaks as shown in Fig. 4—4.

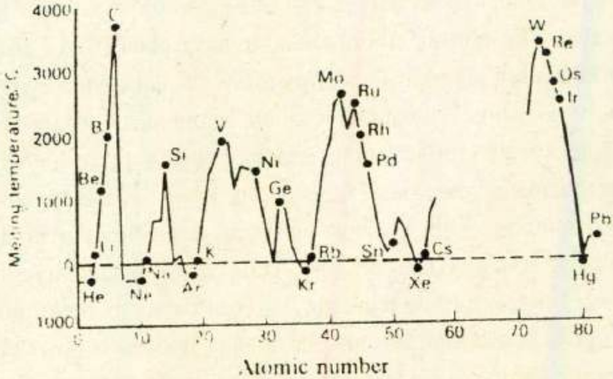


Fig. 4—4. Periodicity of melting points.

Many other physical properties such as hardness, malleability, compressibility, coefficient of expansion, thermal conductivity and electrical resistance likewise show periodic variations.

Borderline elements mostly in the middle region of the Periodic Table exhibit both metallic and non-metallic properties and are known as metalloids. They usually act as electron donors with non-metals, and as electron acceptors with metals. It is not very well-defined as to which elements should be included in this class. But they generally occur near about the middle of the Periodic Table. Such elements are boron, silicon, germanium, tellurium etc. They are all solids at room temperature, somewhat brittle and poor conductors of heat and electricity.

Usefulness of the Periodic Table

The systematic arrangement of the elements found in the Periodic Table has greatly simplified the task of organising the extensive mass of knowledge relating to the chemistry of the elements as a whole. The following important applications of the Periodic Table may be mentioned :—

1. Classification of the Elements : The classification of elements of similar properties into groups simplified their study. For instance, sodium, a member of the alkali metals group reacts with water vigorously giving hydrogen gas and forming sodium hydroxide which is a strong base. The other alkali metals, lithium, potassium, rubidium, cesium and francium also react with water in a similar manner. Halogens, again, show properties which are all alike.

It may be noted that similarities of properties in a group actually show gradation. In some cases this gradation is very well-marked.

2. Prediction of Undiscovered Elements : At present all the elements from atomic number 1 to 105 have been discovered and their properties are more or less known. But a very remarkable use of the Periodic Table was made by Mendeleeff in predicting a number of undiscovered elements which were shown by a number of gaps in the then Periodic Table. It may be remembered that Mendeleeff's Table contained only 65 elements with a large number of vacant places. Mendeleeff predicted the existence and properties of 6 elements corresponding to the gaps. These elements have since been discovered and are scandium, gallium, germanium, technetium, rhenium and polonium. It is surprising that these elements have properties quite similar to those predicted by Mendeleeff.

Elements having atomic number 43, 61,85 and 87 were also missing from the Mendeleef's Table and discovered later.

3. Correction of Atomic Weight : Atomic weights of some of the elements at the time of Mendeleeff gave a wrong position to some of the elements in the Periodic Table. The properties of these elements required their placement somewhere else. These discrepancies have been a matter of great research by chemists and physicists. For instance, the element 'indium' was placed in a vacant place in the Periodic Table between Cd (112.4) and Sn (118.7) and indium with atomic weight of about 114 fitted very well in between Cd and Sn.

4. Periodic Table in Industrial Research : The Periodic Table has been found to be quite useful in industrial researches. Several of the light metals and their alloys used in modern mechanical equipments, jet engines and air-crafts were first studied in detail because of their position in the Periodic Table. The search for tetraethyl lead as an anti-knock compound to be added to modern ethyl gasoline, was found as the result of great need for such materials by looking through the Periodic Table for elements having such properties. Another classical example of the application of the Periodic Table to an industrial problem was in connection with the development of Freon, a non-toxic, non-inflammable refrigerant. It is easily visualized by a look at the Periodic Table that compounds of the non-metallic elements in the upper right-hand region of the table are volatile enough to act as refrigerant. Thus, fluorine compounds would possess such properties and as a result Freon, CF_2Cl_2, was discovered.

Limitation of the Periodic Table

There are certain inherent weakness in the Periodic Table although it has been immensely successful in producing a systematic classification of chemical knowledge.

1. Position of Hydrogen : The position of hydrogen in the periodic table is left undecided. It has similarities in properties with both the alkali metals and the halogens. According to the atomic number or atomic weight, hydrogen should occupy a position just before helium.

Hydrogen is a gas like fluorine and chlorine and forms compounds like CH_4, SiH_4 which are like CCl_4 and $SiCl_4$ respectively. Even solid hydrogen is a non-metal resembling iodine. The hydrogen molecule is diatomic like halogen.

On the other hand, hydrogen resembles lithium and other alkali metals in having one electron $1s^1$ which can be lost in forming the hydrogen ion. Under most conditions, however, hydrogen does not lose this electron, but shares it with other atoms. Again, sodium hydride and sodium fluoride are both crystalline ionic solids, a point which shows similarity of hydrogen with fluorine. But in most cases it assumes a +1 oxidation state. For this reason, hydrogen is usually included in group IA of the table. Actually, hydrogen shows no relationship with any other element.

*2. **Anomalies in the Mendeleeff's Table*** : When the atomic weights of the elements were adopted as a basis for periodic classification, a number of anomalies were observed with regard to the placement of some elements of similar properties. Thus potassium (39.1) should come before argon (39.94). Similarly, tellurium (127.5) comes before iodine (126.93) and cobalt (58.4) should be placed after nickel (55.69). These anomalies disapeared automatically when atomic number was adopted as the basis of periodic classification and these elements occupy positions justified by their atomic numbers.

*3. **The Position of Rare Earths*** : The rare earths are also known as lanthanides. These elements have the two outermost energy levels identically occupied by electrons which give them great similarity in properties. All of them are metals. Their compounds are very closely related to one another which involved tremendous difficulties in their separation. All these elements are, therefore, placed in one and the same group. Starting from lanthanum (57) to lutecium (71), these fifteen elements actually have only one place in the Periodic Table and they are generally omitted from the main table and placed by themselves at the bottom of the table starting from Ce(58). It may be assumed that these elements form a sort of bridge between the preceding and the following elements, i.e. barium and hafnium.

*4. **Position of the Actinides*** : This group of elements starting from actimium (89) include all the trans-uranium elements which have been discovered within the last few years. The electronic configurations of these elements have been found to be very similar to that of lanthanides. Both of these groups of elements contain **f** energy levels which are being systematically filled. Thus cerium to lutecium contains $4f^2$ to $4f^{14}$ and the actinide series of the $5f^2$ to $5f^{14}$ is being completed at lawrencium (103). For the same reason, as in lanthanides, the actinides are also placed in the same position of the Periodic Table and are tabulated at the bottom.

*5. **Oxidation states and the Periodic Table*** : The position of each element in the Periodic Table emphasizes only one oxidation number for each element. But most of the elements show more than one oxidation numbers.

*6. **Properties which are not Periodic functions*** : Certain properties have no relationship with the periodic classification : (i) The activities of the elements expressed in terms of electromotive series (e.m.f. series) do not show periodic variations although this is very useful in explaining many properties of the elements. Elements arranged in the e.m.f. series do not follow any order in the Periodic Table but are scattered throughout the table.

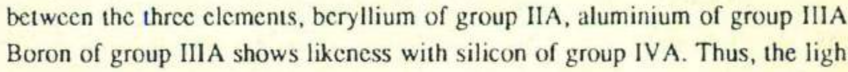
(ii) Some of the elements in the sub-group do not show any likeness in the properties with others. For example, group B copper, silver and gold (IB) have many properties different from those of the alkali metals (IA).

(iii) The specific heat of elements do not give periodic curve but a hyperbolic curve when plotted against atomic numbers.

(iv) Some of the elements in the same group of periodic classification do not belong to the same analytical scheme in qualitative analysis. There are elements widely scattered in the Periodic Table but are included in the same analytical group. For instance, Ba, Sr and Ca of group IIA of the Periodic Table are placed in the same group in the analytical scheme. On the other hand, Pb, Bi, Cu, Cd, Hg, As, Sb, which are widely separated in the Periodic Table, are included in the same group of qualitative analysis. This is mainly due to the different basis of classification. The analytical scheme is based upon the formation of insoluble compounds under identical conditions by group reagents.

(v) Isotopes and Periodic Table : Isotopes are elements possessing the same atomic numbers but different atomic weights. There are over 1000 isotopes of all the elements occurring in nature or made artificially. Obviously, all these isotopes cannot be accommodated in their respective places. However, the classification based on atomic number has solved this problem.

7. Diagonal Relationships : Lithium, a member of the alkali metal of group IA, in some respects respects resembles magnesium of group IIA. Thus, lithium salts usually occur in hydrated form unlike other alkhali metal salts. Moreover, unlike other alkali metal carbonates and phosphates Li_2CO_3 and Li_3PO_4 are insoluble in water, as are the corresponding magnesium carbonate and phosphate. Lithium is the only alkali metal to form ionic lithium nitride, Li_3N, like magnesium nitride. Thus, Li of group IA resembles Mg of group IIA in many respects contrary to its group properties. Similar relationship exists between the three elements, beryllium of group IIA, aluminium of group IIIA. Boron of group IIIA shows likeness with silicon of group IVA. Thus, the light elements of one group shows similarity in properties with the second elements of the following groups. This similarity is generally referred to as *diagonal relationship* in the Periodic Table as shown below.



The diagonal relationship between the elements may be explained in terms of the electropositive character of the elements. Although an element present in a given group is more electropositive than the corresponding element of the next higher group, the elements become more electropositive in passing down the group. Thus, Li in group IA is more electropositive than Be in group IIA, but Mg is also more electropositive than Be. Thus, both Li and Mg are more electropositive than Be and less electropositive than Na.

The other explanation is based on the sizes of the ions formed by the removal of valence electrons. Thus, Li^+ ion is almost of the same size as Mg^{+2} ion. Similarly, H^+, Be^{+2} and Al^{+3} ions have approximately the same ionic size.

B^{+3} and Si^{+4} also present the same situation. Compounds having similar properties of the elements showing diagonal relationship are formed due to the effect of ionic sizes and their distorting influence on the same anions.

IUPAC approved names of new elements

IPUAC has approved the names for elements 101-109. The final table of names was recommended to IUPAC by the Committee on Nomenclature of Inorganic Chemistry (CNIC) which drew up its original list of names for these elements in 1994.

Atomic number	*Name*	*Symbol*	*Named after*
101	Mendelevium	Md	Dimitri Ivanovich Mendeleev
102	Nobelium	No	Alfred Bernhard Nobel
103	Lawrencium	Lr	Ernest Orlando Lawrence
104	Rutherfordium	Rf	Ernest Rutherford
105	Dubnium	Db	Dubna, site of Russian Laboratory
106	Seaborgium	Sg	Glenn Theodore Seaborg
107	Bohrium	Bh	Neils Bohr
108	Hassium	Hs	Latin for Hesse, the German state
109	Meitnerium	Mt	Lise Meitner

Some of you may be surprised to see that element 105 is here called *dubnium*, because in many textbooks it has been called *hahnium* (Ha) for years. Hahnium was the name proposed by the American researchers, in honour of Otto Hahn.
The names for the recently discovered elements 110 to 112 have yet to be decided. (Chemistry Review, Vol 7, No. 4 P. 4, 1994).

QUESTIONS AND PROBLEMS

1. Write an essay on the periodic classification of the elements.
2. Write a note on transition elements.
3. Write a note on periodic law.
4. Discuss the general feature of the Periodic Table and show that these are in conformity with the atomic structure of the elements.

5. Give a brief account of the periodic classification of the elements and discuss how this has systematised the vast informations regarding the chemistry of the elements.

6. Discuss some of the limitations of the Mendeleeffs's periodic classification of the elements.

7. Explain the usefulness of the Periodic Table.

8. Discuss the Periodic Table in terms of the electronic structure of the elements.

9. Discuss the variation of properties of elements in groups and also in periods in the periodic classification of the elements.

10. Write notes on :—(a) Diagonal relationships between elements. (b) The position of rare earth elements in the Periodic Table. (c) Periodic variation of valence electrons. (d) The position of hydrogen in the Periodic Table.

11. Discuss the so-called diagonal relationships in the Periodic Table, with particular reference to the elements Li and Mg, B and Si, O and Cl

12. (a) Discuss briefly the arrangement of extra-nuclear electrons in the different atoms and hence explain the terms "transition" and "inner transition element."

    (b) Describe the properties of rare earths and the position of these elements in the Periodic Table.

13. Write a brief note on diagonal relationship in the Periodic Table.

14. Write detailed notes on group properties of elements.

15. Discuss the following :—

    (a) Alkali metals are highly reactive.

    (b) Elements of zero group are inert.

    (c) Properties of B and Si are similar in many respects.

16. Write explanatory notes on :

    (a) Transition elements.

    (b) Periodic Law.

    (c) Variable oxidation states.

17. Explain the anomalous properties of Li in relation to other alkali metals.

18. Explain why alkali metals react vigorously with water and chlorine.

19. Plot the quantities of the reciprocal values of the first ionization potential for each of the first 18 elements. What is the significance of this graph.

20. Find the relationship between the atomic weights of the following triads of elements :

    Li, Na, K

    F , Cl, Br

    Fe , Ru, Os

CHAPTER 5

THE SHAPES OF MOLECULES

It has been mentioned before that the chemical bonds are directed in space. Thus the electron-pairs forming the chemical bonds are distributed in space around a central metal atom. The electron-pairs, whether they form chemical bonds or not, appear to be responsible for the shapes of the molecules. It has been seen that a molecule has bonding pairs of electrons (shared) and in some cases also non-bonding pairs of electrons. Both the bonding-pairs and lone-pairs of electrons in a molecule around a central atom determine the shape of the molecule. Recently a simple theory has been put forward by Nyholm and Gillespie on the basis of Pauli Exclusion Principles and electron-pair repulsions and has been found to be of great value in accounting for the shapes of a large number of inorganic compounds. With some modifications, this has been found to be quite suitable for the elementary students to understand the basis of molecular structures.

Imagine a system having a positive nucleus round which there are two electrons having the same spin. The positive nucleus will attract the electrons and the two electrons will repel each other. Even the pairing up of the two electrons is not expected since the two electrons have the same spin. Due to the mutual repulsion of the two electrons, they arrange themselves in such a way in the system that the repulsion between these is minimum. The electrostatic repulsion between the two electrons will be minimum when they are separated as far apart as possible. The only way in which these two electrons can have minimum repulsion is to be present on the opposite sides of the nucleus in a straight line passing through the nucleus as shown in Fig. 5—1(a). The situation is the same if two electron-pairs are considered instead of two isolated electrons. The two pairs of electrons will arrange themselves in a similar position in a straight line in order to minimize the repulsion between them. If the electron pairs are forming two bonds with the central atom, the two bonds will lie in a straight line or at an angle of 180°, because at this position the

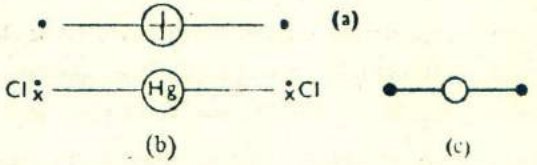


Fig. 5—1 Linear structure : (a) Linear arrangement of two electrons of the same spin around central atom. (b) Linear arrangement of two electron-pair bonds as in $HgCl_2$. (c) Symbolic representation of a linear molecule.

electron-pairs will have minimum of mutual repulsion. Thus the shape of the molecule may be explained on the basis of electrostatic repulsion between-electron pairs.

The pairs of electrons in the valence shell of the central atom in a molecule are always arranged in the same way, i.e., they are as far apart as possible and the molecules assume different shapes which depend only on the number of electron-pairs. The electron pairs may be shared pairs or lone pairs and have great influence in determining the shapes of molecules. It is noted that two electrons-pairs have a linear arrangement, three pairs, a triangular arrangement, four pairs, a tetrahedral, five pairs, in the form of a trigonal bipyramid and six pairs have octahedral arrangement. These arrangements hold good for the non-transition elements, i.e., those which do not use **d** electrons in bond formation. But valence electrons of d° and d^{10} behave like non-transition elements as regards the shapes of molecules. It must be remembered that the regular shapes are obtained only when all the electron-pairs are forming bonds with the same kind of atom or group. If some of the electrons are lone pairs or if there are two or more different kinds of atoms or groups attached to the central atom, the regular geometrical shapes become distorted. The geometrical shapes are the consequence of the tendency of the electron-pairs to be apart at a maximum distance so that the interaction between them is minimum. The repulsion between free electron-pairs will be obviously greater than that of repulsion between free electron pairs and a bond pair whereas the repulsion between a bond pair and another bond pair will be least. This theory is known as Valence Shell Electron Pair Repulsion (VSEPR) Theory. The interaction between electron-pairs in the valence shell of the central atom when forming chemical bonds follows the order:

$$\underset{\text{repulsion}}{\text{lone pair—lone pair}} > \underset{\text{repulsion}}{\text{lone pair—bond pair}} > \underset{\text{repulsion}}{\text{bond pair—bond pair}}$$

In short lp—lp > lp—bp > bp — bp (lp = lone pair, bp = bond pair)

Mercury has two electrons in the valence shell ($6s^2$). These electron are used to form two covalent bonds with, say, Cl atoms giving mercuric chloride, $HgCl_2$, as shown in Fig. 5—1 (b). The two bond pairs in $HgCl_2$ arrange themselves as far apart as possible in order to minimize the repulsion between them and the only arrangement is that in which the molecule is linear :

Cl : Hg : Cl Cl—Hg—Cl

Similarly, Be, Zn, Cd, Hg having two electrons in the valence shell form linear molecules of the type A : M : A (i.e. A—M—A). In terms of the molecular orbital they exhibit **sp** hybridization. The case is similar for $[Ag(NH_3)_2]^+$ or $[Ag(CN)_2]^-$ complex ions in which Ag^+ has the completed $4d^{10}$ electron level.

$$[NC : Ag : CN]^- \qquad [H_3N : Ag : NH_3]^+$$

The linear bonds may be represented symbolically as in Fig. 5—1 (c).

The three electron pairs in BF_3 are bond pairs and are situated at the corners of an equilateral triangle for minimum interaction at maximum distance from

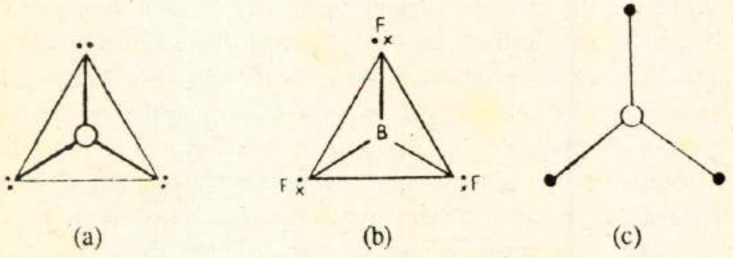
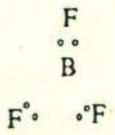
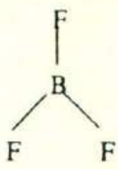


Fig. 5—2. Tringular shape : (a) Tringular arrangement of three electron-pairs : (b) Traingular shape of BF_3 ; (c) Symbolic representation of plane triangular molecule.

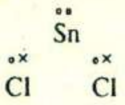
one another as shown in Fig 5—2(a) and (b) and symbolically represented in Fig. 5—2 (c).

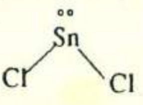




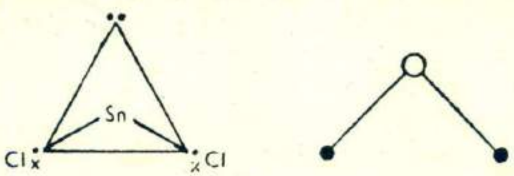
The angle between F—B—F is 120° which gives the greatest possible separation between the bonded electron-pairs. In terms of molecular orbital B uses sp^2 hybrid orbitals to form the three bonds.

In the case of tin compounds, such as stannous chloride, there is distortion because of the presence of a lone pair. Sn has the valence electrons $5s^2\ 5p^2$. The lone pair occupies one corner of the triangle and the two corners are occupied by





the two bond pairs as given in Fig. 5—3 (a). The lone pair exerts a greater repulsion on the bond pairs resulting in the shortening of the angle Cl—Sn—Cl. Thus the effective shape of $SnCl_2$ molecule in the vapour phase is



(a) (b)

Fig. 5—3 (b). Distortion in triangular molecules : (a) V-shape of $SnCl_2$ due to the presence of a lone pair in plane triangular arrangement. (b) Symbolic representation of a V-shaped molecule.

a V-shape as given in Fig. 5—3 (a) and symbolically represented in Fig. 5—3 (b). The molecular orbital is given by sp^2 hybridization : one of the three m.o. is occupied by the lone pair electrons.

The electrostatic repulsions between four pairs of electrons are at a minimum when these are situated at the corners of a regular tetrahedron as in the case of CH_4 and $SiCl_4$. The angle between H—C—H bond is 109°28′ and is known as the tetrahedral angle. The Figures 5—4 (a) and (b) represent the tetrahedral shape of the molecule and the geometry of the tetrahedron is given in Fig. 5—4 (c) which gives the perspective view of the distances of the 4 corners from the centre. A very large number of molecules have the tetrahedral shape including complex ions, such as $Zn(NH_3)_4^{+2}$, $Cd(CN)_4^{-2}$ etc. As mentioned before in terms of molecular orbital, the central atom uses sp^3 hybrid orbitals for bond formation. Note that the square planar arrangement of 4 electron-pairs is ruled out because the angles between electron-pairs are 90° which is smaller than the approximate tetrahedral angle 109.5°.

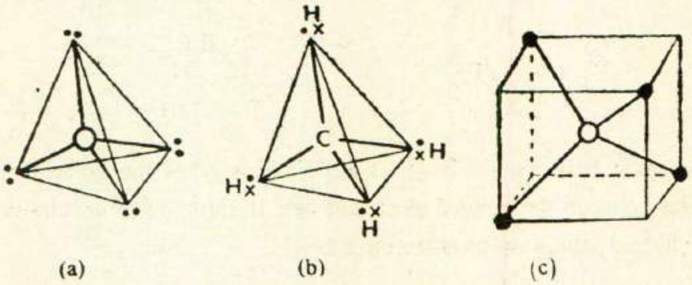
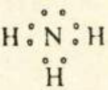


Fig. 5—4. Tetrahedral shape : (a) Tetrahedral arrangement of 4 electron-pairs. (b) Tetrahedral shape of CH_4. (c) Tetrahedral orientation of bonds in space.

In a molecule of ammonia, there is one lone pair and three bond pairs. The lonepair-bondpair repulsion in ammonia gives it a distorted tetrahedral shape as



$$\begin{array}{c}\mathrm{H}\,\overset{\circ}{\cdot}\,\overset{\circ\circ}{\mathrm{N}}\,\overset{\circ}{\cdot}\,\mathrm{H}\\ \overset{\circ\circ}{\mathrm{H}}\end{array}$$

shown in Fig. 5—5(a) and the molecule assumes a trigonal pyramidal arrangement as illustrated in Fig. 5—5 (b). Many other molecules such as PCl_3

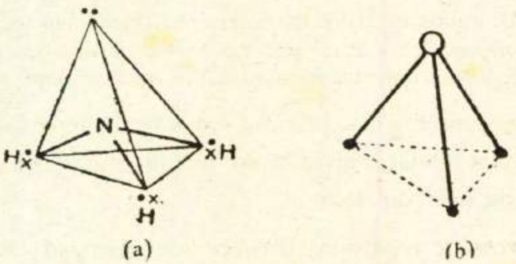
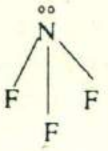


Fig. 5—5. Distortion in tetrahedral molecules due to one lone pair : (a) Trigonal pyramidal shape of NH_3. (b) Symbolic representation of a trigonal pyramidal molecule.

and NF_3 etc. have the same general shape as shown in Fig. 5—5 (b). The bond pairs are under the influence of two positive charge centres of N and H and occupy less volume than the lone pair which is under the influence of only one positive charge centre of N. The lone pair is also close to the central atom, N. Therefore, the lone pair exerts a greater repulsion on the bond pairs in NH_3 distoting the tetrahedral structure and the bond angle H—N—H comes closer to 107.3° instead of the tetrahedral angle 109.5°. If the three H in NH_3 is replaced by F which is more electronegative than H, the charge concentration of the bond pair is shifted towards F atoms in NF_3. The lone pair on N in NF_3 exerts a greater repulsion on the bond pairs and the N—F bonds are further shrunk

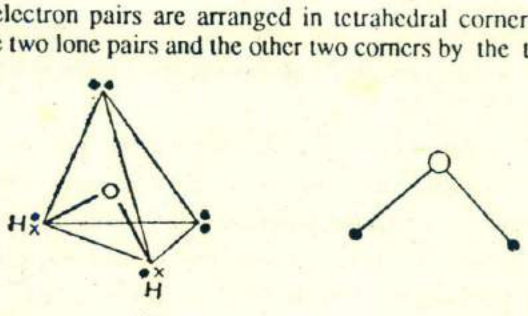


giving F—N—F angle in NF_3 of only 102.1° smaller than H—N—H angle in NH_3. NF_3 like NH_3 has triangular pyramidal shape. In fact, all molecules with three bond pairs and one lone pair have this geometry.

When we look into the electron distributions in water molecules we find that there are four electron pairs around oxygen and these consist of two lone pairs and two bond pairs.

$$H:\overset{..}{\underset{..}{O}}:\atop H$$

The four electron pairs are arranged in tetrahedral corners, two corners occupied by the two lone pairs and the other two corners by the two bond-pairs



(a) (b)

Fig. 5—6. Distortion in tetrahedral molecule due to two lone pairs : (V-shape of H_2O ; (b) Symbolic representation of V-shaped molecule.

[Fig. 5—6(a)]. The water molecule has, therefore, a V-shaped structure [Fig. 5—6 (b)]. But the two lone pairs will exert a greater repulsion not only between themselves but also on the two bond pairs and the two O—H in H_2O bonds are forced together closer than N—H bond in NH_3 molecule. The bond angle H—O—H in water molecule is decreased to 104.5°. The situation is the same in F_2O molecule, generally represented by Fig. 5—6(b). Thus an account of the decrease of bond angle in NH_3 and H_2O can be obtained on the consideration that the lone pairs repel the bond pairs increasingly as the number of lone pairs increases.

A central atom having five electron pairs presents a complicated situation. The shape of the molecule with regular arrangement in which there is minimum of repulsion between electron pairs is a trigonal bipyramid as given in Fig. 5—7 (a). The shape of PCl_5 is a regular triangular bipyramid shown in Fig. 5—7 (b), generally representated by Fig. 5—7 (c) for such molecules like PCl_5, $NbCl_5$, $TaCl_5$ etc. In a trigonal bipyramid, the atoms at the apex (top and bottom) are differently situated as compared to the three equatorial atoms at the corners of a planar triangle. Thus in PCl_5, the angles Cl—P—Cl at the three corners of the planar positions are 120°, whereas the angle Cl—P—Cl involving one Cl at the apex of the bipyramid is 90°. The total number of angles are : 6 angles of 90° each and 3 angles of 120 each.

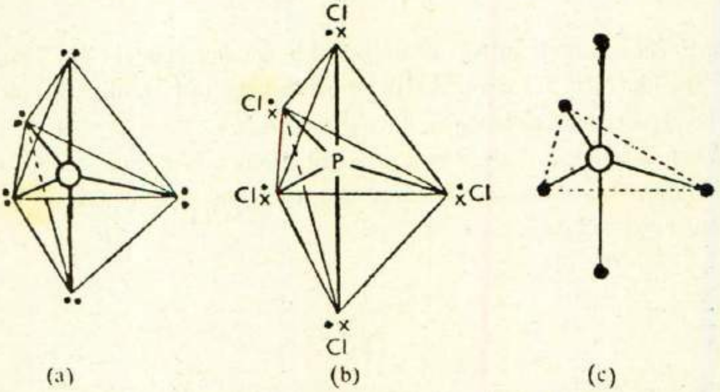
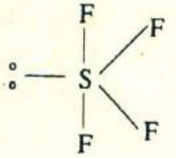
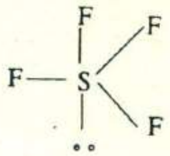


Fig. 5—7. Trigonal bipyramidal shape : (a) Trigonal bipyramidal arrangement of 5 electron pairs. (b) Trigonal bipyramidal shape of PCl_5. (c) symbolic representation.

Now, in the molecules of SF_4, SeF_4 or $TeCl_4$, the valence shell of S, Se and Te contains $3s^23p^4$ and $5s^25p^4$ electron arrangements respectively. The molecules each have total number of 10 electrons involved in bond formation, the same as in PCl_5 but with one lone pair. The bonds in SF_4, TeF_4 or TeF_4 should be directed at the corners of a trigonal bipyramid. But there are two possibilities of the arrangement of the lone pair which may be placed either, (a) at the equatorial position (base) of the pyramid or, (b) at the axial or apical position as shown below :

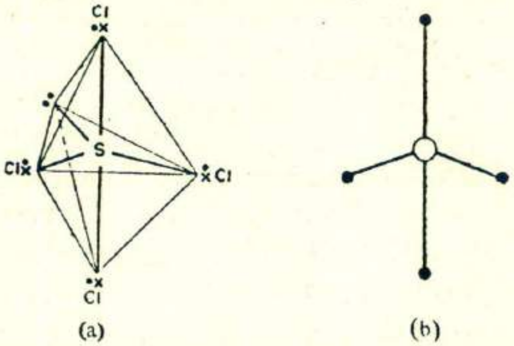


(a) equatorial



(b) axial

In (a) there are four (4) bp—bp angles of 90° and two (2) lp—bp angles of 90°. Also there are one (1) bp—bp angle of 120° and two (2) lp—bp angles of 120°. In (b) There are three (3) bp—bp angles of 90° and three (3) lp—bp angles of 90°. Also there are three (3) bp—bp angles of 120°. Since lp—bp repulsions are greater than bp—bp repulsions it is evident that shape (a) is the preferred arrangement and proved experimentally. Thus the molecules of SF_4, SeF_4 and SCl_4 have four bond pairs and a lone pair as shown in Fig. 5—8(a) for SCl_4. The lone pair occupies an equatorial position because it is at an angle of 90° to two bond pairs only. If the lone pairs is at the apex, this will make an angle

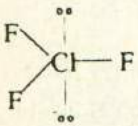


(a) (b)

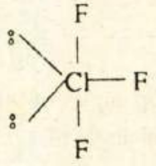
Fig. 5—8. Distotion in trigonal bipyramidal shape due to one lone pair : (a) Irregular tetrahedral shape of SCl_4. (b) Irregular tetrahedral molecule.

of 90° to three equatorial bond pairs. The lonepair-bondpair repulsion is less when the lone pair is at the equatoprial position and hence the molecules have an irregular tetradedral shape derived from the distortion of trigonal bipyramid as shown in fig. 5—8(b). The six valence electrons each of S, Se and Te might have been distributed in an octahedral positions with bond angles of 90° with the central atom, but there are not enough electron pairs in SF_4, SeF_4 or $TeCl_4$ to form this shape.

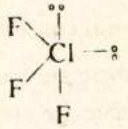
Molecules like ClF_3 and BrF_3 in which Cl and Br have **s^2p^5** valence electrons have the two lone pairs in the trigonal bipyramid arrangement at the following position ; (i) The two lone pairs at the apical positions at 180°, (ii) the two lone pairs at the equatorial position at 120°, (iii) one lone pair at the apex and the other lone pair at the equatorial position at 90°.



(i)



(ii)



(iii)

In this case the bondpair-bondpair repulsion is more significant as is seen by the following considerations :—

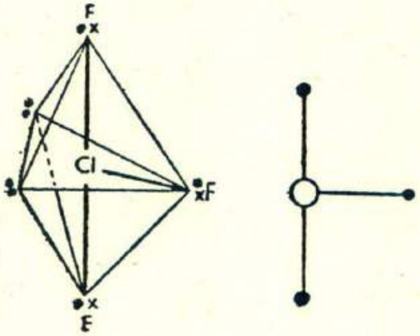
In (i) the 6 lonepair-bondpair angles are at 90°.

In (ii) there are four lonepair-bondpair angles of 90°and two lonepair-bondpair angles of 120° and lonepair-lonepair angle is 120°.

In (iii) the lonepair-lonepair angle is 90° and, three lonepair-bondpair angles of 90° and two bondpair-bondpair angles of 90°.

Out of the above three possibilities, the most probable shape of the molecule, ClF_3, is that one in which the electrostatic repulsion is minimum and the electron pairs are situated as far apart as possible. From this consideration the two lone pairs must be situated in the equatorial position as shown in Fig. 5—9 (a) or (ii) above, giving the molecule a T-shape, generally represented as in Fig. 5—9 (b). In terms of molecular orbitals the central atom uses sp^3d hybrid bonds.

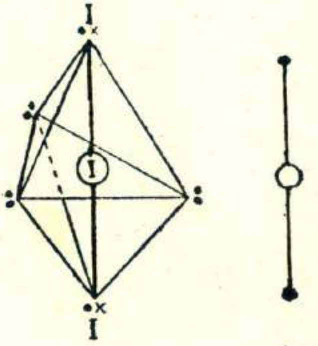
When the number of lone pairs increases to three in the trigonal bipyramidal structure with five electron pairs as in the case of ICl_2^- ion or tri-iodide I_3^- ion (as in KI_3), the only possible arrangement for the three lone pairs are the equatorial positions in which these will have minimum of repulsion as given in



(a) (b)

Fig. 5—9. Distortion in trigonal bipyramidal shape due to lone pairs : (a) T-shape of ClF_3 ; (b) Symbolic representation of T-Shaped molecule.

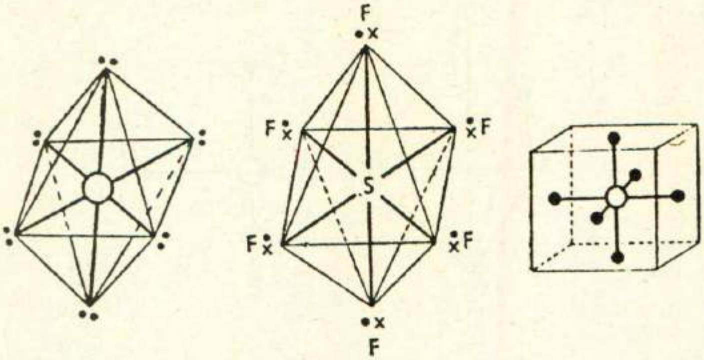
Fig. 5—10 (a). The two iodine atoms are at an angle of 180° and hence the molecule is linear in shape as shown in Fig. 5—10 (b).



(a) (b)

Fig. 5—10. Distortion in trigonal bipyramidal shape due to three lone pairs : (a) Linear shape of I_3^- ion. (b) Symbolic representation.

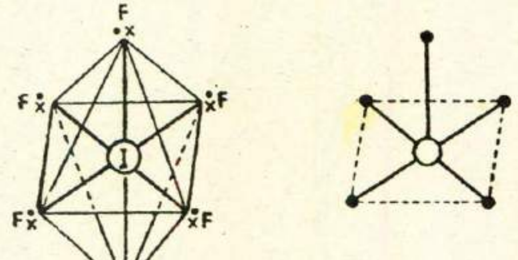
Molecules, in which the central atom has six electron pair bonds as in SF_6, MoF_6^-, PCl_6^- etc., assume the shape of a regular octahedron as shown in Fig.5—11 (b). It is be evident that the electrostaric repulsion is minimum for this arrangement of 6 electron pairs and that the bond angles are all 90° as is generally illustrated in Fig. 5—11 (c). In terms of molecular orbital, the central atom uses $\mathbf{d^2sp^3}$ or $\mathbf{sp^3d^2}$ orbitals for bond formation.



(a) (b) (c)

Fig. 5—11. Octahedral shape ; (a) Octahedral arrangement of 6 electron pairs ; (b) Shape of SF_6 molecule ; (c) Octahedral orientation of bonds in space.

However, if the 6 electron pairs consist of one lone pair and 5 bond pairs, the molecule will assumes the shape of square pyramid as in the case of IF_5, BrF_5, $SbCl_5^{-2}$ shown in Fig. 5—12 (a) and 5—12 (b). If there are 2 lone pairs and 4 bond pairs, obviously the two lone pairs have minimum repulsion if they



(a) (b)

Fig. 5—12. Distortion in octahedral shape due to one lone pair : (a) Square pyramidal shape of IF_5. (b) Symbolic representation of a square pyramidal molecule.

are situated at 180° angle to each other at the two opposite corners. The molecule then assumes a square planar shape as in the case of ICl_4^-, BrF_4^-. Taking BrF_4^- as an example, the valence shell of Br contains s^2p^5 electron arrangement. The formation of BrF_4^- ion can be shown as follows :—

	s^2	p^5			d°					
Br (ground state)	⇅	⇅	⇅	↑						d°
Br (excited state)	⇅	⇅	↑	↑	↑					d^1
Br^- (excited state)	⇅	⇅	↑	↑	↑	↑				d^2
BrF_4^- ion formed	⇅	⇅	⇅	⇅	⇅	⇅				d^4
			F	F	F	F				

sp^3d^2

Thus the six pairs of electrons in BrF_4^- or ICl_4^- ions (2 lone pairs and 4 bond pairs) are distributed at the corners of an octahedron. The most probable arrangement for the minimum repulsion between the lone pairs is that in which these are situated at a maximum distance apart at the opposite corners giving square planar structure for ICl_4^- ion as shown in Fig. 5—13(a) and 5—13(b). Thus the square planar shape of a molecule is the result of distortion in the octahedral arrangement. XeF_4 molecule has similar square planar shape [Fig. 5—13 (c)].

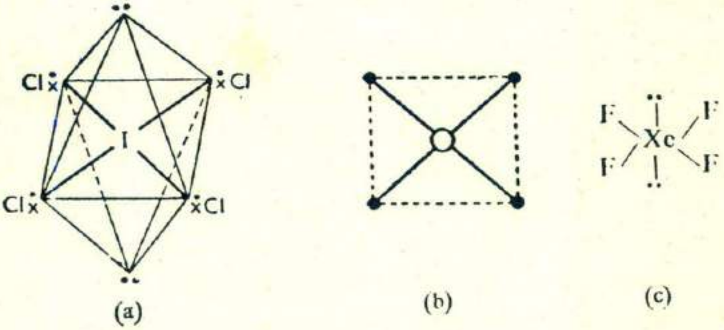


Fig. 5—13. Distortion in octahedral shape due to two lone pairs. : (a) Square planar shape of ICl_4^- ion. (b) Symbolic representation. (c) XeF_4 molecule.

Seven pairs of electrons in a molecule having all the 7 pairs as bond pairs appear to have a pentagonal bipyramidal shape as in the case of IF_7 and ZrF_7^{-3} ion. This is illustrated in Fig. 5—14(a) and 5—14(b). If one of the bond pairs is a lone pair, as in the case of $(SbBr_6)^{-3}$ ion, the shape is distorted to irregular octahedron.

Molecules with more than 6 pairs of electrons have rather complicated shape and are not discussed in this book.

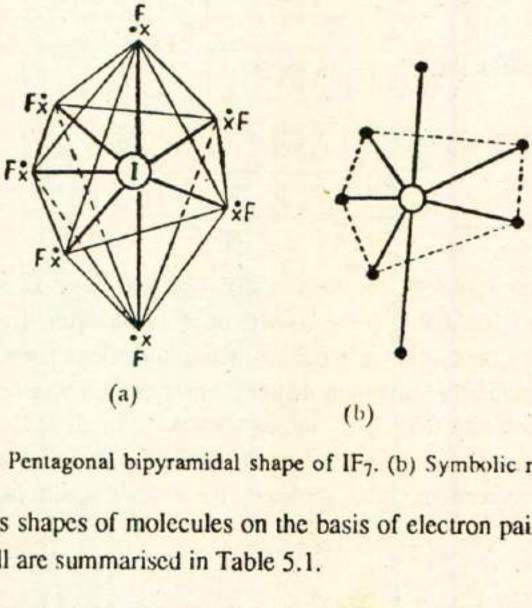


Fig. 5—14. (a) Pentagonal bipyramidal shape of IF_7. (b) Symbolic representation.

The various shapes of molecules on the basis of electron pairs repulsion in the valence shell are summarised in Table 5.1.

Molecules having double and triple bonds have almost similar shapes as those with only single bond. It is to be remembered that double and triple bonds are generally formed by using both σ and π bonds. The shape of a molecule containing an atom with a double or triple bonds is generally determined only by the number of pairs of σ electrons in the valence shell. The effect of π electrons is just ignored. Thus in the molecule of C_2H_4, each C atom has three σ bond pairs and one π bond pair. The most probable arrangement of three σ bond pairs is that in which these are situated with a plane triangular shape. Hence ethylene molecule has a plane triangular shape with the two C atoms at the two centres of the two triangles joined by a double bond.

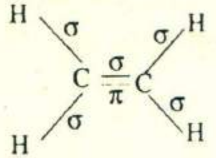
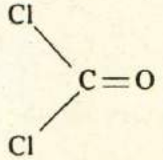


Table 5.1. Shapes of molecules on the basis of electron pairs.

No. of valence shell electron pairs	*Arrangement*	*No. of bond pairs*	*No. of lone pairs*	*Shapes of molecules*	*Examples*
2.	Linear	2	0	Linear	$BeCl_2$, $HgCl_2$, $[Ag(CN)_2]^-$
3	Equilateral	3	0	Triangular plane	BCl_3, BF_3
		2	1	V-shape	$SnCl_2$ (gas)
4	Tetrahedron	4	0	Tetrahedral	CH_4, BF_4^-, $SiCl_4$
		3	1	Trigonal pyramid	NH_3, PCl_3
		2	2	V-shape	H_2O, F_2O
5	Trigonal bipyramid	5	0	Trigonal bipyramidal	PCl_5, $NbCl_5$
		4	1	Irregular tetrahedron	SeF_4, $TeCl_4$, SF_4
		3	2	T-shape	ClF_3, BrF_3
		2	3	Linear	ICl_2^-, I_3^-
6	Octahedron	6	0	Octahedral	SF_6, $M_oF_6^-$
		5	1	Square pyramid	IF_5
		4	2	Square plane	XeF_4, ICl_4^-
7	Pentagonal bipyramid	7	0	Pentagonal bipyramidal	IF_7
		6	1	Irregular octahedral	$[SbBr_6]^{-3}$

Similarly, $COCl_2$ has a planar triangular shape based on the most probable arrangement of three σ electron pairs of C atom.

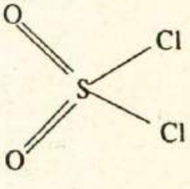


CO_2 has a linear structure because the two σ electron pairs of C are situated at an angle of 180°. In HCN molecule there are two σ bond pairs and two π bond pairs giving a single σ bond between C and H and a single σ bond between C and N and two π bonds between C and N :

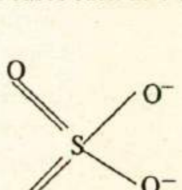
$$H—C \equiv N$$

Since π bond pairs are ineffective, the shape of HCN is linear on the basis of the arrangement of the two σ bond pairs.

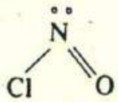
The molecule of SO_2Cl_2 has a tetrahedral shape since the four σ bond pairs of S atom are arranged in this manner :



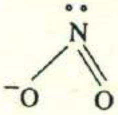
But a double bond consists of two electron pairs, and due to greater repulsion the angle between two adjacent double bonds is greater than that between two single bonds. The angle O=S=O is larger than Cl—S—Cl in SO_2Cl_2. This is applicable in all cases such as SO_4^{-2} ion :

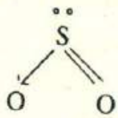


Molecules containing double bonds and also lone pairs are subjected to distortions. But the shapes of such molecules depend mostly on the number of σ bond pairs and are distorted according to the repulsion between the lone pairs and σ bond pairs and also due to lonepair-lonepair repulsion. Thus, NOCl assumes a V-shape or angular structure since the most probable arrangement of three σ electron pairs (two σ bond pairs and one lone pair) is plane triangular but distorted to angular shape because of the presence of a lone pair in the molecule :

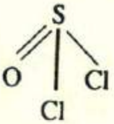


Similar is the case with SO_2 molecule and NO_2^- ion

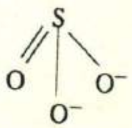




As mentioned before, molecules consisting of four σ electron pairs are tetrahedral in shape. But the presence of lone pair or pairs distort the structure in a similar manner. Thus in the molecule $SOCl_2$ and SO_3^{-2} ion, there are four σ electron pairs (three σ bond pairs and one σ lone pair). The original tetrahedral structures are distorted to triangular pyramidal shape giving :



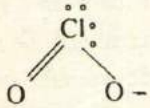
($SOCl_2$)



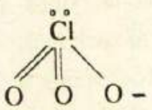
(SO_3^{-2} ion)

ClO_2^- ion having two σ bond pairs and two lone pairs (total of four σ electron pairs) is distorted to V-shape :

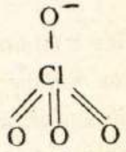
The molecules with five and six σ electron pairs containing σ lone pairs bring about distortions of trigonal bipyramidal and octahedral shapes respectively. Some of the examples of the shapes of molecules containing double bonds are given in Table 5.2.



(ClO_2^- ion)



(ClO_3^- ion)



(ClO_4^- ion)

Thus the shapes of molecules containing double and tripe bonds can be predicted by assuming that the two pairs and three pairs of electrons in a double and triple bonds respectively occupy only one of the positions in the various arrangements as predicted in the case of single electron pair bond (single bond) molecules. π electron pairs of double or triple bonds are ignored in determining the shapes of molecules.

Table 5.2 Shapes of molecules containing double and triple bonds.

No. of σ electron pairs	*Theoretical arrangement*	*No. of σ bond pairs*	*No. of lone pairs*	*Shapes of molecules*	*Examples*
2	Linear	2	0	Linear	CO_2, HCN
3	Equilateral triangle	3	0	Plane triangular	$COCl_2$, SO_3 NO_3^-, C_2H_4
		2	1	V-shaped	SO_2, NOCl
4	Tetrahedral	4	0	Tetrahedral	SO_2Cl_2, SO_4^{-2}
		3	1	Triangular pyramidal	$SOCl_2$ SO_3^{-2}
		2	2	V-shaped	ClO_2^-

Thus the important considerations in predicting the shapes of molecules boil down to the following main points :—

(1) The σ bond pairs and lone pairs of electrons in molecules arrange themselves at a maximum distance from one another to minimize the repulsion between them.

(3) The lonepair-lonepair repulsion is much greater than bondpair-bondpair repulsion giving rise to maximum distortion in the shape.

(4). Lone pair also repels bond pairs giving rise to some distortions.

(2) π bond pairs of electrons do not generally determine the shapes of molecules.

(5) A double bond pair repels another double bond pair more than the repulsion between single bond pairs or a double bond pairs-singlebond pair.

(6) Repulsion between bond pair is influenced by the electronegativity of the atoms forming the bonds. The repulsion decreases as the electronegativity values increases.

Shapes of more complicated molecules involving **d** electrons are not discussed in this chapter (see chapter 24 on Complex Compounds).

Comparison of bond hybridization and electron repulsion model of molecules

The bond angles in molecules could be predicted on the basis of hybridization of bond orbitals or the result of electron pair repulsion in valence shell. There appears to be good agreement between the results of the two theories as given in Table 5.3 but departures occur in many cases.

Table 5.3. Bond angles prediction by orbital hybridization and electron pair repulsion.

Number of bonds	*Hybridization*	*Bond angle predicted*	*Number of electron pairs*	*Bond angle predicted*
2	**sp**	180°	2	180°
3	**sp^2**	120°	3	120°
2	**p^2**	90°	4	109°28′
3	**p^3**	90°	4	109°28′
4	**sp^3**	109°28′	4	109°28′
5	**sp^3d, dsp^3**	Trigonal bipyramid	5	Trigonal bipyramid
6	**sp^3d^2 d^2sp^3**	Octahedral	6	Octahedral

Thus in H_2O (105°) NH_3 (107°), the electron pair repulsion gives closer prediction to the tetrahedral angle 109°28′ than the results of bond hybridization model. But the bond angles in H_2S, H_2Se, H_2Te and in PH_3, AsH_3, are closer to those predicted by simple **p** orbital involvement in bond formation. As the central atom becomes larger in size as in O, S, Se Te or N, P, As and Sb, the electron repulsion appears to decrease to a marked extent and the bond angles in H_2S, H_2Se, H_2Te and in PH_3, AsH_3, SbH_3 molecules approach the value of simple orbital prediction. Some of the values of bond angles are given in Table 5.4 for comparison.

Table 5.4. Actual bond angles in hydrides and halides.

Predicted : by Hybrid orbitals 90°

by Electron repulsion 109°28′

Molecule	*Bond angle*	*Molecule*	*Bond angle*
H_2O	104.5°	NF_3	102°
H_2S	92.2°	PF_3	104°
H_2Se	91.0°	AsF_3	102°
H_2Te	88.5°	SbF_3	88°
NH_3	107.3°	PCl_3	100°
PH_3	93°	$AsCl_3$	99.5°
AsH_3	91.5°	$BiCl_3$	100°
SbH_3	91.3°	PBr_3	101.5°
		$AsBr_3$	101°
		$SbBr_3$	97°
		$BiBr_3$	100°
		PI_3	98°
		AsI_3	98.5°
		SbI_3	99°

QUESTIONS AND PROBLEMS

1. Show that Al_2Cl_6 molecule is made of two tetrahedra with aluminium atoms at the two centres. Why should it have this structure ?

2. What is the geometry of ozone (O_3) ? How do you explain the shape on the basis of 2 σ bond pairs and 1 lone pair of electrons ?
3. Predict the shape of the following on the basis of electron pair repulsion : N_2O, $SnCl_4$, AsH_3, PH_4^+, CCl_4, XeF_4, XeF_2, PF_5, SeF_6, $PbCl_2$, H_2S and PO_4^{-3}.
4. What shapes do you assign to SO_2 and SO_3 ? The fact that SO_3 has zero dipole moment has been used to conclude about the geometry of the molecule. Explain.
5. What is the effect of lone pair of electrons (non-bonding electrons) on the shapes of molecules ? Illustrate with examples.
6. How the presence of double bonds influences the shapes of the molecules ?
7. The presence of π-bondings has generally been ignored in determining the shapes of a molecule. Why ?
8. Discuss the properties and bonding in water molecule.
9. Give the structure of Al_2Cl_6, PCl_6^-, AlH_4^-, NH_3, SF_4, $PtCl_5$, $SiCl_4$
10. Draw the three-dimensional pictures of the following chemical species showing lone pairs of electrons that occur in a valence level

    SF_6, AsF_5, ClF_3, PCl_4^{-2}
11. Draw the three-dimentional pictures of the following chemical species. Estimate bond angles from the type of symmetry present in each case.

    ClO^- CCl_4, ClO_2^-, ClO_3^-
    ClO_4^- CO_2, N_2, CO
    CN^- C_2^{-2}

CHAPTER 6

TYPES OF CHEMICAL REACTIONS

There are actually quite a large number of different types of chemical reactions that can be distinguished from one another. Attempts have, therefore, been made to classify them into groups. It may be noted that there are again different basis of classification of chemical reactions. Thus chemical reactions may be classified as—

(I) reactions among the atoms and molecules of the same kind;

(II) reactions among the atoms and molecules of different kinds of substances ;

(III) miscellaneous types of reactions.

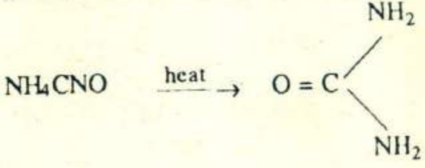
Chemical reactions may also be classified on the basis of electron transfer phenomenon. Thus we have examples of,

(i) reactions in which there in no electron transfer, and

(ii) reactions in which there is electron transfer from one atom to another.

I. Reactions among the Atoms and Molecules of the Same Kind

1. Isomeric Transformations : In this process the atoms in the molecule of a substance undergo a rearrangement producing a new substance of the same compositions as the original one but with different properties The well-known case of the conversion of ammonium cyanate, NH_4CNO, into urea, $CO(NH_2)_2$, by heat is an example of isomeric change.

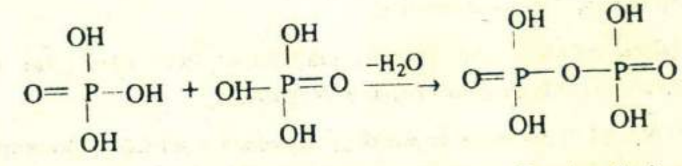


The composition of the two substances are the same but arrangements of the atoms in the molecules are different. The cis-and trans-isomers of complexes and organic compounds are other examples.

2. Polymerisation : This process consists of the formation of a large molecule by the combinations of large number of small molecules of the same kind. The product is known as a polymer. Thus ethylene, C_2H_4, is a monomer and polyethylene, $(\text{—HC}_2\text{—CH}_2\text{—})n$, is a polymer. Sulphur trioxide is a trimer $(SO_3)_3$ and phosphorus pentoxide is a dimer $(P_2O_5)_2$. Sulphur atoms also polymerise to form a chain of sulphur atoms in plastic sulphur. Phosphate, borate and silicate also give polymeric structures.

3. Depolymerisation : In this process a polymer or a complex molecule breaks up to give two or more molecules of the same kind. Thus N_2O_4, a dimer, breaks up into two molecules of NO_2.

4. Condensation : This process consists of the formation of molecules of a compound with the elimination of water. For instance; two molecules of phosphoric acid combine to form pyrophosphoric acid with elimination of one molecule of water.

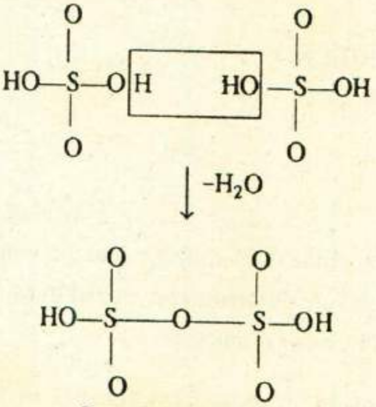


$$O{=}P(OH)_2{-}OH + OH{-}P(OH)_2{=}O \xrightarrow{-H_2O} O{=}P(OH)_2{-}O{-}P(OH)_2{=}O$$

2 molecules of orthophosphoric acid

Pyrophosphoric acid

Similarly, 2 molecules of H_2SO_4 undergo condensation :



Pyrosulphuric acid

5. Decomposition : In this reaction the molecule of a substance breaks up into two or more molecules of different substances. Thus when mercuric oxide in strongly heated it breaks up into mercury and oxygen. Similarly, potassium chlorate gives potassium chloride and oxygen on strong heating.

$$2HgO = 2Hg + O_2$$

$$2KClO_3 = 2KCl + 3O_2$$

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

6. Association : In this process two or more molecules of a substance combine together to form a large aggregate. The substance remains unaltered after association and no new substance is formed (compare from polymerisation). for instance, water is an associated liquid whereas H_2S is not and is therefore, a gas at ordinary temperature. The association in water is due to hydrogen bonding. Similarly, acetic acid is an associated liquid in which 2 molecules become associated through hydrogen bonding.

7. Dissociation : This process may be of two types : (a) Thermal dissociation and (b) Ionic dissociation in solution.

(a) Thermal dissociation is a process in which a substance decomposes on heating and the products recombine on cooling. Thus when ammonium chaloride is heated, it dissociates into ammonia and hydrochloric acid. The latter two recombine again on cooling to produce ammonium chloride.

$$NH_4Cl \underset{\text{cooling}}{\overset{\text{heating}}{\rightleftharpoons}} HCl + NH_3$$

It may be noted that dissociation is a reversible reaction in which the dissociating substance and the products of dissociation are present together in the system in a state of equilibrium. Similarly, the dissociation of PCl_5 follows the equation :

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

(b) Ionic dissociation is a process when a substance breaks up into cations and anions in solutions (say, in water or other solvents). The two ions recombine when the solvent is removed,

$$NaCl \underset{\text{water removed}}{\overset{\text{in water}}{\rightleftharpoons}} Na^+ + Cl^-$$

$$KNO_3 \rightleftharpoons K^+ + NO_3^-$$

The ionic dissociation also gives examples of reversible reactions.

8. Disproportionation : In this reaction a compound undergoes simultaneously oxidation and reduction due to the presence of an element of variable oxidation states. In this process a compound of an element breaks up into two new substances, one containing the element in a lower oxidation and the other containing the same element in a higher state of oxidation. Thus cuprous chloride disproportionates into cupric chloride and elementary copper. Other examples are disproportionation of gold chloride into auric chloride and gold.

Similarly, sodium hypochlorite in solution on heating changes to sodium chlorate and sodium chloride.

From the above examples it is evident that changes in oxidation states of the elements occur during disproportionation reaction. When $\overset{+1}{Cu}$ disproportionates

$$\overset{+1}{Cu_2}Cl_2 = \overset{+2}{Cu}Cl_2 + \overset{\circ}{Cu}$$

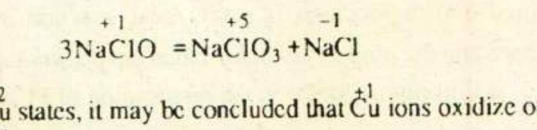
$$3\overset{+1}{Au}Cl = 2\overset{\circ}{Au} + \overset{+3}{Au}Cl_3$$

$$3Na\overset{+1}{Cl}O = Na\overset{+5}{Cl}O_3 + Na\overset{-1}{Cl}$$

into $\overset{\circ}{Cu}$ and $\overset{+2}{Cu}$ states, it may be concluded that $\overset{+1}{Cu}$ ions oxidize other $\overset{+1}{Cu}$ ions to form $\overset{+2}{Cu}$ and $\overset{\circ}{Cu}$. Another definition of disproportionation reaction may be put forward as follows :-

A reaction in which a substance oxidizes itself and also reduces itself is known as disproportionation reaction.

A disproportionation reaction can occur if the standard electrode potential of the couple, say, M^{o}/M^{+1}, is more negative than that of the couple, M^{+1}/M^{+2}, for a system involving M^{o}, M^{+1} and M^{+2} ions. Thus the values for coper ions are :-



Thus the force for the conversion of $\overset{+1}{Cu}$ to $\overset{\circ}{Cu}$ is numerically 0.52 volts. This can happen only if another $\overset{+1}{Cu}$ is converted to $\overset{+2}{Cu}$ for which the value is 0.15V. Since the driving force for conversion of $\overset{+2}{Cu}$ to $\overset{0}{Cu}$ (0.52 volts) is greater than the force required for $\overset{+1}{Cu}$ to $\overset{+2}{Cu}$ (0.15), hence $\overset{+1}{Cu}$ is capable to go spontaneously to $\overset{\circ}{Cu}$ and Cu^{+2} ion.

II. Reactions Between Atoms and Molecules of different Substances

1. Synthesis : Union of atoms or molecules of two or more different substances to produce a new compound is known as synthesis or synthetic reaction. Thus when sulphur combines with iron on heating to produce ferrous sulphide, the process involved is synthesis :

$$S + Fe = FeS$$

Similarly, the following examples also show synthetic reactions :

$$2H_2 + O_2 = 2H_2O$$

$$CaO + CO_2 = CaCO_3$$

2. Metathesis or Exchange Reactions : In these reactions two or more substances react which involve displacement of partners to form new substances. These are divided into two groups :

(a) Simple displacement or substitution : In this process one element displaces or substitutes another element from a compound. Thus zinc displaces hydrogen from dilute sulphuric acid to form zinc sulphate and hydrogen is set free :

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

Similarly, iron reacts with copper sulphate solution displacing copper to form ferrous sulphate :

$$Fe + CuSO_4 = Cu + FeSO_4$$

(b) Double decomposition or double displacement : In this process the components of two reacting compounds change places, i. e., doubly displaced. Thus when silver nitrate solution is added to a solution of sodium chloride, sodium nitrate and silver chloride are formed by double displacement :

$$AgNO_3 + NaCl = NaNO_3 + AgCl$$

It may be mentioned that neutralization reactions and hydrolysis may be included in the double displacement type of reactions.

(c) Neutralization : Acids and bases react with one another to form water and ionic compounds known as salts. Thus NaOH reacts with HCl to produce water and NaCl :

$$NaOH + HCl = H_2O + NaCl$$

(d) Hydrolysis : This reaction is more generally defined as the process in which an ion reacts with water to form either H^+ ions or OH^- ions. The effect of water on different substances produces different results. Examples of hydrolytic reactions are :

$$Na_2CO_3 + 2H_2O = 2NaOH + H_2CO_3$$

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

(e) Ammonolysis : This tuype of reaction is analogous to hydrolysis. This is a reaction in which an ion reacts with NH_3 producing compounds containing ammonia residues, i. e., NH_2, NH or N and releasing H^+ ion. Thus when ammonia is added to a solution of mercuric chloride, a white precipitate is obtained which is $Hg(NH_2)Cl$.

III. Miscellaneous Types of Chemical Reactions

There are a large number of chemical reactions which may be classified as miscellaneous types. These, of course, may be included in one or other of the various types described before. Some of them are of great importance in chemistry and are described below.

1. Addition reaction : This is a chemical reaction that involves the addition of the atoms of a molecule to a molecule containing a double bond or a triple bond. These also include reactions in which a molecule is added to another molecule during chemical reaction :

$$CH_2 = CH_2 + H_2 = CH_3—CH_3$$

$FeSO_4, 7H_2O$; $CuSO_4, 5H_2O$ etc. are formed by the addition of water molecules to $FeSO_4$ and $CuSO_4$ respectively and are known as hydrates. This particular type of addition reaction is known as "hydration" reaction. This occurs during crystallization of the products from aqueous solutions.

2. Cracking or Pyrolysis : In this process the thermal decomposition of a large molecule into many different small molecules takes place. Thus C_3H_8 may give by cracking a mixture of C_2H_4 and CH_4 :

$$CH_3—CH_2—CH_3 \longrightarrow C_2H_4 + CH_4$$

Another example is the cracking of petroleum hydrocarbons for the manufacture of gasoline which is a complicated mixture of smaller hydrocarbon molecules.

*3. **Catalytic reaction*** : This type of reaction is effected in the presence of a foreign substance which remains practically unchanged at the end. Some reactions which proceed very slowly or do not occur are generally enhanced in presence of the foreign substance. There are also reactions in which the progress of the reaction is arrested or retarded by the foreign substance. Such types of reactions are known as catalytic reactions and the foreign substance is called a catalyst.

Catalysts or catalytic agents can, therefore, accelerate or retard the speed of chemical reactions.

Synthesis of ammonia from nitrogen and hydrogen in presence of tungsten or iron as catalyst is well-known example :

$$N_2 + H_2 \xrightarrow{\text{W or Fe}} NH_3$$

Similarly, $$SO_2 + O_2 \xrightarrow[V_2O_5]{\text{Pt or}} SO_3$$

The change of catalyst may produce different types of catalytic reactions giving different products from the same starting reactants. Thus,

$$CO \quad + \quad 2H_2 \xrightarrow{ZnO\ Cr_2O_3} CH_3OH$$

$$CO \quad + \quad 3H_2 \xrightarrow{Ni} CH_4 + H_2O$$

An example of the retardation of a chemical reaction in presence of catalyst is the inhibition of the decomposition of H_2O_2 by addition of a trace amount of acetanilide or borax. Similarly, addition of lead tetraethyl inhibits the explosion rates of gasoline.

*4. **Chain reaction*** : In this type of reaction the products of the reaction cause the reaction to continue further. One of the products of reaction is activated by some means and reacts with more molecules and so a chain is formed. Thus reaction between chlorine and huydrogen molecules takes place in presence of sunlight giving rise to the following chain reaction :

$$Cl_2 \xrightarrow{+\text{ light } (h\nu)} 2Cl$$

$$Cl + H_2 = HCl + H$$

$$H + Cl_2 = HCl + Cl$$

$$Cl + H_2 = HCl + H, \text{ etc.}$$

*5. **Photochemical reaction*** : Certain reactions take place quite readily when the reactants are exposed to light. Such reactions are known as photochemical reactions. A well-known example is the darkening of a photographic film when it is exposed to light and the effect of sunlight on growing plants. The example given in the chain reaction of hydrogen and chlorine forming HCl is also included in the photochemical reaction.

The branch of chemistry that deals with photochemical reactions is known as photochemistry.

*6. **Induced reaction*** : Two substances which do not react directly with one another, do, however, react in presence of a third substance which reacts with one of them. Such reactions are known as induced reactions. For example, sodium arsenite and sodium sulphite do not react with each other in aqueous solution. But a solution of sodium sulphite reacts with oxygen of the air when present alone to produce Na_2SO_4. But a mixed solution of Na_2SO_3 and Na_3AsO_3 reacts with each other in presence of air and Na_3AsO_3 is oxidized to Na_3AsO_4 by means of induced reaction :

$$Na_3AsO_3 + Na_2SO_3 \xrightarrow[\text{(air)}]{O_2} Na_2SO_4 + Na_3AsO_4$$

Similarly, green $Ni(OH)_2$ is oxidized to black $NiO_2.H_2O$ in presence of Na_2SO_3 :

$$\underset{\text{green}}{Ni(OH)_2} + Na_2SO_3 + O_2 \longrightarrow \underset{\text{black}}{NiO_2.H_2O} + Na_2SO_4$$

7. Exothermic reaction : Reactions accompanied by the evolution of heat are said to be exothermic reactions. The burning of magnesium, carbon, sulphur, methane etc. in air, are all exothermic reactions. Once started, exothermic reaction may proceed in the absence of any supply of energy from outside. Thus, carbon continue to burn in oxygen with the evolution of heat until the supply of carbon or oxygen is exhausted :

$$C + O_2 = CO_2 + 97 \text{ Kcal}$$

$$2Mg + O_2 = 2MgO + 148 \text{ Kcal}$$

$$8Al + 3Fe_3O_4 = 4Al_2O_3 + 9Fe + 800 \text{ Kcal}$$

8. Endothermic reaction : Reactions accompanied by the absorption of heat are known as endothermic reactions. For example, the decomposition of potassium chlorate into potassium chloride and oxygen take place only so long as the compound is heated from outside. Similarly, the reaction of hydrogen and iodine to form hydroiodic acid takes place with absorption of heat. Reactions of this type require a continuous supply of energy from the outside to keep them going :

$$H_2 + I_2 = 2HI - 1.2 \text{ Kcal}$$

$$C + 2S = CS_2 - 1.5 \text{ Kcal}$$

9. Explosion : This is a special type of exothermic combustion reaction which takes place with extreme rapidity. The heat of reaction is liberated almost instantly and usually a large increase in volume results. Thus a mixture of gasoline and air when ignited explodes with great violence. Similarly, the rapid burning of gunpowder results in an explosion.

10. Oxidation and Reduction : In addition to the above reactions there are other types of reactions which may not be included here but are discussed in the appropriate places in this text book. It may be noted that quite a large number of reactions involve electron transfer phenomenon. For this reason the particular type of reactions, known as oxidation and reduction reactions, are dealt in the next chapter separately with some details since these are the most important reactions in chemistry both from the theoretical and practical points of view.

11. The "electrophilic" and "nucleophilic" reactions : The terms "electrophilic" and "nucleophilic" are often used to describe reactions where covalent bonds are formed.

There are many reactions that result in the formation of new covalent bond and rupture of an old covalent bond. An acid or a base functions as the bond-breaking reagent. Lewis acids are generally known as electrophilic reagents because of the attraction to the electron-rich part of basic molecule. Lewis base behaves as nucleophilic reagent because it attacks the electron-poor region of the acid molecule and supplies electron pair to the nucleus. Base displacements are, therefore, nucleophilic displacement reactions. In the reaction :

$$H_3N : + BF_3 = H_3N : BF_3$$

an electrophilic attack on N by B and also a nucleophilic attack on B by N take place. Similarly, a nucleophilic displacement takes place when H^+ ions react with OH^- ions; $OH^- + H_3O^+ \rightarrow H_2O + H_2O$

Similarly, the displacement of base H_2O from the hydrated complex $[Cu(H_2O)_4]^{+2}$ by a stronger base NH_3 is an example of nucleophilic displacement :

$$[Cu(H_2O)_4]^{+2} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{+2} + 4H_2O$$

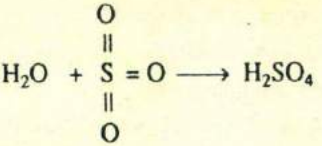
An electronphilic displacement occurs when BF_3 reacts with I_2 when I in displaced by B.

$$BF_3 + I_2 \longrightarrow BF_3I + I^+$$

Electrophilic displacement or acid displacement reactions are not so common as the nucleophilic reactions.

Generally, the two types of reaction may be represented as electrophilic displacement :

When H_2O reacts with SO_3, it represents a nucleophilic attack on a double bond :



$$H_2O + O{=}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}{=}O \longrightarrow H_2SO_4$$

When an aqueous HF reacts with BF_3 an interesting type of reaction known as "push pull reaction" occurs. In this case H_2O pushes HF and BF_3 pulls HF :

$$H_2O + HF + BF_3 \rightarrow [H_3O]^+ + BF_4^-$$

The electrophilic and nucleophilic displacements occur involving electrons in pairs. Sometimes an unpaired electron also gives rise to displacement reactions which is known as "Radical displacement" because upaired electrons give species which are radicals. Thus, when F atoms react with HCl we have Cl° radical. Similarly, OH°- radical is formed during the reaction of Fe^{+2} with H_2O_2:

$$Fe^{+2} + H_2O_2 \longrightarrow Fe(OH)^{+2} + OH^{\circ}$$

$$F + HCl \longrightarrow HF + Cl^{\circ}$$

QUESTIONS AND PROBLEMS

1. How will you classify the different types of chemical reactions? Explain some of the important chemical reactions giving examples.
2. Explain :-
    - (a) Electrolytic and thermal dissociation.
    - (b) Induced reactions.
    - (c) Chain reactions.
3. What are the differences between the following types of chemical reactions? Illustrate with examples :—
    - (a) Polymerisation and condensation.
    - (b) Association and polymerisation.
    - (c) Decomposition and polymerisation.
    - (J) Ammonolysis and hydrolysis.
    - (e) Endothermic and exothermic.

4. Explain the following reactions :—
   - (a) Disproportionation reaction.
   - (b) Displacement reaction.
5. Write note on different types of chemical reactions.
6. Write short notes on :—

   Association, dissociation and disproportionation.
7. Give a brief account of different types of chemical reactions.
8. Write notes on :—(a) Condensation reactions, (b) Exothermic and endothermic reactions, (c) Induced reactions, (d) Disproportionation reaction.