

valence electron in an atom will be less than the actual charge on the nucleus because of “**shielding**” or “**screening**” of the valence electron from the nucleus by the intervening core electrons. For example, the 2s electron in lithium is shielded from the nucleus by the inner core of 1s electrons. As a result, the valence electron experiences a net positive charge which is less than the actual charge of +3. In general, shielding is effective when the orbitals in the inner shells are completely filled. This situation occurs in the case of alkali metals which have single outermost *ns*-electron preceded by a noble gas electronic configuration.

When we move from lithium to fluorine across the second period, successive electrons are added to orbitals in the same principal quantum level and the shielding of the nuclear charge by the inner core of electrons does not increase very much to compensate for the increased attraction of the electron to the nucleus. Thus, across a period, increasing nuclear charge outweighs the shielding. Consequently, the outermost electrons are held more and more tightly and the ionization enthalpy increases across a period. As we go down a group, the outermost electron being increasingly farther from the nucleus, there is an increased shielding of the nuclear charge by the electrons in the inner levels. In this case, increase in shielding outweighs the increasing nuclear charge and the removal of the outermost electron requires less energy down a group.

From Fig. 3.6(a), you will also notice that the first ionization enthalpy of boron ($Z = 5$) is slightly less than that of beryllium ($Z = 4$) even though the former has a greater nuclear charge. When we consider the same principal quantum level, an s-electron is attracted to the nucleus more than a p-electron. In beryllium, the electron removed during the ionization is an s-electron whereas the electron removed during ionization of boron is a p-electron. The penetration of a 2s-electron to the nucleus is more than that of a 2p-electron; hence the 2p electron of boron is more shielded from the nucleus by the inner core of electrons than

the 2s electrons of beryllium. Therefore, it is easier to remove the 2p-electron from boron compared to the removal of a 2s-electron from beryllium. Thus, boron has a smaller first ionization enthalpy than beryllium. Another “anomaly” is the smaller first ionization enthalpy of oxygen compared to nitrogen. This arises because in the nitrogen atom, three 2p-electrons reside in different atomic orbitals (Hund’s rule) whereas in the oxygen atom, two of the four 2p-electrons must occupy the same 2p-orbital resulting in an increased electron-electron repulsion. Consequently, it is easier to remove the fourth 2p-electron from oxygen than it is, to remove one of the three 2p-electrons from nitrogen.

Problem 3.6

The first ionization enthalpy ($\Delta_i H$) values of the third period elements, Na, Mg and Si are respectively 496, 737 and 786 kJ mol⁻¹. Predict whether the first $\Delta_i H$ value for Al will be more close to 575 or 760 kJ mol⁻¹? Justify your answer.

Solution

It will be more close to 575 kJ mol⁻¹. The value for Al should be lower than that of Mg because of effective shielding of 3p electrons from the nucleus by 3s-electrons.

(d) Electron Gain Enthalpy

When an electron is added to a neutral gaseous atom (X) to convert it into a negative ion, the enthalpy change accompanying the process is defined as the **Electron Gain Enthalpy** ($\Delta_{eg} H$). Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion as represented by equation 3.3.



Depending on the element, the process of adding an electron to the atom can be either endothermic or exothermic. For many elements energy is released when an electron is added to the atom and the electron gain enthalpy is negative. For example, group 17 elements (the halogens) have very high

Table 3.7 Electron Gain Enthalpies* / (kJ mol⁻¹) of Some Main Group Elements

Group 1	$\Delta_{eg}H$	Group 16	$\Delta_{eg}H$	Group 17	$\Delta_{eg}H$	Group 0	$\Delta_{eg}H$
H	-73					He	+48
Li	-60	O	-141	F	-328	Ne	+116
Na	-53	S	-200	Cl	-349	Ar	+96
K	-48	Se	-195	Br	-325	Kr	+96
Rb	-47	Te	-190	I	-295	Xe	+77
Cs	-46	Po	-174	At	-270	Rn	+68

negative electron gain enthalpies because they can attain stable noble gas electronic configurations by picking up an electron. On the other hand, noble gases have large positive electron gain enthalpies because the electron has to enter the next higher principal quantum level leading to a very unstable electronic configuration. It may be noted that electron gain enthalpies have large negative values toward the upper right of the periodic table preceding the noble gases.

The variation in electron gain enthalpies of elements is less systematic than for ionization enthalpies. As a general rule, electron gain enthalpy becomes more negative with increase in the atomic number across a period. The effective nuclear charge increases from left to right across a period and consequently it will be easier to add an electron to a smaller atom since the added electron on an average would be closer to the positively charged nucleus. We should also expect electron gain enthalpy to become less negative as we go down a group because the size of the atom increases and the added electron would be farther from the nucleus. This is generally the case (Table 3.7). However, electron gain enthalpy of O or F is less negative than that of the succeeding element. This is because when an electron is added to O or F, the added electron goes to the smaller $n = 2$ quantum level and suffers significant repulsion from the other electrons present in this level. For the $n = 3$ quantum level (S or Cl), the added electron occupies a larger region of space and the electron-electron repulsion is much less.

Problem 3.7

Which of the following will have the most negative electron gain enthalpy and which the least negative?
P, S, Cl, F.

Explain your answer.

Solution

Electron gain enthalpy generally becomes more negative across a period as we move from left to right. Within a group, electron gain enthalpy becomes less negative down a group. However, adding an electron to the 2p-orbital leads to greater repulsion than adding an electron to the larger 3p-orbital. Hence the element with most negative electron gain enthalpy is chlorine; the one with the least negative electron gain enthalpy is phosphorus.

(e) Electronegativity

A qualitative measure of the ability of an atom in a **chemical compound** to attract shared electrons to itself is called **electronegativity**. Unlike ionization enthalpy and electron gain enthalpy, it is not a measurable quantity. However, a number of numerical scales of electronegativity of elements viz., Pauling scale, Mulliken-Jaffe scale, Allred-Rochow scale have been developed. The one which is the most widely used is the Pauling scale. Linus Pauling, an American scientist, in 1922 assigned arbitrarily a value of 4.0 to fluorine, the element considered to have the greatest

* In many books, the negative of the enthalpy change for the process depicted in equation 3.3 is defined as the ELECTRON AFFINITY (A_e) of the atom under consideration. If energy is released when an electron is added to an atom, the electron affinity is taken as positive, contrary to thermodynamic convention. If energy has to be supplied to add an electron to an atom, then the electron affinity of the atom is assigned a negative sign. However, electron affinity is defined as absolute zero and, therefore at any other temperature (T) heat capacities of the reactants and the products have to be taken into account in $\Delta_{eg}H = -A_e - 5/2 RT$.

ability to attract electrons. Approximate values for the electronegativity of a few elements are given in Table 3.8(a)

The electronegativity of any given element is not constant; it varies depending on the element to which it is bound. Though it is not a measurable quantity, it does provide a means of predicting the nature of force that holds a pair of atoms together – a relationship that you will explore later.

Electronegativity generally increases across a period from left to right (say from lithium to fluorine) and decrease down a group (say from fluorine to astatine) in the periodic table. How can these trends be explained? Can the electronegativity be related to atomic radii, which tend to decrease across each period from left to right, but increase down each group? The attraction between the outer (or valence) electrons and the nucleus increases as the atomic radius decreases in a period. The electronegativity also increases.

On the same account electronegativity values decrease with the increase in atomic radii down a group. The trend is similar to that of ionization enthalpy.

Knowing the relationship between electronegativity and atomic radius, can you now visualise the relationship between electronegativity and non-metallic properties? Non-metallic elements have strong tendency

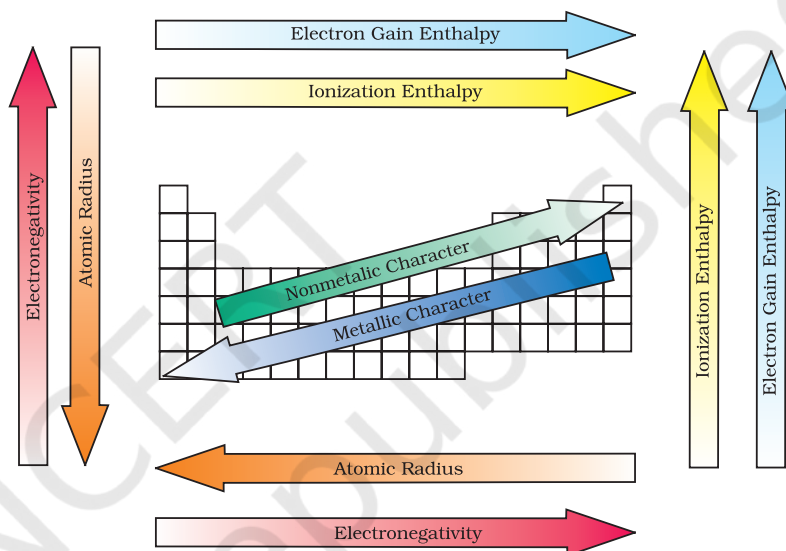


Fig. 3.7 The periodic trends of elements in the periodic table

Table 3.8(a) Electronegativity Values (on Pauling scale) Across the Periods

Atom (Period II)	Li	Be	B	C	N	O	F
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Atom (Period III)	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

Table 3.8(b) Electronegativity Values (on Pauling scale) Down a Family

Atom (Group I)	Electronegativity Value	Atom (Group 17)	Electronegativity Value
Li	1.0	F	4.0
Na	0.9	Cl	3.0
K	0.8	Br	2.8
Rb	0.8	I	2.5
Cs	0.7	At	2.2

to gain electrons. Therefore, electronegativity is directly related to that non-metallic properties of elements. It can be further extended to say that the electronegativity is inversely related to the metallic properties of elements. Thus, the increase in electronegativities across a period is accompanied by an increase in non-metallic properties (or decrease in metallic properties) of elements. Similarly, the decrease in electronegativity down a group is accompanied by a decrease in non-metallic properties (or increase in metallic properties) of elements.

All these periodic trends are summarised in Figure 3.7.

3.7.2 Periodic Trends in Chemical Properties

Most of the trends in chemical properties of elements, such as diagonal relationships, inert pair effect, effects of lanthanoid contraction etc. will be dealt with along the discussion of each group in later units. In this section we shall study the periodicity of the valence state shown by elements and the anomalous properties of the second period elements (from lithium to fluorine).

(a) Periodicity of Valence or Oxidation States

The valence is the most characteristic property of the elements and can be understood in terms of their electronic configurations. The valence of representative elements is usually (though not necessarily) equal to the number of electrons in the outermost orbitals and/or equal to eight minus the number of outermost electrons as shown below.

Nowadays the term oxidation state is frequently used for valence. Consider the two oxygen containing compounds: OF_2 and Na_2O . The order of electronegativity of the three elements involved in these compounds is $\text{F} > \text{O} > \text{Na}$. Each of the atoms of fluorine,

with outer electronic configuration $2s^2 2p^5$, shares one electron with oxygen in the OF_2 molecule. Being highest electronegative element, fluorine is given oxidation state -1 . Since there are two fluorine atoms in this molecule, oxygen with outer electronic configuration $2s^2 2p^4$ shares two electrons with fluorine atoms and thereby exhibits oxidation state $+2$. In Na_2O , oxygen being more electronegative accepts two electrons, one from each of the two sodium atoms and, thus, shows oxidation state -2 . On the other hand sodium with electronic configuration $3s^1$ loses one electron to oxygen and is given oxidation state $+1$. Thus, the oxidation state of an element in a particular compound can be defined as the charge acquired by its atom on the basis of electronegative consideration from other atoms in the molecule.

Problem 3.8

Using the Periodic Table, predict the formulas of compounds which might be formed by the following pairs of elements; (a) silicon and bromine (b) aluminium and sulphur.

Solution

- (a) Silicon is group 14 element with a valence of 4; bromine belongs to the halogen family with a valence of 1. Hence the formula of the compound formed would be SiBr_4 .
- (b) Aluminium belongs to group 13 with a valence of 3; sulphur belongs to group 16 elements with a valence of 2. Hence, the formula of the compound formed would be Al_2S_3 .

Some periodic trends observed in the valence of elements (hydrides and oxides) are shown in Table 3.9. Other such periodic trends which occur in the chemical behaviour of the elements are discussed elsewhere in

Group	1	2	13	14	15	16	17	18
Number of valence electron	1	2	3	4	5	6	7	8
valence	1	2	3	4	3,5	2,6	1,7	0,8

Table 3.9 Periodic Trends in Valence of Elements as shown by the Formulas of Their Compounds

Group	1	2	13	14	15	16	17
Formula of hydride	LiH NaH KH	CaH ₂	B ₂ H ₆ AlH ₃	CH ₄ SiH ₄ GeH ₄ SnH ₄	NH ₃ PH ₃ AsH ₃	H ₂ O H ₂ S H ₂ Se H ₂ Te	HF HCl HBr HI
Formula of oxide	Li ₂ O Na ₂ O K ₂ O	MgO CaO SrO BaO	B ₂ O ₃ Al ₂ O ₃ Ga ₂ O ₃ In ₂ O ₃	CO ₂ SiO ₂ GeO ₂ SnO ₂ PbO ₂	N ₂ O ₃ , N ₂ O ₅ P ₄ O ₆ , P ₄ O ₁₀ As ₂ O ₃ , As ₂ O ₅ Sb ₂ O ₃ , Sb ₂ O ₅ Bi ₂ O ₃ –	SO ₃ SeO ₃ TeO ₃ –	– Cl ₂ O ₇ – –

this book. There are many elements which exhibit variable valence. This is particularly characteristic of transition elements and actinoids, which we shall study later.

(b) Anomalous Properties of Second Period Elements

The first element of each of the groups 1 (lithium) and 2 (beryllium) and groups 13-17 (boron to fluorine) differs in many respects from the other members of their respective group. For example, lithium unlike other alkali metals, and beryllium unlike other alkaline earth metals, form compounds with pronounced covalent character; the other members of these groups predominantly form ionic compounds. In fact the behaviour of lithium and beryllium is more similar with

the second element of the following group i.e., magnesium and aluminium, respectively. This sort of similarity is commonly referred to as **diagonal relationship** in the periodic properties.

What are the reasons for the different chemical behaviour of the first member of a group of elements in the **s-** and **p-blocks** compared to that of the subsequent members in the same group? The anomalous behaviour is attributed to their small size, large charge/radius ratio and high electronegativity of the elements. In addition, the first member of group has only four valence orbitals (2s and 2p) available for bonding, whereas the second member of the groups have nine valence orbitals (3s, 3p, 3d). As a consequence of this, the maximum covalency of the first member of each group is 4 (e.g., boron can only form [BF₄][–], whereas the other members of the groups can expand their valence shell to accommodate more than four pairs of electrons e.g., aluminium [AlF₆]^{3–} forms). Furthermore, the first member of p-block elements displays greater ability to form p_π – p_π multiple bonds to itself (e.g., C = C, C ≡ C, N = N, N ≡ N) and to other second period elements (e.g., C = O, C = N, C ≡ N, N = O) compared to subsequent members of the same group.

Property	Element		
Metallic radius M/pm	Li	Be	B
	152	111	88
	Na	Mg	Al
	186	160	143
Ionic radius M ⁺ /pm	Li	Be	
	76	31	
	Na	Mg	
	102	72	

Problem 3.9

Are the oxidation state and covalency of Al in $[\text{AlCl}(\text{H}_2\text{O})_5]^{2+}$ same ?

Solution

No. The oxidation state of Al is +3 and the covalency is 6.

3.7.3 Periodic Trends and Chemical Reactivity

We have observed the periodic trends in certain fundamental properties such as atomic and ionic radii, ionization enthalpy, electron gain enthalpy and valence. We know by now that the periodicity is related to electronic configuration. That is, all chemical and physical properties are a manifestation of the electronic configuration of elements. We shall now try to explore relationships between these fundamental properties of elements with their chemical reactivity.

The atomic and ionic radii, as we know, generally decrease in a period from left to right. As a consequence, the ionization enthalpies generally increase (with some exceptions as outlined in section 3.7.1(a)) and electron gain enthalpies become more negative across a period. In other words, the ionization enthalpy of the extreme left element in a period is the least and the electron gain enthalpy of the element on the extreme right is the highest negative (note : noble gases having completely filled shells have rather positive electron gain enthalpy values). This results into high chemical reactivity at the two extremes and the lowest in the centre. Thus, the maximum chemical reactivity at the extreme left (among alkali metals) is exhibited by the loss of an electron leading to the formation of a cation and at the extreme right (among halogens) shown by the gain of an electron forming an anion. This property can be related with the reducing and oxidizing behaviour of the elements which you will learn later. However,

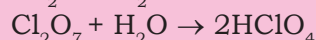
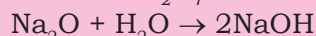
here it can be directly related to the metallic and non-metallic character of elements. Thus, the metallic character of an element, which is highest at the extremely left decreases and the non-metallic character increases while moving from left to right across the period. The chemical reactivity of an element can be best shown by its reactions with oxygen and halogens. Here, we shall consider the reaction of the elements with oxygen only. Elements on two extremes of a period easily combine with oxygen to form oxides. The normal oxide formed by the element on extreme left is the most basic (e.g., Na_2O), whereas that formed by the element on extreme right is the most acidic (e.g., Cl_2O_7). Oxides of elements in the centre are amphoteric (e.g., Al_2O_3 , As_2O_3) or neutral (e.g., CO , NO , N_2O). Amphoteric oxides behave as acidic with bases and as basic with acids, whereas neutral oxides have no acidic or basic properties.

Problem 3.10

Show by a chemical reaction with water that Na_2O is a basic oxide and Cl_2O_7 is an acidic oxide.

Solution

Na_2O with water forms a strong base whereas Cl_2O_7 forms strong acid.



Their basic or acidic nature can be qualitatively tested with litmus paper.

Among transition metals (3d series), the change in atomic radii is much smaller as compared to those of representative elements across the period. The change in atomic radii is still smaller among inner-transition metals (4f series). The ionization enthalpies are intermediate between those of s- and p-blocks. As a consequence, they are less electropositive than group 1 and 2 metals.

In a group, the increase in atomic and ionic radii with increase in atomic number generally results in a gradual decrease in ionization enthalpies and a regular decrease (with exception in some third period elements as shown in section 3.7.1(d)) in electron gain enthalpies in the case of main group elements. Thus, the metallic character

increases down the group and non-metallic character decreases. This trend can be related with their reducing and oxidizing property which you will learn later. In the case of transition elements, however, a reverse trend is observed. This can be explained in terms of atomic size and ionization enthalpy.

SUMMARY

In this Unit, you have studied the development of the **Periodic Law** and the **Periodic Table**. Mendeleev's **Periodic Table** was based on atomic masses. Modern **Periodic Table** arranges the elements in the order of their atomic numbers in seven horizontal rows (**periods**) and eighteen vertical columns (**groups** or **families**). Atomic numbers in a period are consecutive, whereas in a group they increase in a pattern. Elements of the same group have similar **valence shell** electronic configuration and, therefore, exhibit similar chemical properties. However, the elements of the same period have incrementally increasing number of electrons from left to right, and, therefore, have different valencies. Four types of elements can be recognized in the periodic table on the basis of their electronic configurations. These are **s-block**, **p-block**, **d-block** and **f-block** elements. **Hydrogen** with one electron in the 1s orbital occupies a unique position in the periodic table. **Metals** comprise more than seventy eight per cent of the known elements. **Non-metals**, which are located at the top of the periodic table, are less than twenty in number. Elements which lie at the border line between metals and non-metals (e.g., Si, Ge, As) are called **metalloids** or **semi-metals**. Metallic character increases with increasing atomic number in a group whereas decreases from left to right in a period. The physical and chemical properties of elements vary periodically with their atomic numbers.

Periodic trends are observed in **atomic sizes**, **ionization enthalpies**, **electron gain enthalpies**, **electronegativity** and **valence**. The atomic radii decrease while going from left to right in a period and increase with atomic number in a group. Ionization enthalpies generally increase across a period and decrease down a group. Electronegativity also shows a similar trend. Electron gain enthalpies, in general, become more negative across a period and less negative down a group. There is some periodicity in valence, for example, among representative elements, the valence is either equal to the number of electrons in the outermost orbitals or eight minus this number. **Chemical reactivity** is highest at the two extremes of a period and is lowest in the centre. The reactivity on the left extreme of a period is because of the ease of electron loss (or low ionization enthalpy). Highly reactive elements do not occur in nature in free state; they usually occur in the combined form. Oxides formed of the elements on the left are basic and of the elements on the right are acidic in nature. Oxides of elements in the centre are amphoteric or neutral.

EXERCISES

- 3.1 What is the basic theme of organisation in the periodic table?
- 3.2 Which important property did Mendeleev use to classify the elements in his periodic table and did he stick to that?
- 3.3 What is the basic difference in approach between the Mendeleev's Periodic Law and the Modern Periodic Law?
- 3.4 On the basis of quantum numbers, justify that the sixth period of the periodic table should have 32 elements.
- 3.5 In terms of period and group where would you locate the element with $Z=114$?
- 3.6 Write the atomic number of the element present in the third period and seventeenth group of the periodic table.
- 3.7 Which element do you think would have been named by
- (i) Lawrence Berkeley Laboratory
 - (ii) Seaborg's group?
- 3.8 Why do elements in the same group have similar physical and chemical properties?
- 3.9 What does atomic radius and ionic radius really mean to you?
- 3.10 How do atomic radius vary in a period and in a group? How do you explain the variation?
- 3.11 What do you understand by isoelectronic species? Name a species that will be isoelectronic with each of the following atoms or ions.
- (i) F^- (ii) Ar (iii) Mg^{2+} (iv) Rb^+
- 3.12 Consider the following species :
- N^{3-} , O^{2-} , F^- , Na^+ , Mg^{2+} and Al^{3+}
- (a) What is common in them?
 - (b) Arrange them in the order of increasing ionic radii.
- 3.13 Explain why cation are smaller and anions larger in radii than their parent atoms?
- 3.14 What is the significance of the terms — 'isolated gaseous atom' and 'ground state' while defining the ionization enthalpy and electron gain enthalpy?
- Hint :** Requirements for comparison purposes.
- 3.15 Energy of an electron in the ground state of the hydrogen atom is $-2.18 \times 10^{-18} J$. Calculate the ionization enthalpy of atomic hydrogen in terms of $J mol^{-1}$.
- Hint:** Apply the idea of mole concept to derive the answer.
- 3.16 Among the second period elements the actual ionization enthalpies are in the order $Li < B < Be < C < O < N < F < Ne$.
Explain why
- (i) Be has higher $\Delta_i H$ than B
 - (ii) O has lower $\Delta_i H$ than N and F?

- 3.17 How would you explain the fact that the first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium?
- 3.18 What are the various factors due to which the ionization enthalpy of the main group elements tends to decrease down a group?
- 3.19 The first ionization enthalpy values (in kJ mol^{-1}) of group 13 elements are :
- | B | Al | Ga | In | Tl |
|-----|-----|-----|-----|-----|
| 801 | 577 | 579 | 558 | 589 |
- How would you explain this deviation from the general trend ?
- 3.20 Which of the following pairs of elements would have a more negative electron gain enthalpy?
(i) O or F (ii) F or Cl
- 3.21 Would you expect the second electron gain enthalpy of O as positive, more negative or less negative than the first? Justify your answer.
- 3.22 What is the basic difference between the terms electron gain enthalpy and electronegativity?
- 3.23 How would you react to the statement that the electronegativity of N on Pauling scale is 3.0 in all the nitrogen compounds?
- 3.24 Describe the theory associated with the radius of an atom as it
(a) gains an electron
(b) loses an electron
- 3.25 Would you expect the first ionization enthalpies for two isotopes of the same element to be the same or different? Justify your answer.
- 3.26 What are the major differences between metals and non-metals?
- 3.27 Use the periodic table to answer the following questions.
(a) Identify an element with five electrons in the outer subshell.
(b) Identify an element that would tend to lose two electrons.
(c) Identify an element that would tend to gain two electrons.
(d) Identify the group having metal, non-metal, liquid as well as gas at the room temperature.
- 3.28 The increasing order of reactivity among group 1 elements is $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ whereas that among group 17 elements is $\text{F} > \text{Cl} > \text{Br} > \text{I}$. Explain.
- 3.29 Write the general outer electronic configuration of s -, p -, d - and f -block elements.
- 3.30 Assign the position of the element having outer electronic configuration
(i) ns^2np^4 for $n=3$ (ii) $(n-1)d^2ns^2$ for $n=4$, and (iii) $(n-2)f^7(n-1)d^1ns^2$ for $n=6$, in the periodic table.

- 3.31 The first ($\Delta_i H_1$) and the second ($\Delta_i H_2$) ionization enthalpies (in kJ mol^{-1}) and the ($\Delta_{eg} H$) electron gain enthalpy (in kJ mol^{-1}) of a few elements are given below:

Elements	ΔH_1	ΔH_2	$\Delta_{eg} H$
I	520	7300	-60
II	419	3051	-48
III	1681	3374	-328
IV	1008	1846	-295
V	2372	5251	+48
VI	738	1451	-40

Which of the above elements is likely to be :

- the least reactive element.
 - the most reactive metal.
 - the most reactive non-metal.
 - the least reactive non-metal.
 - the metal which can form a stable binary halide of the formula MX_2 (X=halogen).
 - the metal which can form a predominantly stable covalent halide of the formula MX (X=halogen)?
- 3.32 Predict the formulas of the stable binary compounds that would be formed by the combination of the following pairs of elements.
- Lithium and oxygen
 - Magnesium and nitrogen
 - Aluminium and iodine
 - Silicon and oxygen
 - Phosphorus and fluorine
 - Element 71 and fluorine
- 3.33 In the modern periodic table, the period indicates the value of :
- atomic number
 - atomic mass
 - principal quantum number
 - azimuthal quantum number.
- 3.34 Which of the following statements related to the modern periodic table is incorrect?
- The p -block has 6 columns, because a maximum of 6 electrons can occupy all the orbitals in a p -shell.
 - The d -block has 8 columns, because a maximum of 8 electrons can occupy all the orbitals in a d -subshell.
 - Each block contains a number of columns equal to the number of electrons that can occupy that subshell.
 - The block indicates value of azimuthal quantum number (l) for the last subshell that received electrons in building up the electronic configuration.

- 3.35 Anything that influences the valence electrons will affect the chemistry of the element. Which one of the following factors does not affect the valence shell?
- (a) Valence principal quantum number (n)
 - (b) Nuclear charge (Z)
 - (c) Nuclear mass
 - (d) Number of core electrons.
- 3.36 The size of isoelectronic species — F^- , Ne and Na^+ is affected by
- (a) nuclear charge (Z)
 - (b) valence principal quantum number (n)
 - (c) electron-electron interaction in the outer orbitals
 - (d) none of the factors because their size is the same.
- 3.37 Which one of the following statements is incorrect in relation to ionization enthalpy?
- (a) Ionization enthalpy increases for each successive electron.
 - (b) The greatest increase in ionization enthalpy is experienced on removal of electron from core noble gas configuration.
 - (c) End of valence electrons is marked by a big jump in ionization enthalpy.
 - (d) Removal of electron from orbitals bearing lower n value is easier than from orbital having higher n value.
- 3.38 Considering the elements B, Al, Mg, and K, the correct order of their metallic character is :
- (a) $B > Al > Mg > K$
 - (b) $Al > Mg > B > K$
 - (c) $Mg > Al > K > B$
 - (d) $K > Mg > Al > B$
- 3.39 Considering the elements B, C, N, F, and Si, the correct order of their non-metallic character is :
- (a) $B > C > Si > N > F$
 - (b) $Si > C > B > N > F$
 - (c) $F > N > C > B > Si$
 - (d) $F > N > C > Si > B$
- 3.40 Considering the elements F, Cl, O and N, the correct order of their chemical reactivity in terms of oxidizing property is :
- (a) $F > Cl > O > N$
 - (b) $F > O > Cl > N$
 - (c) $Cl > F > O > N$
 - (d) $O > F > N > Cl$



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UNIT 4

CHEMICAL BONDING AND MOLECULAR STRUCTURE

Objectives

After studying this Unit, you will be able to

- understand Kössel-Lewis approach to chemical bonding;
- explain the octet rule and its limitations, draw Lewis structures of simple molecules;
- explain the formation of different types of bonds;
- describe the VSEPR theory and predict the geometry of simple molecules;
- explain the valence bond approach for the formation of covalent bonds;
- predict the directional properties of covalent bonds;
- explain the different types of hybridisation involving *s*, *p* and *d* orbitals and draw shapes of simple covalent molecules;
- describe the molecular orbital theory of homonuclear diatomic molecules;
- explain the concept of hydrogen bond.

“Scientists are constantly discovering new compounds, orderly arranging the facts about them, trying to explain with the existing knowledge, organising to modify the earlier views or evolve theories for explaining the newly observed facts.”

Matter is made up of one or different type of elements. Under normal conditions no other element exists as an independent atom in nature, except noble gases. However, a group of atoms is found to exist together as one species having characteristic properties. Such a group of atoms is called a molecule. Obviously there must be some force which holds these constituent atoms together in the molecules. **The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.** Since the formation of chemical compounds takes place as a result of combination of atoms of various elements in different ways, it raises many questions. Why do atoms combine? Why are only certain combinations possible? Why do some atoms combine while certain others do not? Why do molecules possess definite shapes? To answer such questions different theories and concepts have been put forward from time to time. These are Kössel-Lewis approach, Valence Shell Electron Pair Repulsion (VSEPR) Theory, Valence Bond (VB) Theory and Molecular Orbital (MO) Theory. The evolution of various theories of valence and the interpretation of the nature of chemical bonds have closely been related to the developments in the understanding of the structure of atom, the electronic configuration of elements and the periodic table. Every system tends to be more stable and bonding is nature's way of lowering the energy of the system to attain stability.

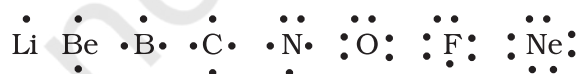
4.1 KÖSSEL-LEWIS APPROACH TO CHEMICAL BONDING

In order to explain the formation of chemical bond in terms of electrons, a number of attempts were made, but it was only in 1916 when Kössel and Lewis succeeded independently in giving a satisfactory explanation. They were the first to provide some logical explanation of valence which was based on the inertness of noble gases.

Lewis pictured the atom in terms of a positively charged 'Kernel' (the nucleus plus the inner electrons) and the outer shell that could accommodate a maximum of eight electrons. He, further assumed that these eight electrons occupy the corners of a cube which surround the 'Kernel'. Thus the single outer shell electron of sodium would occupy one corner of the cube, while in the case of a noble gas all the eight corners would be occupied. This octet of electrons, represents a particularly stable electronic arrangement.

Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds. In the case of sodium and chlorine, this can happen by the transfer of an electron from sodium to chlorine thereby giving the Na^+ and Cl^- ions. In the case of other molecules like Cl_2 , H_2 , F_2 , etc., the bond is formed by the sharing of a pair of electrons between the atoms. In the process each atom attains a **stable outer octet of electrons**.

Lewis Symbols: In the formation of a molecule, only the outer shell electrons take part in chemical combination and they are known as **valence electrons**. The inner shell electrons are well protected and are generally not involved in the combination process. G.N. Lewis, an American chemist introduced simple notations to represent valence electrons in an atom. These notations are called **Lewis symbols**. For example, the Lewis symbols for the elements of second period are as under:



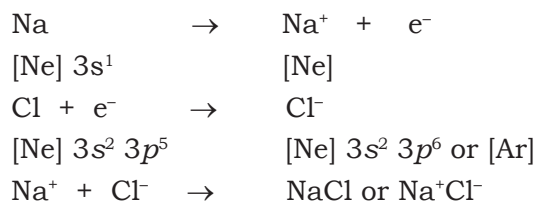
Significance of Lewis Symbols : The number of dots around the symbol represents

the number of valence electrons. This number of valence electrons helps to calculate the common or **group valence** of the element. The group valence of the elements is generally either equal to the number of dots in Lewis symbols or 8 minus the number of dots or valence electrons.

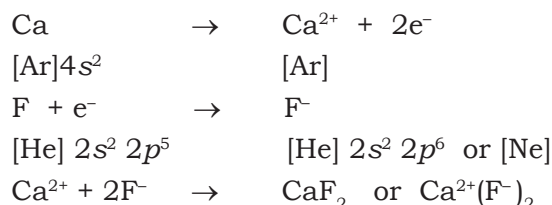
Kössel, in relation to chemical bonding, drew attention to the following facts:

- In the periodic table, the highly electronegative halogens and the highly electropositive alkali metals are separated by the noble gases;
- The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with the gain and loss of an electron by the respective atoms;
- The negative and positive ions thus formed attain stable noble gas electronic configurations. The noble gases (with the exception of helium which has a duplet of electrons) have a particularly stable outer shell configuration of eight (octet) electrons, ns^2np^6 .
- The negative and positive ions are stabilized by electrostatic attraction.

For example, the formation of NaCl from sodium and chlorine, according to the above scheme, can be explained as:



Similarly the formation of CaF_2 may be shown as:



The bond formed, as a result of the electrostatic attraction between the positive and negative ions was termed as

the electrovalent bond. The electrovalence is thus equal to the number of unit charge(s) on the ion. Thus, calcium is assigned a positive electrovalence of two, while chlorine a negative electrovalence of one.

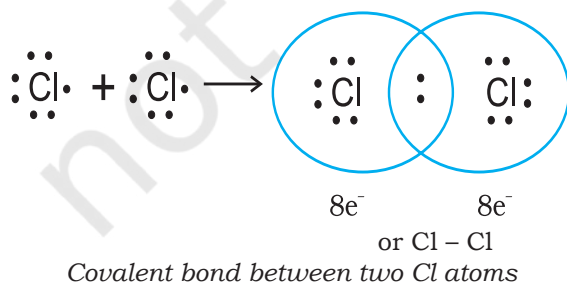
Kössel's postulations provide the basis for the modern concepts regarding ion-formation by electron transfer and the formation of ionic crystalline compounds. His views have proved to be of great value in the understanding and systematisation of the ionic compounds. At the same time he did recognise the fact that a large number of compounds did not fit into these concepts.

4.1.1 Octet Rule

Kössel and Lewis in 1916 developed an important theory of chemical combination between atoms known as **electronic theory of chemical bonding**. According to this, atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells. This is known as **octet rule**.

4.1.2 Covalent Bond

Langmuir (1919) refined the Lewis postulations by abandoning the idea of the stationary cubical arrangement of the octet, and by introducing the term **covalent bond**. The Lewis-Langmuir theory can be understood by considering the formation of the chlorine molecule, Cl_2 . The Cl atom with electronic configuration, $[\text{Ne}]3s^2 3p^5$, is one electron short of the argon configuration. The formation of the Cl_2 molecule can be understood in terms of the sharing of a pair of electrons between the two chlorine atoms, each chlorine atom contributing one electron to the shared pair. In the process both

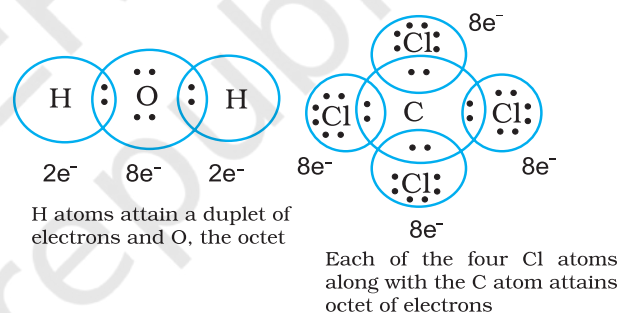


chlorine atoms attain the outer shell octet of the nearest noble gas (i.e., argon).

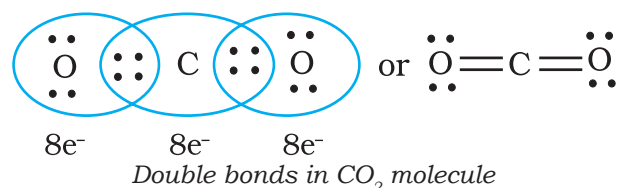
The dots represent electrons. Such structures are referred to as Lewis dot structures.

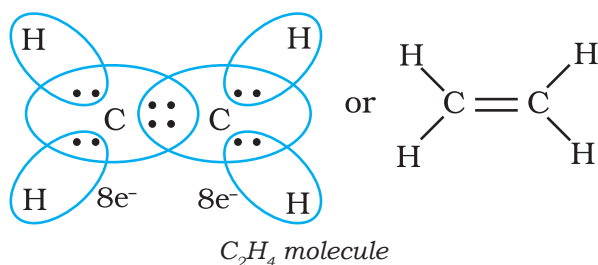
The Lewis dot structures can be written for other molecules also, in which the combining atoms may be identical or different. The important conditions being that:

- Each bond is formed as a result of sharing of an electron pair between the atoms.
- Each combining atom contributes at least one electron to the shared pair.
- The combining atoms attain the outer-shell noble gas configurations as a result of the sharing of electrons.
- Thus in water and carbon tetrachloride molecules, formation of covalent bonds can be represented as:

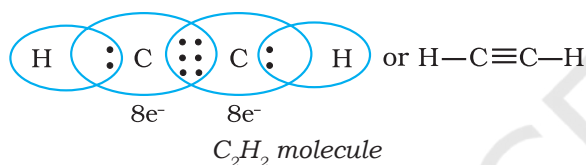
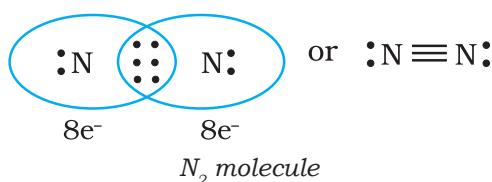


Thus, when two atoms share one electron pair they are said to be joined by a single covalent bond. In many compounds we have **multiple bonds** between atoms. The formation of multiple bonds envisages sharing of more than one electron pair between two atoms. **If two atoms share two pairs of electrons, the covalent bond between them is called a double bond.** For example, in the carbon dioxide molecule, we have two double bonds between the carbon and oxygen atoms. Similarly in ethene molecule the two carbon atoms are joined by a double bond.





When combining atoms share three electron pairs as in the case of two nitrogen atoms in the N_2 molecule and the two carbon atoms in the ethyne molecule, a triple bond is formed.



4.1.3 Lewis Representation of Simple Molecules (the Lewis Structures)

The Lewis dot structures provide a picture of bonding in molecules and ions in terms of the shared pairs of electrons and the octet rule. While such a picture may not explain the bonding and behaviour of a molecule completely, it does help in understanding the formation and properties of a molecule to a large extent. Writing of Lewis dot structures of molecules is, therefore, very useful. The Lewis dot structures can be written by adopting the following steps:

- The total number of electrons required for writing the structures are obtained by adding the valence electrons of the combining atoms. For example, in the CH_4 molecule there are eight valence electrons available for bonding (4 from carbon and 4 from the four hydrogen atoms).
- For anions, each negative charge would mean addition of one electron. For cations, each positive charge would result in subtraction of one electron from the total

number of valence electrons. For example, for the CO_3^{2-} ion, the two negative charges indicate that there are two additional electrons than those provided by the neutral atoms. For NH_4^+ ion, one positive charge indicates the loss of one electron from the group of neutral atoms.

- Knowing the chemical symbols of the combining atoms and having knowledge of the skeletal structure of the compound (known or guessed intelligently), it is easy to distribute the total number of electrons as bonding shared pairs between the atoms in proportion to the total bonds.
- In general the least electronegative atom occupies the central position in the molecule/ion. For example in the NF_3 and CO_3^{2-} , nitrogen and carbon are the central atoms whereas fluorine and oxygen occupy the terminal positions.
- After accounting for the shared pairs of electrons for single bonds, the remaining electron pairs are either utilized for multiple bonding or remain as the lone pairs. The basic requirement being that each bonded atom gets an octet of electrons.

Lewis representations of a few molecules/ions are given in Table 4.1.

Table 4.1 The Lewis Representation of Some Molecules

Molecule/Ion	Lewis Representation	
H_2	$H : H^*$	$H - H$
O_2	$:\ddot{O}::\ddot{O}:$	$:\ddot{O}=\ddot{O}:$
O_3	$\begin{array}{c} \cdot\ddot{O}^+ \\ \cdot\ddot{O}::\ddot{O}^- \end{array}$	$\begin{array}{c} \cdot\ddot{O}^+ \\ :\ddot{O}::\ddot{O}^- \end{array}$
NF_3	$\begin{array}{c} :\ddot{F}: \\ :\ddot{N}::\ddot{F}: \\ :\ddot{F}: \end{array}$	$\begin{array}{c} :\ddot{F}-\ddot{N}-\ddot{F}: \\ :\ddot{F}: \end{array}$
CO_3^{2-}	$\left[\begin{array}{c} :\ddot{O}: \\ :\ddot{O}::\ddot{C}::\ddot{O}: \end{array} \right]^{2-}$	$\left[\begin{array}{c} :\ddot{O}: \\ :\ddot{O}-\ddot{C}::\ddot{O}: \end{array} \right]^{2-}$
HNO_3	$\begin{array}{c} + \\ \ddot{O}::\ddot{N}::\ddot{O}:H \\ :\ddot{O}:^- \end{array}$	$\begin{array}{c} + \\ \ddot{O}=\ddot{N}-\ddot{O}-H \\ :\ddot{O}:^- \end{array}$

* Each H atom attains the configuration of helium (a duplet of electrons)

Problem 4.1

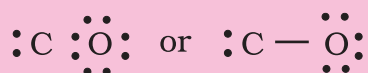
Write the Lewis dot structure of CO molecule.

Solution

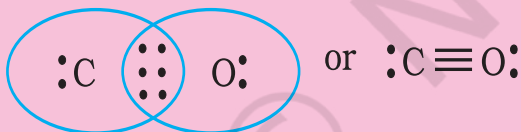
Step 1. Count the total number of valence electrons of carbon and oxygen atoms. The outer (valence) shell configurations of carbon and oxygen atoms are: $2s^2 2p^2$ and $2s^2 2p^4$, respectively. The valence electrons available are $4 + 6 = 10$.

Step 2. The skeletal structure of CO is written as: C O

Step 3. Draw a single bond (one shared electron pair) between C and O and complete the octet on O, the remaining two electrons are the lone pair on C.



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

**Problem 4.2**

Write the Lewis structure of the nitrite ion, NO_2^- .

Solution

Step 1. Count the total number of valence electrons of the nitrogen atom, the oxygen atoms and the additional one negative charge (equal to one electron).

$$\text{N}(2s^2 2p^3), \text{O}(2s^2 2p^4) \\ 5 + (2 \times 6) + 1 = 18 \text{ electrons}$$

Step 2. The skeletal structure of NO_2^- is written as: O N O

Step 3. Draw a single bond (one shared electron pair) between the nitrogen and

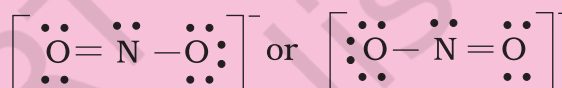
each of the oxygen atoms completing the octets on oxygen atoms. This, however, does not complete the octet on nitrogen if the remaining two electrons constitute lone pair on it.



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



or

**4.1.4 Formal Charge**

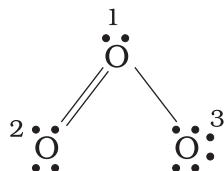
Lewis dot structures, in general, do not represent the actual shapes of the molecules. In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is, however, feasible to assign a formal charge on each atom. The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure. It is expressed as :

Formal charge (F.C.)
on an atom in a Lewis
structure =

$$\left[\begin{array}{l} \text{total number of valence} \\ \text{electrons in the free} \\ \text{atom} \end{array} \right] - \left[\begin{array}{l} \text{total number of non} \\ \text{bonding (lone pair)} \\ \text{electrons} \end{array} \right] \\ - (1/2) \left[\begin{array}{l} \text{total number of} \\ \text{bonding (shared)} \\ \text{electrons} \end{array} \right]$$

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

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



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

- The central O atom marked 1

$$= 6 - 2 - \frac{1}{2} (6) = +1$$

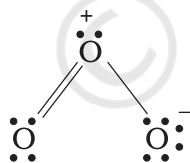
- The end O atom marked 2

$$= 6 - 4 - \frac{1}{2} (4) = 0$$

- The end O atom marked 3

$$= 6 - 6 - \frac{1}{2} (2) = -1$$

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



We must understand that formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule. Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species. **Generally the lowest energy structure is the one with the smallest formal charges on the atoms. The formal charge is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighbouring atoms.**

4.1.5 Limitations of the Octet Rule

The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are three types of exceptions to the octet rule.

The incomplete octet of the central atom

In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are $LiCl$, BeH_2 and BCl_3 .



Li, Be and B have 1, 2 and 3 valence electrons only. Some other such compounds are $AlCl_3$ and BF_3 .

Odd-electron molecules

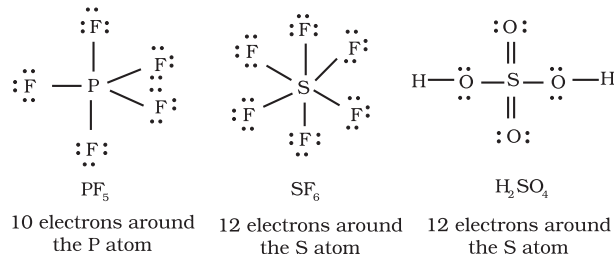
In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, NO_2 , the octet rule is not satisfied for all the atoms



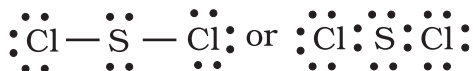
The expanded octet

Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases.

Some of the examples of such compounds are: PF_5 , SF_6 , H_2SO_4 and a number of coordination compounds.



Interestingly, sulphur also forms many compounds in which the octet rule is obeyed. In sulphur dichloride, the S atom has an octet of electrons around it.



Other drawbacks of the octet theory

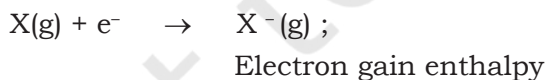
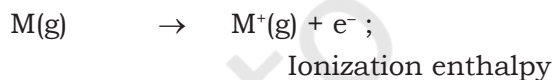
- It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2 , KrF_2 , XeOF_2 etc.
- This theory does not account for the shape of molecules.
- It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

4.2 IONIC OR ELECTROVALENT BOND

From the Kössel and Lewis treatment of the formation of an ionic bond, it follows that the formation of ionic compounds would primarily depend upon:

- The ease of formation of the positive and negative ions from the respective neutral atoms;
- The arrangement of the positive and negative ions in the solid, that is, the lattice of the crystalline compound.

The formation of a positive ion involves ionization, i.e., removal of electron(s) from the neutral atom and that of the negative ion involves the addition of electron(s) to the neutral atom.



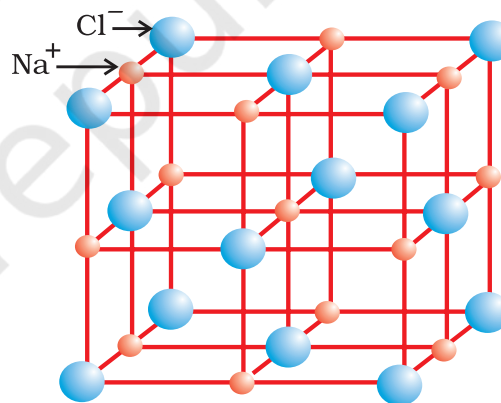
The **electron gain enthalpy**, $\Delta_{\text{eg}} H$, is the enthalpy change (Unit 3), when a gas phase atom in its ground state gains an electron. The electron gain process may be exothermic or endothermic. The ionization, on the other hand, is always endothermic. Electron

affinity, is the negative of the energy change accompanying electron gain.

Obviously ionic bonds will be formed more easily between elements with comparatively low ionization enthalpies and elements with comparatively high negative value of electron gain enthalpy.

Most ionic compounds have cations derived from metallic elements and anions from non-metallic elements. The ammonium ion, NH_4^+ (made up of two non-metallic elements) is an exception. It forms the cation of a number of ionic compounds.

Ionic compounds in the crystalline state consist of orderly three-dimensional arrangements of cations and anions held together by coulombic interaction energies. These compounds crystallise in different crystal structures determined by the size of the ions, their packing arrangements and other factors. The crystal structure of sodium chloride, NaCl (rock salt), for example is shown below.



Rock salt structure

In ionic solids, the sum of the electron gain enthalpy and the ionization enthalpy may be positive but still the crystal structure gets stabilized due to the energy released in the formation of the crystal lattice. For example: the ionization enthalpy for $\text{Na}^+(\text{g})$ formation from Na(g) is $495.8 \text{ kJ mol}^{-1}$; while the electron gain enthalpy for the change $\text{Cl(g)} + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$ is, $-348.7 \text{ kJ mol}^{-1}$ only. The sum of the two, $147.1 \text{ kJ mol}^{-1}$ is more than compensated for by the enthalpy of lattice formation of NaCl(s) (-788 kJ mol^{-1}). Therefore, the energy released in the processes is more than the

energy absorbed. **Thus a qualitative measure of the stability of an ionic compound is provided by its enthalpy of lattice formation and not simply by achieving octet of electrons around the ionic species in gaseous state.**

Since lattice enthalpy plays a key role in the formation of ionic compounds, it is important that we learn more about it.

4.2.1 Lattice Enthalpy

The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. For example, the lattice enthalpy of NaCl is 788 kJ mol^{-1} . This means that 788 kJ of energy is required to separate one mole of solid NaCl into one mole of Na^+ (g) and one mole of Cl^- (g) to an infinite distance.

This process involves both the attractive forces between ions of opposite charges and the repulsive forces between ions of like charge. The solid crystal being three-dimensional; it is not possible to calculate lattice enthalpy directly from the interaction of forces of attraction and repulsion only. Factors associated with the crystal geometry have to be included.

4.3 BOND PARAMETERS

4.3.1 Bond Length

Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule. Bond lengths are measured by spectroscopic, X-ray diffraction and electron-diffraction techniques about which you will learn in higher classes. Each atom of the bonded pair contributes to the bond length (Fig. 4.1). In the case of a covalent bond, the contribution from each atom is called the covalent radius of that atom.

The covalent radius is measured approximately as the radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation. The covalent radius is half of the distance between two similar atoms joined by a covalent bond

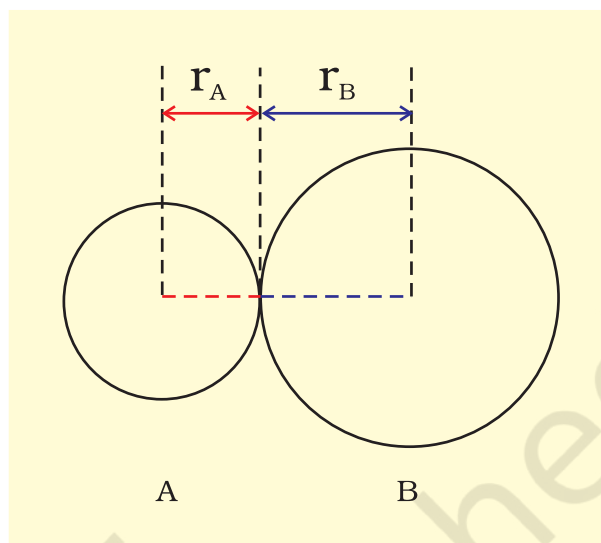


Fig. 4.1 The bond length in a covalent molecule AB.

$R = r_A + r_B$ (R is the bond length and r_A and r_B are the covalent radii of atoms A and B respectively)

in the same molecule. **The van der Waals radius represents the overall size of the atom which includes its valence shell in a nonbonded situation.** Further, the van der Waals radius is half of the distance between two similar atoms in separate molecules in a solid. Covalent and van der Waals radii of chlorine are depicted in Fig. 4.2.

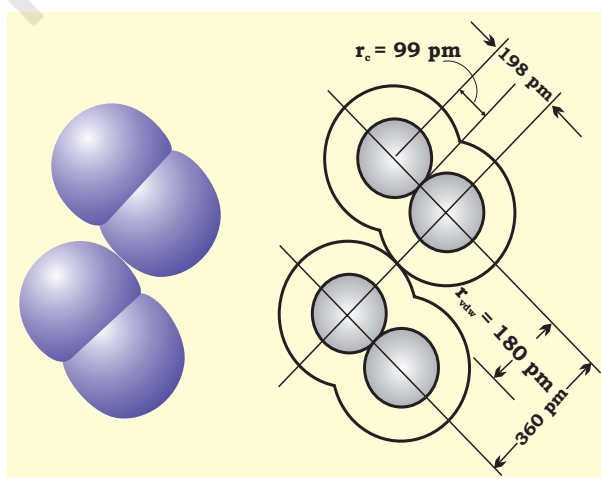


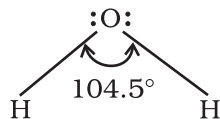
Fig. 4.2 Covalent and van der Waals radii in a chlorine molecule. The inner circles correspond to the size of the chlorine atom (r_{vdw} and r_c are van der Waals and covalent radii respectively).

Some typical average bond lengths for single, double and triple bonds are shown in Table 4.2. Bond lengths for some common molecules are given in Table 4.3.

The covalent radii of some common elements are listed in Table 4.4.

4.3.2 Bond Angle

It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion. Bond angle is expressed in degree which can be experimentally determined by spectroscopic methods. It gives some idea regarding the distribution of orbitals around the central atom in a molecule/complex ion and hence it helps us in determining its shape. For example H–O–H bond angle in water can be represented as under :

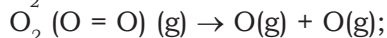


4.3.3 Bond Enthalpy

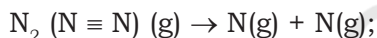
It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. The unit of bond enthalpy is kJ mol^{-1} . For example, the H–H bond enthalpy in hydrogen molecule is $435.8 \text{ kJ mol}^{-1}$.



Similarly the bond enthalpy for molecules containing multiple bonds, for example O_2 and N_2 will be as under :

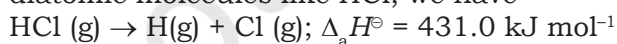


$$\Delta_a H^\ominus = 498 \text{ kJ mol}^{-1}$$



$$\Delta_a H^\ominus = 946.0 \text{ kJ mol}^{-1}$$

It is important that larger the bond dissociation enthalpy, stronger will be the bond in the molecule. For a heteronuclear diatomic molecules like HCl, we have



In case of polyatomic molecules, the measurement of bond strength is more complicated. For example in case of H_2O molecule, the enthalpy needed to break the two O–H bonds is not the same.

Table 4.2 Average Bond Lengths for Some Single, Double and Triple Bonds

Bond Type	Covalent Bond Length (pm)
O–H	96
C–H	107
N–O	136
C–O	143
C–N	143
C–C	154
C=O	121
N=O	122
C=C	133
C=N	138
C≡N	116
C≡C	120

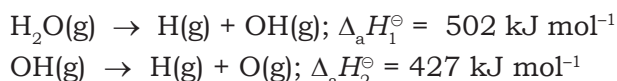
Table 4.3 Bond Lengths in Some Common Molecules

Molecule	Bond Length (pm)
H_2 (H – H)	74
F_2 (F – F)	144
Cl_2 (Cl – Cl)	199
Br_2 (Br – Br)	228
I_2 (I – I)	267
N_2 (N ≡ N)	109
O_2 (O = O)	121
HF (H – F)	92
HCl (H – Cl)	127
HBr (H – Br)	141
HI (H – I)	160

Table 4.4 Covalent Radii, r_{cov}^* /(pm)

H	37				
C	77(1)	N	74 (1)	O	66(1)
	67 (2)		65(2)		57 (2)
	60(3)		55(3)		
		P	110	S	104(1)
					95(2)
		As	121	Se	104
				I	133
		Sb	141	Te	137

* The values cited are for single bonds, except where otherwise indicated in parenthesis. (See also Unit 3 for periodic trends).



The difference in the $\Delta_a H^\ominus$ value shows that the second O – H bond undergoes some change because of changed chemical environment. This is the reason for some difference in energy of the same O – H bond in different molecules like $\text{C}_2\text{H}_5\text{OH}$ (ethanol) and water. Therefore in polyatomic molecules the term **mean or average bond enthalpy** is used. It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken as explained below in case of water molecule,

$$\begin{aligned} \text{Average bond enthalpy} &= \frac{502 + 427}{2} \\ &= 464.5 \text{ kJ mol}^{-1} \end{aligned}$$

4.3.4 Bond Order

In the Lewis description of covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule. The bond order, for example in H_2 (with a single shared electron pair), in O_2 (with two shared electron pairs) and in N_2 (with three shared electron pairs) is 1, 2, 3 respectively. Similarly in CO (three shared electron pairs between C and O) the bond order is 3. For N_2 , bond order is 3 and its $\Delta_a H^\ominus$ is 946 kJ mol^{-1} ; being one of the highest for a diatomic molecule.

Isoelectronic molecules and ions have identical bond orders; for example, F_2 and O_2^{2-} have bond order 1. N_2 , CO and NO^+ have bond order 3.

A general correlation useful for understanding the stabilities of molecules is that: with increase in bond order, bond enthalpy increases and bond length decreases.

4.3.5 Resonance Structures

It is often observed that a single Lewis structure is inadequate for the representation of a molecule in conformity with its experimentally determined parameters. For example, the ozone, O_3 molecule can be equally represented by the structures I and II shown below:

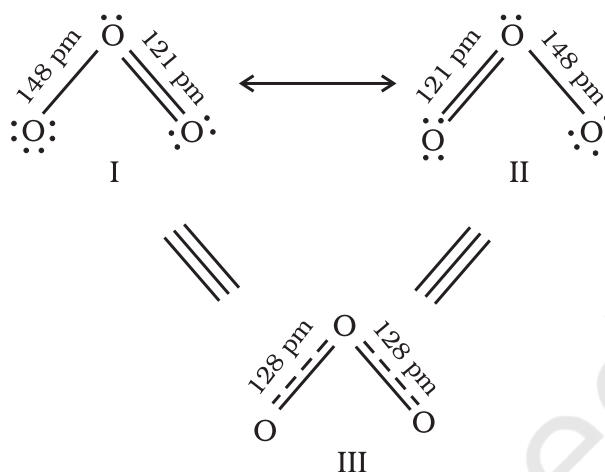


Fig. 4.3 Resonance in the O_3 molecule

(structures I and II represent the two canonical forms while the structure III is the resonance hybrid)

In both structures we have a O–O single bond and a O=O double bond. The normal O–O and O=O bond lengths are 148 pm and 121 pm respectively. Experimentally determined oxygen-oxygen bond lengths in the O_3 molecule are same (128 pm). Thus the oxygen-oxygen bonds in the O_3 molecule are intermediate between a double and a single bond. Obviously, this cannot be represented by either of the two Lewis structures shown above.

The concept of resonance was introduced to deal with the type of difficulty experienced in the depiction of accurate structures of molecules like O_3 . **According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately.** Thus for O_3 , the two structures shown above constitute the canonical structures or resonance structures and their hybrid i.e., the III structure represents the structure of O_3 more accurately. This is also called **resonance hybrid**. Resonance is represented by a double headed arrow.

Some of the other examples of resonance structures are provided by the **carbonate ion** and the **carbon dioxide molecule**.

Problem 4.3

Explain the structure of CO_3^{2-} ion in terms of resonance.

Solution

The single Lewis structure based on the presence of two single bonds and one double bond between carbon and oxygen atoms is inadequate to represent the molecule accurately as it represents unequal bonds. According to the experimental findings, all carbon to oxygen bonds in CO_3^{2-} are equivalent. Therefore the carbonate ion is best described as a resonance hybrid of the canonical forms I, II, and III shown below.

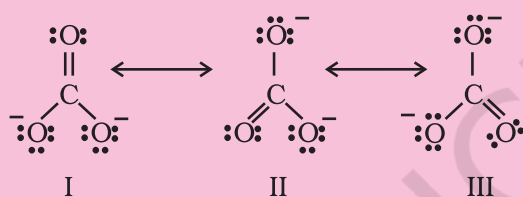


Fig. 4.4 Resonance in CO_3^{2-} , I, II and III represent the three canonical forms.

Problem 4.4

Explain the structure of CO_2 molecule.

Solution

The experimentally determined carbon to oxygen bond length in CO_2 is 115 pm. The lengths of a normal carbon to oxygen double bond ($\text{C}=\text{O}$) and carbon to oxygen triple bond ($\text{C}\equiv\text{O}$) are 121 pm and 110 pm respectively. The carbon-oxygen bond lengths in CO_2 (115 pm) lie between the values for $\text{C}=\text{O}$ and $\text{C}\equiv\text{O}$. Obviously, a single Lewis structure cannot depict this position and it becomes necessary to write more than one Lewis structures and to consider that the structure of CO_2 is best described as a hybrid of the canonical or resonance forms I, II and III.

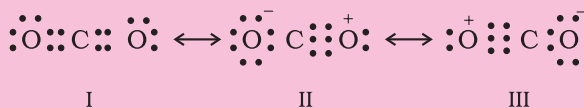


Fig. 4.5 Resonance in CO_2 molecule, I, II and III represent the three canonical forms.

In general, it may be stated that

- Resonance stabilizes the molecule as the energy of the resonance hybrid is less than the energy of any single canonical structure; and,
- Resonance averages the bond characteristics as a whole.

Thus the energy of the O_3 resonance hybrid is lower than either of the two canonical forms I and II (Fig. 4.3).

Many **misconceptions** are associated with resonance and the same need to be dispelled. You should remember that :

- The canonical forms have no real existence.
- The molecule does not exist for a certain fraction of time in one canonical form and for other fractions of time in other canonical forms.
- There is no such equilibrium between the canonical forms as we have between tautomeric forms (*keto* and *enol*) in tautomerism.
- The molecule as such has a single structure which is the resonance hybrid of the canonical forms and which cannot as such be depicted by a single Lewis structure.

4.3.6 Polarity of Bonds

The existence of a hundred percent ionic or covalent bond represents an ideal situation. In reality no bond or a compound is either completely covalent or ionic. Even in case of covalent bond between two hydrogen atoms, there is some ionic character.

When covalent bond is formed between two similar atoms, for example in H_2 , O_2 , Cl_2 , N_2 or F_2 , the shared pair of electrons is equally attracted by the two atoms. As a result

electron pair is situated exactly between the two identical nuclei. The bond so formed is called nonpolar covalent bond. Contrary to this in case of a heteronuclear molecule like HF, the shared electron pair between the two atoms gets displaced more towards fluorine since the electronegativity of fluorine (Unit 3) is far greater than that of hydrogen. The resultant covalent bond is a polar covalent bond.

As a result of polarisation, the molecule possesses the **dipole moment** (depicted below) which can be defined as the product of the magnitude of the charge and the distance between the centres of positive and negative charge. It is usually designated by a Greek letter ' μ '. Mathematically, it is expressed as follows :

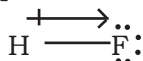
Dipole moment (μ) = charge (Q) \times distance of separation (r)

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

$$1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m}$$

where C is coulomb and m is meter.

Further dipole moment is a vector quantity and by convention it is depicted by a small arrow with tail on the negative centre and head pointing towards the positive centre. But in chemistry presence of dipole moment is represented by the crossed arrow (\rightarrow) put on Lewis structure of the molecule. The cross is on positive end and arrow head is on negative end. For example the dipole moment of HF may be represented as :

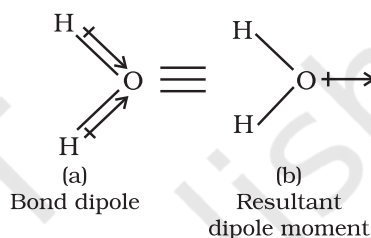


This arrow symbolises the direction of the shift of electron density in the molecule. Note that the direction of crossed arrow is opposite to the conventional direction of dipole moment vector.



Peter Debye, the Dutch chemist received Nobel prize in 1936 for his work on X-ray diffraction and dipole moments. The magnitude of the dipole moment is given in Debye units in order to honour him.

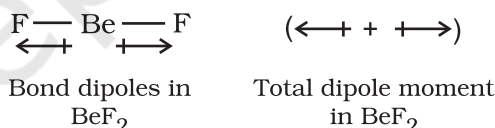
In case of polyatomic molecules the dipole moment not only depend upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such case, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. For example in H_2O molecule, which has a bent structure, the two O-H bonds are oriented at an angle of 104.5° . Net dipole moment of $6.17 \times 10^{-30} \text{ C m}$ ($1\text{D} = 3.33564 \times 10^{-30} \text{ C m}$) is the resultant of the dipole moments of two O-H bonds.



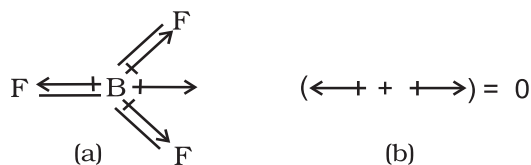
Net Dipole moment, $\mu = 1.85 \text{ D}$

$$= 1.85 \times 3.33564 \times 10^{-30} \text{ C m} = 6.17 \times 10^{-30} \text{ C m}$$

The dipole moment in case of BeF_2 is zero. This is because the two equal bond dipoles point in opposite directions and cancel the effect of each other.



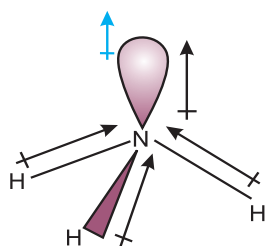
In tetra-atomic molecule, for example in BF_3 , the dipole moment is zero although the B - F bonds are oriented at an angle of 120° to one another, the three bond moments give a net sum of zero as the resultant of any two is equal and opposite to the third.



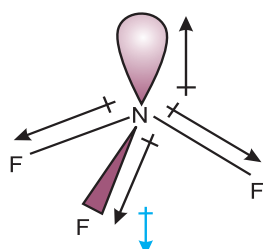
BF_3 molecule; representation of (a) bond dipoles and (b) total dipole moment

Let us study an interesting case of NH_3 and NF_3 molecule. Both the molecules have pyramidal shape with a lone pair of electrons on nitrogen atom. Although fluorine is more electronegative than nitrogen, the resultant

dipole moment of NH_3 ($4.90 \times 10^{-30} \text{ C m}$) is greater than that of NF_3 ($0.8 \times 10^{-30} \text{ C m}$). This is because, in case of NH_3 the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N – H bonds, whereas in NF_3 the orbital dipole is in the direction opposite to the resultant dipole moment of the three N – F bonds. The orbital dipole because of lone pair decreases the effect of the resultant N – F bond moments, which results in the low dipole moment of NF_3 as represented below :



Resultant dipole moment
in $\text{NH}_3 = 4.90 \times 10^{-30} \text{ C m}$



Resultant dipole moment
in $\text{NF}_3 = 0.80 \times 10^{-30} \text{ C m}$

Dipole moments of some molecules are shown in Table 4.5.

Just as all the covalent bonds have some partial ionic character, the ionic bonds also have partial covalent character. The partial covalent character of ionic bonds was discussed by Fajans in terms of the following rules:

- The smaller the size of the cation and the larger the size of the anion, the greater the covalent character of an ionic bond.
- The greater the charge on the cation, the greater the covalent character of the ionic bond.
- For cations of the same size and charge, the one, with electronic configuration $(n-1)d^n ns^0$, typical of transition metals, is more polarising than the one with a noble gas configuration, $ns^2 np^6$, typical of alkali and alkaline earth metal cations.

The cation polarises the anion, pulling the electronic charge toward itself and thereby increasing the electronic charge between the two. This is precisely what happens in a covalent bond, i.e., buildup of electron charge density between the nuclei. The polarising power of the cation, the polarisability of the anion and the extent of distortion (polarisation) of anion are the factors, which determine the per cent covalent character of the ionic bond.

4.4 THE VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

As already explained, Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict the shapes of covalent molecules. Sidgwick

Table 4.5 Dipole Moments of Selected Molecules

Type of Molecule	Example	Dipole Moment, $\mu(\text{D})$	Geometry
Molecule (AB)	HF	1.78	linear
	HCl	1.07	linear
	HBr	0.79	linear
	HI	0.38	linear
	H_2	0	linear
Molecule (AB_2)	H_2O	1.85	bent
	H_2S	0.95	bent
	CO_2	0	linear
Molecule (AB_3)	NH_3	1.47	trigonal-pyramidal
	NF_3	0.23	trigonal-pyramidal
	BF_3	0	trigonal-planar
Molecule (AB_4)	CH_4	0	tetrahedral
	CHCl_3	1.04	tetrahedral
	CCl_4	0	tetrahedral

and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Nyholm and Gillespie (1957).

The main postulates of VSEPR theory are as follows:

- The shape of a molecule depends upon the number of valence shell electron pairs (bonded or nonbonded) around the central atom.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

The repulsive interaction of electron pairs decrease in the order:

Lone pair (lp) – Lone pair (lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) – Bond pair (bp)

Nyholm and Gillespie (1957) refined the VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons. While the lone pairs are localised on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons. This results in greater repulsion between lone pairs of electrons as compared to the lone pair – bond pair and bond pair – bond pair repulsions. These repulsion effects

result in deviations from idealised shapes and alterations in bond angles in molecules.

For the prediction of geometrical shapes of molecules with the help of VSEPR theory, it is convenient to divide molecules into two categories as **(i) molecules in which the central atom has no lone pair and (ii) molecules in which the central atom has one or more lone pairs.**

Table 4.6 (page 114) shows the arrangement of electron pairs about a central atom A (without any lone pairs) and geometries of some molecules/ions of the type AB. Table 4.7 (page 115) shows shapes of some simple molecules and ions in which the central atom has one or more lone pairs. Table 4.8 (page 116) explains the reasons for the distortions in the geometry of the molecule.

As depicted in Table 4.6, in the compounds of AB₂, AB₃, AB₄, AB₅ and AB₆, the arrangement of electron pairs and the B atoms around the central atom A are : **linear, trigonal planar, tetrahedral, trigonal-bipyramidal and octahedral**, respectively. Such arrangement can be seen in the molecules like BF₃ (AB₃), CH₄ (AB₄) and PCl₅ (AB₅) as depicted below by their ball and stick models.

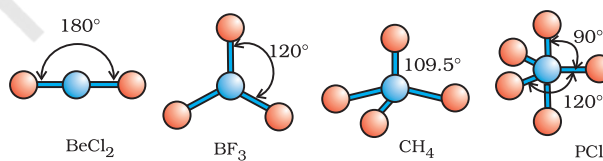


Fig. 4.6 The shapes of molecules in which central atom has no lone pair

The VSEPR Theory is able to predict geometry of a large number of molecules, especially the compounds of *p*-block elements accurately. It is also quite successful in determining the geometry quite-accurately even when the energy difference between possible structures is very small. The theoretical basis of the VSEPR theory regarding the effects of electron pair repulsions on molecular shapes is not clear and continues to be a subject of doubt and discussion.