

# **UNIT 2 PERIODICITY**

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## **2.1 INTRODUCTION**

In the preceding unit, you have studied that the properties of elements are a periodic function of their atomic numbers. As a result of their similar valence-shell electronic configuration, elements belonging to the same group of periodic table exhibit similarities in properties like valence and formulae of their highest oxides, hydrides and chlorides. Further, they also exhibit a gradation in properties with their position in the group because of the valence electrons occupying different electronic levels. For example, in Group 14 (IVA) of the periodic table, C is a non-metal, Si and Ge are semi-metals, whereas Sn and Pb are metallic elements. All these elements exhibit the highest oxidation state of 4, as the valence shells in all of these belong to  $s^2 p^2$  type. However, the stability of tetravalent species decreases down the group and bivalent species become more stable.

In Group 1 (IA) having highly electropositive alkali metals, the reactivity of elements towards water increases down the group. At 298 K, Li reacts slowly, Na reacts vigorously, K inflames whereas Rb and Cs react explosively with water. These differences in the properties arise due to differences in the atomic properties like the atomic size, ionisation energy, electron affinity and electronegativity. These atomic properties are directly related to the total electronic configurations of the elements and form an important link between the properties of elements and their electronic configuration. In this unit you will study the periodicity in these atomic properties in general and in the following units, you will learn to make use of these in explaining the trends in the properties of elements in a particular group.

### **Objectives**

After studying this unit, you should be able to:

- define atomic radii, ionisation energy, electron affinity and electronegativity,
- discuss the factors affecting atomic radii,
- describe the relationship of atomic radii with ionisation energy and electron affinity,
- describe the periodicity in atomic radii, ionisation energy, electron affinity and electronegativity.

## 2.2 ATOMIC RADII

Atomic radii are a measure of the size of the atoms. Atomic radii are important, because other atomic properties like ionisation energy, electron affinity and electronegativity can be related to them. You have studied the wave mechanical picture of an atom, according to which an atom is composed of a compact nucleus surrounded by an electron cloud. This electron cloud does not have a definite boundary surface similar to that of a ball. There is a definite but very small probability of finding an electron at an infinite distance from the nucleus of the atom. Does this mean that atom is infinitely large? This just does not make any sense. Thus, we have to find a way to define the size of an atom. **The radius of an atom can be defined as the distance from the centre of the nucleus to the point where the electron density is virtually zero.**

After we have defined the size of an atom, the problem arises as to how we are going to measure it? Thus, if we are measuring the size of an atom when it is occupying a lattice site in the crystal, the value will be different from the one when it is colliding with another atom in the gaseous state. Furthermore, the size of the neutral atom will be different from the one when it is present as a cation or anion. Consequently, we cannot have one set of atomic radii applicable under all conditions. It, therefore, becomes necessary to specify the bonding conditions under which the size is being measured. Pertaining to four major types of bonding, atomic radii are of following four types:

- i) Covalent radius
- ii) Crystal or Metallic radius
- iii) van der Waals radius
- iv) Ionic radius.

### 2.2.1 Covalent Radius

**Covalent radius is defined as one half of the distance between the nuclei of two like atoms bonded together by a single covalent bond.** If in a homonuclear diatomic molecule of A<sub>2</sub> type (e.g., F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub>),  $r_{A-A}$  is bond length or internuclear distance and  $r_A$  is the covalent radius of atom A, then  $r_A = \frac{1}{2} r_{A-A}$ .

The internuclear distance  $r_{C-C}$  between two carbon atoms in diamond is 154 pm, so the covalent radius of carbon,  $r_C$ , is equal to 77 pm. Similarly, the  $r_{Cl-Cl}$  for solid Cl<sub>2</sub> is 198 pm,  $r_{Cl}$  is, therefore, 99 pm. In a heteronuclear, diatomic molecule of AB type, if the bonding is purely covalent, then the bond length  $r_{A-B}$  is equal to the sum of covalent radii of A and B, i.e.,

$$r_{A-B} = r_A + r_B$$

Thus covalent radii are additive. It is possible to calculate the radius of one of the atoms in a heteronuclear diatomic molecule of AB type if we know the internuclear distance  $r_{A-B}$  and radius of the other atom. For example, the Si-C bond length in carborundum is 193 pm and covalent radius of C is 77 pm; so you can calculate the covalent radius of Si as follows:

$$\begin{aligned} r_{Si-C} &= r_{Si} + r_C \text{ or } r_{Si} = r_{Si-C} - r_C \\ \text{or } r_{Si} &= 193 - 77 = 116 \text{ pm} \end{aligned}$$

As stated earlier, the above relation holds good only if the bond between the atoms A and B is purely covalent. If there is a difference in the electronegativities of the bonded atoms, it causes shortening of the bonds. Schomaker and Stevenson have proposed the following relationship between the shortening of the bond and the electronegativity difference of the atoms:

$$r_{A-B} = r_A + r_B - 0.07 (X_A - X_B)^2$$

Here  $X_A$  and  $X_B$  are the electronegativities of A and B, respectively, about which you will study in Section 2.5 of this unit.

Multiplicity of the bond also causes a shortening of the bond. Usually a double bond is about 0.86 times and a triple bond about 0.78 times the single bond length for the second period elements. Covalent radii of the elements are listed in Table 2.1.

Table 2.1: Covalent and van der Waals radii of elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18				
I A	II A	III B	IV B	V B	VI B	VII B	VIIIB			I B	II B	III A	IV A	V A	VIA	VII A	VIIIA				
<b>H</b>	Covalent radius in pm van der Waals radius in pm															<b>He</b>	120				
37<																					
Li 123	Be 89															B 82	C 77	N 70 150	O 66 140	F 64 135	Ne 131
Na 156	Mg 136															Al 125	Si 117	P 110 180	S 104 190	Cl 99 185	Ar 174
K 203	Ca 174	Sc 144	Ti 132	V 122	Cr 118	Mn 117	Fe 117	Co 116	Ni 115	Cu 117	Zn 125	Ga 125	Ge 122	As 121 200	Se 117 200	Br 114 195	Kr 189				
Rb 216	Sr 191	Y 162	Zr 145	Nb 134	Mo 130	Tc 127	Ru 125	Rh 125	Pd 128	Ag 134	Cd 144	In 144	Sn 140	Sb 141 220	Te 137 220	I 133 215	Xe 210				
Cs 235	Ba 198	La 169	Hf 144	Ta 134	W 130	Re 128	Os 126	Ir 127	Pt 130	Au 134	Hg 147	Tl 155	Pb 154	Bi 148	Po 146	At —	Rn 215				
			Ce 165	Pr 165	Nd 164	Pm —	Sm 166	Eu 185	Gd 161	Tb 159	Dy 159	Ho 158	Er 157	Tm 156	Yb 170	Lu 156					

### SAQ 1

Assuming that the atoms are touching each other, what would be the internuclear distance between two fluorine atoms in  $\text{F}_2$ ?

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### 2.2.2 van der Waals Radius

In the solid state, the non-metallic elements usually exist as aggregates of molecules. The bonding within a non-metal molecule is largely covalent, yet individual molecules are held to each other by what is called van der Waals force. **Half of the distance between the nuclei of two atoms belonging to two adjacent molecules in the crystal lattice is called van der Waals radius.** Table 2.1 also lists the values of van der Waals radii of some elements.

Figure 2.1 illustrates the difference between the covalent and van der Waals radii of chlorine. It is evident from the figure that half of the distance between the nuclei X and  $X'$  of the two non-bonded neighbouring chlorine atoms of adjacent molecules A and B is the van der Waals radius of chlorine atom, whereas half of the distance between the two nuclei X and Y in the same molecule is the covalent radius of chlorine atom. Thus van der Waals radii represent the distance of the closest approach of an atom to another atom it is in contact with, but not covalently bound to it. Values of van der Waals radii are larger than those of covalent radii because the van der Waals forces are much weaker than the forces operating between atoms in a covalently bonded molecule.

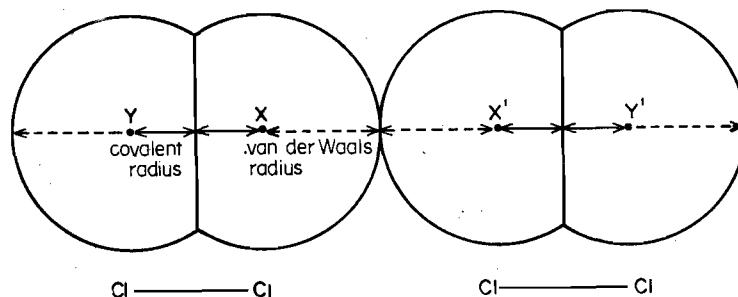


Fig. 2.1: Covalent and van der Waals radii of solid chlorine

### 2.2.3 Metallic or Crystal Radius

Metallic or crystal radius is used to describe the size of metal atoms which are assumed to be closely packed spheres in the metallic crystal. The metal atoms are supposed to touch one another in the crystal. **Metallic radius is defined as one-half of the distance between the nuclei of two adjacent metal atoms in the close packed crystal lattice.** For example, the internuclear distance between two adjacent Na atoms in a crystal of sodium metal is 382 pm, so the metallic radius of Na metal is  $382/2$ , i.e., 191 pm.

The metallic radius depends to some extent on the crystal structure of the metal. Most metals adopt a close packed lattice, either hexagonal close packed (hcp) or cubic close packed (ccp) lattice (Fig. 2.2).

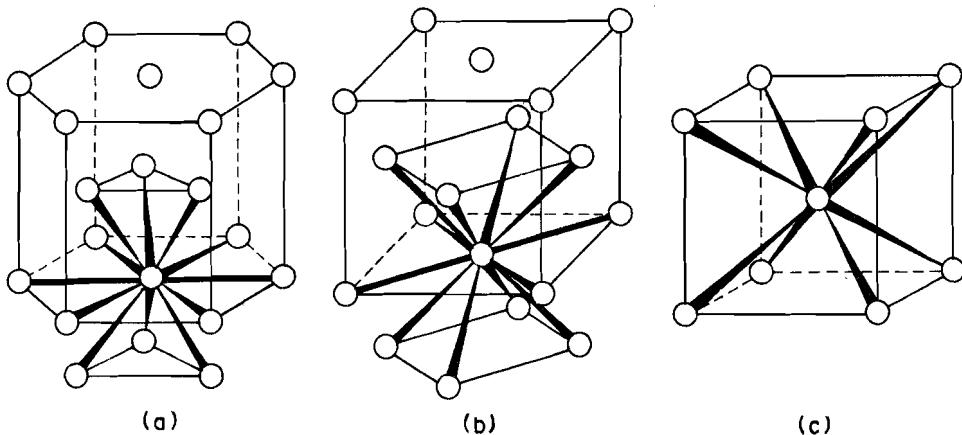


Fig. 2.2: Types of metal lattices: (a) hexagonal; (b) cubic close packed (c) body-centred cubic

In both these structures, a given metal atom has twelve nearest neighbours. However, a significant number of metals adopt a body centred cubic lattice (bcc) in which the number of nearest neighbours is eight. The number of nearest neighbours of a metal atom in a lattice is known as the **coordination number** of the metal. Experimental studies on a number of metals having more than one crystal lattice have shown that the radius of a metal in a eight coordinate lattice is about 0.97 of the radius of the same metal in a twelve coordinate environment. Table 2.2 gives a set of twelve coordinate radii for metal atoms which can be compared with the covalent radii or van der Waals radii in Table 2.1.

The metallic radii are generally larger than the corresponding covalent radii, although both involve a sharing of electrons. This is because the average **bond order** of an individual metal-metal bond is considerably less than one and therefore, the individual bond is weaker and longer than a covalent bond. This does not mean that the overall bonding is weak, as there is a large number of these bonds, eight or twelve per metal atom. On the other hand, the metallic radii are smaller than the van der Waals radii, since the bonding forces in the metallic crystal lattice are much stronger than the van der Waals forces.

### 2.2.4 Ionic Radius

Ionic radius is defined as the distance between the nucleus of an ion and the point upto which the nucleus has influence on the electron cloud. In other words, it may also be defined as the distance of the closest approach from the centre of ion by another ion. Ionic radius is usually evaluated from the distance determined experimentally between the centres of nearest neighbours. Thus, if we wish to estimate the ionic radius of  $\text{Na}^+$ , we may measure the internuclear distance between  $\text{Na}^+$  and  $\text{Cl}^-$  ions in the  $\text{NaCl}$  crystal lattice. This distance is the sum of radii of  $\text{Na}^+$  and  $\text{Cl}^-$  ions. From the electron density maps obtained by X-ray analysis, it has become possible, in some cases, to apportion the internuclear distance into the radius of cation and anion. A small number of ionic crystals have thus been studied and the ionic radii of some of the elements have been determined. These radii have become the basis for assigning the ionic radii of most of the other elements.

Ionic radii are of two types: cation radii and anion radii. All common cations are smaller than all common anions except for the rubidium and caesium cations (largest single atom cations) which are larger than oxide and fluoride anions (smallest single atom anions). This is not too surprising, since not only there is a loss of electron(s) from a partially filled outer

shell on cation formation, but there is also an increase in the overall positive charge on the ion. Conversely, in anion formation, the addition of an electron to an atom increases the size due to increase in inter-electronic repulsion in the valence-shell and decrease in effective nuclear charge. In general, there is a decrease in size from anions, to covalent radii of corresponding atoms to cations. Thus in a series of isoelectronic species (e.g.,  $\text{N}^{3-}$ ,  $\text{O}^{2-}$ ,  $\text{Ne}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ), the greater the effective nuclear charge, the smaller is the radius of the species. In Table 2.2 radii of some of the common ions have been listed.

Table 2.2: Metallic and ionic radii of elements.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18				
IA	IIA	IIIB	IVB	V	VIIB	VIIIB		VIIIIB		IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA				
<b>H</b> 208(-1)																<b>He</b>					
<b>Li</b> 155 60(+1)	<b>Be</b> 112 31(+2)															<b>B</b> 98 20(+3)	<b>C</b> 91 15(+4) 260(-4)	<b>N</b> 11(+5) 171(-3)	<b>O</b> 9(+6) 140(-2)	<b>F</b> 7(+7) 136(-1)	<b>Ne</b>
<b>Na</b> 190 95(+1)	<b>Mg</b> 160 65(+2)															<b>Al</b> 143 50(+3)	<b>Si</b> 132 41(+4) 271(-4)	<b>P</b> 128 34(+5) 212(-3)	<b>S</b> 29(+6) 184(-2)	<b>Cl</b> 26(+7) 181(-1)	<b>Ar</b>
<b>K</b> 235 133(+1)	<b>Ca</b> 197 99(+2)	<b>Sc</b> 164 81(+3)	<b>Ti</b> 147 76(+3) 68(+4)	<b>V</b> 135 74(+3) 60(+4)	<b>Cr</b> 130 84(+2) 69(+3)	<b>Mn</b> 135 80(+2) 66(+3)	<b>Fe</b> 126 76(+2) 64(+3)	<b>Co</b> 125 74(+2) 63(+3)	<b>Ni</b> 125 72(+2) 62(+3)	<b>Cu</b> 128 96(+1) 69(+2)	<b>Zn</b> 137 74(+2) 62(+3)	<b>Ga</b> 141 113(+1) 53(+4)	<b>Ge</b> 137 93(+2) 53(+4)	<b>As</b> 129 47(+5) 222(-3)	<b>Se</b> 140 42(+6) 198(-2)	<b>Br</b> 39(+7) 195(-1)	<b>Kr</b>				
<b>Rb</b> 248 148(+1)	<b>Sr</b> 215 113(+2)	<b>Y</b> 178 93(+3)	<b>Zr</b> 160 80(+4)	<b>Nb</b> 146 70(+5)	<b>Mo</b> 139 68(+4) 62(+6)	<b>Tc</b> 136 69(+3) 67(+4)	<b>Ru</b> 134 69(+3)	<b>Rh</b> 134 86(+2)	<b>Pd</b> 137 86(+2)	<b>Ag</b> 144 126(+1)	<b>Cd</b> 154 97(+2) 81(+3)	<b>In</b> 166 132(+1) 71(+4)	<b>Sn</b> 162 112(+2) 71(+4)	<b>Sb</b> 159 62(+5) 245(-3)	<b>Te</b> 160 56(+6) 221(-2)	<b>I</b> 50(+7) 216(-1)	<b>Xe</b>				
<b>Cs</b> 267 169(+1)	<b>Ba</b> 222 135(+2)	<b>La</b> 188 115(+3)	<b>Hf</b> 160 81(+4)	<b>Ta</b> 149 73(+5)	<b>W</b> 141 68(+4) 64(+6)	<b>Re</b> 137 69(+4)	<b>Os</b> 135 69(+4)	<b>Ir</b> 136 66(+4)	<b>Pt</b> 139 96(+2)	<b>Au</b> 146 137(+1)	<b>Hg</b> 157 110(+2) 95(+3)	<b>Tl</b> 171 140(+1)	<b>Pb</b> 175 120(+3) 84(+4)	<b>Bi</b> 170 120(+3) 74(+5)	<b>Po</b> 176 120(+3)	<b>At</b>	<b>Rn</b>				

### SAQ 2

Fill in the blanks in the following statements about atomic radii:

- Atomic radii are of four types:
  - .....
  - .....
  - .....
  - .....
- van der Waals radii are always ..... than the covalent radii of the same atoms.
- Covalent radius of an atom is larger than the ..... radius and ..... than the anion radius of the same atom.
- In isoelectronic species, anion radius is always ..... than the cation radius.

### 2.2.5 Factors Affecting the Atomic Radii

So far we have defined different types of atomic radii. Before describing periodicity in atomic radii, we shall first discuss two of the factors which affect them.

- Principal Quantum Number ( $n$ ):** As the principal quantum number ( $n$ ) increases, the outer electrons get farther and farther away from the nucleus and hence the atomic radius generally increases.
- Effective Nuclear Charge ( $Z^*$ ):** You know that the magnitude of effective nuclear

charge determines the magnitude of the force of attraction exerted by the nucleus on the outermost electrons. Greater the magnitude of effective nuclear charge, greater is the force exerted by the nucleus on the outermost electrons. Hence, the electron cloud of the outermost shell is pulled inward nearer to the nucleus and consequently its distance from the nucleus, i.e., atomic radius decreases.

Effective nuclear charge,  $Z^*$ , is the amount of positive charge felt by the outer electrons in an atom. It is always less than the actual charge,  $Z$ , of the nucleus of the atom. This is because electrons in inner shells partially shield the electrons in the outer shell from nuclear attraction. The effective nuclear charge felt by an outer electron depends upon the actual nuclear charge and the number and type of inner screening electrons. It can be calculated by subtracting the screening or shielding constant,  $S$ , from the atomic number,  $Z$ . Thus,

$$Z^* = Z - S$$

You can estimate the value of screening constant,  $S$ , with the help of Slater's rules in the following manner:

- i) Write out the electronic configuration of the element in the following order and groupings: (1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) (5d) (5f) (6s, 6p), etc.
- ii) Electrons in any group higher in this sequence than the electron under consideration contribute nothing to  $S$ . For example, in Ti atom (electronic configuration,  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$ ), the two electrons in  $4s$  orbital will contribute nothing towards the screening constant for an electron in  $3d$  orbital.
- iii) Then for an electron in an  $ns$  or  $np$  orbital
  - a) All other electrons in the ( $ns$ ,  $np$ ) group contribute  $S = 0.35$  each except for the electron in  $1s$  which contributes  $S = 0.30$ .
  - b) All electrons in the ( $n-1$ ) shell contribute  $S = 0.85$  each.
  - c) All electrons in ( $n-2$ ) or lower shells contribute  $S = 1.00$  each.
- iv) For an electron in an  $nd$  or  $nf$  orbital,
  - a) All electrons in the same group, i.e.,  $nd$  or  $nf$  contribute  $S = 0.35$  each;
  - b) Those in the groups lying lower in the sequence than the  $nd$  or  $nf$  group contribute  $S = 1.00$  each.

To demonstrate the application of Slater's rules we shall now calculate the  $Z^*$  for an electron in N, K and Zn atoms.

- i) Electronic configuration of N =  $1s^2 2s^2 2p^3$ . Grouping of the orbitals gives  $(1s^2)$  ( $2s^2 2p^3$ ).

Value of screening constant for an electron in  $2p$  orbital will be

$$S = (4 \times 0.35) + (2 \times 0.85) = 3.10. \text{ Hence,}$$

$$Z^* = Z - S = 7 - 3.10 = 3.90$$

- ii) Electronic configuration of K =  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ . Grouping of orbitals will be  $(1s^2)$  ( $2s^2 2p^6$ ) ( $3s^2 3p^6$ ) ( $4s^1$ ). Value of screening constant for an electron in  $4s$  orbital will be  $S = (0.85 \times 8) + (1 \times 10) = 16.80$

Hence, the effective nuclear charge

$$Z^* = Z - S = 19 - 16.80 = 2.20$$

- iii) Electronic configuration of Zn =  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$ . Grouping of the orbitals gives

$$(1s^2) (2s^2 2p^6) (3s^2 3p^6) (3d^{10}) (4s^2)$$

Value of screening constant  $S$  for an electron in  $4s$  orbital will be

$$S = (0.35 \times 1) + (0.85 \times 18) + (1 \times 10) \\ = 25.65$$

Hence, the effective nuclear charge felt by  $4s$  electron will be

$$Z^* = Z - S = 30 - 25.65 = 4.35$$

If we consider a  $3d$  electron in Zn, the grouping is as above, but the effective nuclear charge felt by a  $3d$  electron will be

$$Z^* = Z - S = 30 - [(9 \times 0.35) + (18 \times 1.00)] = 8.85$$

Thus, you can see that an electron in  $3d$  orbitals in Zn is more strongly held by the nucleus than that in  $4s$  orbital.

In Table 2.3 values of effective nuclear charge for electrons in valence shell for the first thirty elements calculated by Slater's rules have been listed. You can see from Table that there is a steady increase in Slater's  $Z^*$  across rows of the periodic table.

Effective nuclear charge felt by electrons also depends on the oxidation state of an atom in a compound. The higher the oxidation state of the atom, the higher will be the effective nuclear charge felt by the electrons and therefore, smaller will be the atomic radius. Thus, the ionic radius of  $\text{Fe}^{3+}$  ion will be smaller than that of the  $\text{Fe}^{2+}$  ion. Similarly the covalent radius of bromine in  $\text{BrCl}_3$  will be smaller than that in  $\text{BrCl}$ .

**Table 2.3: Effective nuclear charge for first 30 elements**

Period	Element	Z	S	$Z^*$
1	H	1	0	1.0
	He	2	0.30	1.70
2	Li	3	1.70	1.30
	Be	4	2.05	1.95
	B	5	2.40	2.60
	C	6	2.75	3.25
	N	7	3.10	3.90
	O	8	3.45	4.55
	F	9	3.80	5.20
	Ne	10	4.15	5.85
3	Na	11	8.80	2.20
	Mg	12	9.15	2.85
	Al	13	9.50	3.50
	Si	14	9.85	4.15
	P	15	10.20	4.80
	S	16	10.55	5.45
	Cl	17	10.90	6.10
	Ar	18	11.25	6.75
4	K	19	16.80	2.20
	Ca	20	17.15	2.85
	Sc	21	18.0	3.0
	Ti	22	18.85	3.15
	V	23	19.70	3.30
	Cr	24	20.55	3.45
	Mn	25	21.40	3.60
	Fe	26	22.25	3.75
	Co	27	23.10	3.90
	Ni	28	23.95	4.05
	Cu	29	24.80	4.20
	Zn	30	25.65	4.35

### SAQ 3

Compare the variation in the values of Slater's effective nuclear charge for the valence electron in the elements of period 2 with that in the elements of 3d series.

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### 2.2.6 Periodicity in the Atomic Radii

After having an overview of the various types of atomic radii and the factors affecting them, we will now consider the periodicity in them. But before doing that, we would like to emphasise that trends observed in one type of radii (e.g., covalent radii) are generally found in the other types of radii also (e.g., ionic and metallic radii). Two general periodic trends are found for all four types of atomic radii. These are: the atomic radii decrease along a period and generally increase down a group in the long form of the periodic table (Fig. 2.3). These changes in the atomic radii can be related to the changes in effective nuclear charge and the principal quantum number in the periodic table.

In Table 2.3, we have listed Slater's values of effective nuclear charge for the first thirty elements. As shown in this Table, there is a steady increase (by 0.65 units) in the value of  $Z^*$  from alkali metals to halogens for the elements of period 2 and 3. But there is no change in

the value of  $n$  because the electrons fill the same principal shell. As a result of this, there is a steady decrease in the covalent radius from 123 and 156 pm, for Li and Na to 64 and 99 pm for F and Cl, respectively.

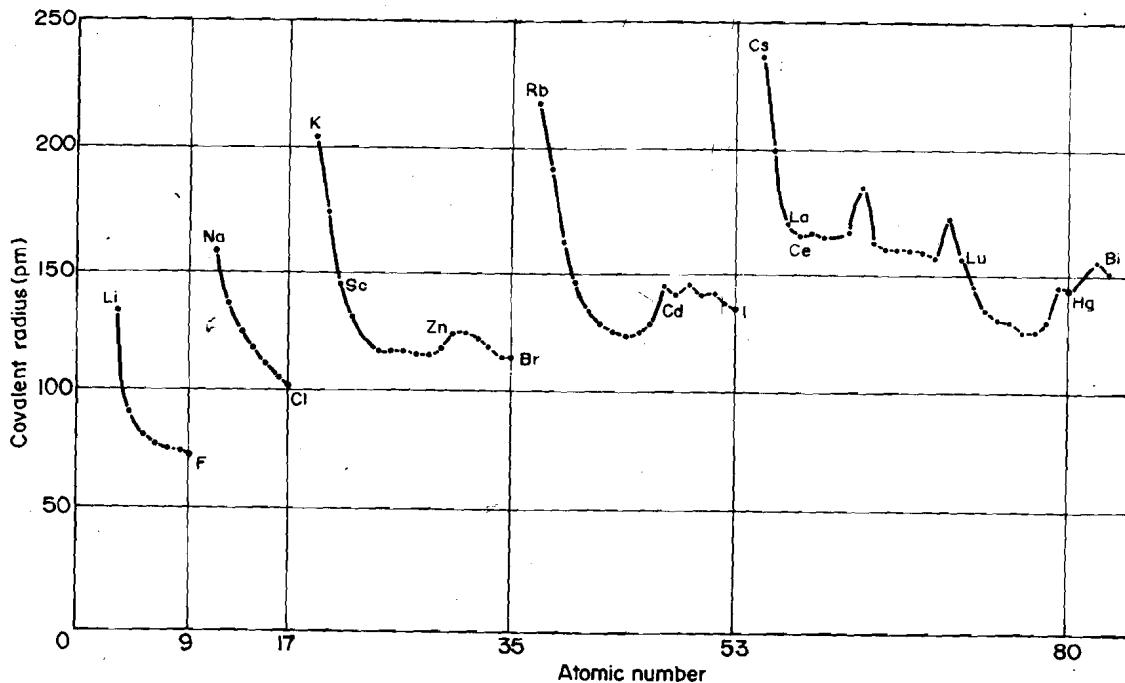


Fig. 2.3: Variation of covalent radius with atomic number

In comparison to the above, the decrease in covalent radii across a transition series is much smaller. As you know, electrons are successively filled in the  $(n-1)d$  orbitals across a transition series and hence screen the size determining  $ns$  electrons from the nuclear charge more effectively. Therefore, across a transition series, there is only a small increase in effective nuclear charge (by 0.15 units), therefore, only a small decrease in atomic radius from one element to another takes place. Thus, in  $3d$  series, covalent radius decreases from 144 pm for Sc to 115 pm for Ni. Then, in copper and zinc due to completion of  $3d$  subshell, the electronic charge density in this subshell becomes very high which increases the interelectronic repulsion. As a result, covalent radii of Cu and Zn increase slightly to 117 and 125 pm, respectively. Thus, across ten elements of the first transition series, there is an overall decrease in covalent radius by 19 pm which is much less than that across seven normal elements of period 2 (59 pm) and period 3 (57 pm). But due to this, the covalent radii of elements from Ga to Kr, following Zn, become much smaller than that expected by simple extrapolation of the values for elements of period 2 and 3. For example, the covalent radii of Al and Ga are equal whereas the covalent radii of elements Ge, As, Se, Br are only slightly larger than those of corresponding elements (Si, P, S, and Cl) of period 3.

The rate of decrease in the size across the lanthanide series is even less than that across the first transition series. In the lanthanide elements, filling of  $(n-2)f$  orbitals takes place, while simultaneously the nuclear charge increases. The electrons in the  $(n-2)f$  orbitals shield the  $ns$  electrons, which largely determine the size, from the increase in nuclear charge almost completely ( $S = 1.00$ ). As a result of this, there is only a small decrease in the atomic radius from one element to another. But there are 14 elements in the series, there is a total contraction of 13 pm across the series from La ( $Z = 57$ ) to Lu ( $Z = 71$ ). This is known as lanthanide contraction, because of which the atoms of elements (Hf to Hg) following Lu are unusually smaller than they would be if the lanthanides had not been built up before them. Lanthanide contraction almost exactly cancels out the effect of the last shell added in the sixth period and therefore, the transition elements of  $4d$  and  $5d$  series have almost the same atomic radii.

On descending any group of the periodic table, the number of electrons in the valence shell remains constant but the number of shells around nucleus increases monotonically. The effective nuclear charge felt by valence electrons stays nearly the same. So, with the increase in principal quantum number ( $n$ ) of the valence shell, an increase in atomic radii is generally observed down any group of the periodic table. For example, as shown in Fig. 2.4, there is

an increase in the atomic radii of alkali and alkaline earth metals as we proceed downwards in the group. But as discussed earlier, with the inclusion of  $3d$  transition elements in period 4, increase in the radii of elements from Ga to Br is smaller than expected. Similarly, because of inclusion of lanthanide elements in period 6, atoms of the transition elements of this period (Hf to Hg) are almost of the same size as the atoms above them in period 5 (Zr to Cd). After that only a small increase in size of the remaining elements of period 6 (Tl to At) as compared to the size of elements above them in period 5 (In to I) is observed.

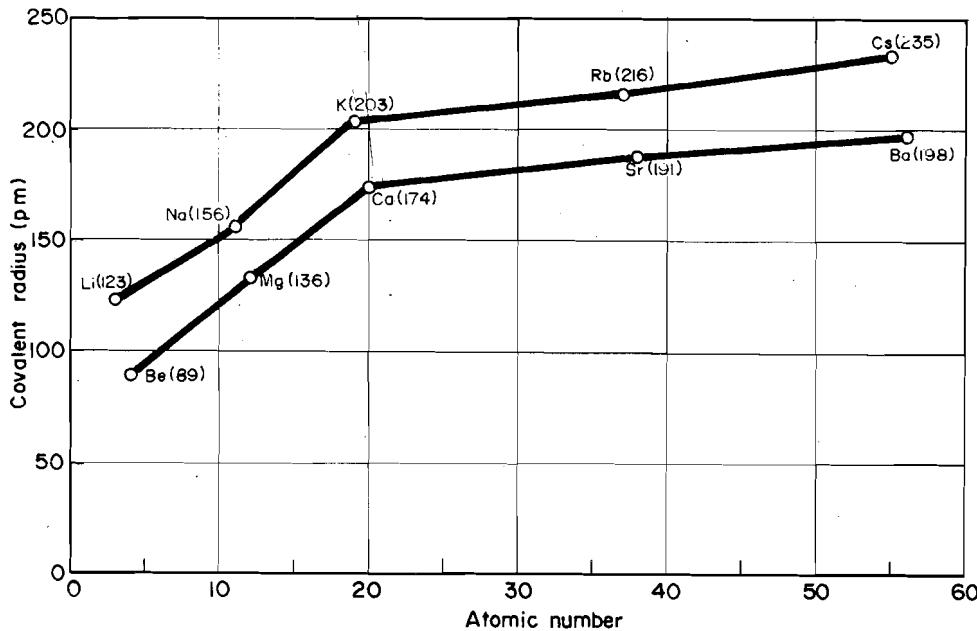


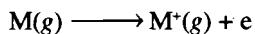
Fig. 2.4: Variation of covalent radius with atomic number down the group.

#### SAQ 4

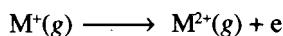
- a) For each of the following pairs, tick ( $\checkmark$ ) the one which is larger in size?
- Na,  $\text{Na}^+$
  - Br,  $\text{Br}^-$
  - Br, I
  - O, S
  - $\text{K}^+$ ,  $\text{Cl}^-$
  - Li, F
- b) Arrange the following isoelectronic species in order of decreasing atomic radius:
- $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Si}^{4+}$ ,  $\text{N}^{3-}$ ,  $\text{O}^{2-}$ ,  $\text{F}^-$ , Ne.
- .....

## 2.3 IONISATION ENERGY

Chemical reactivity of an element has a direct relation with its tendency to gain, lose or share its valence electrons with those of other elements. This process of gain, loss or sharing of electrons is accompanied by energy changes. You know that electrons are bound to the nucleus of an atom by an electrostatic force of attraction. To remove an electron from an atom, this force of attraction would have to be overcome. This can be done by supplying energy. **Energy required to remove the least strongly bound electron from an isolated gaseous atom in its ground state is known as the ionisation energy.** You can represent this process by the following equation:



Since more than one electron may be removed from an atom, the energy required for the above process is called the first ionisation energy. Second ionisation energy is the energy required to remove an electron from a univalent cation, that is, to cause the following reaction to occur:



Second ionisation energy is much larger than the first ionisation energy, as in this case an electron is being removed from a positively charged cation. Similarly you can define third, fourth and higher ionisation energies. **SI unit of ionisation energy which we will use throughout this course is kilojoule per mole.**

### 2.3.1 Factors Affecting Ionisation Energy

The ionisation energy,  $I$ , of an outer valence electron is related to the effective nuclear

charge felt by the electron and its average distance from the nucleus as given below:

$$I = \frac{Z^* \cdot e^2}{2} \cdot (1/r)av$$

where  $Z^*$  is the effective nuclear charge,  $e$  is the charge on electron and  $(1/r)av$  is the average value of  $1/r$ ,  $r$  being the distance of the electron from the nucleus. Thus, the higher is the effective nuclear charge felt by the electron, the higher will be the ionisation energy; also the farther the electron is from the nucleus, the lower will be the ionisation energy and vice versa.

In addition to the above, ionisation energy also depends upon the relative stabilities of the subshells from which the electron is removed. As we have stated before, completely filled and half filled subshells are comparatively more stable. So, removal of an electron from them requires more energy. The valence shell electronic configurations of noble gases are exceptionally stable and, therefore, their ionisation energies are the highest in the respective periods. Try the following SAQ to see whether you understand the effect of various factors on ionisation energy.

#### SAQ 5

Explain briefly why is the second ionisation energy of an element always larger than the first ionisation energy.

.....  
.....  
.....  
.....

### 2.3.2 Periodicity in Ionisation Energy Across Periods

In the above sub-section, we have defined ionisation energy and have identified the factors which affect it. Now, we shall examine the variation in ionisation energy across the periods and down the groups in the periodic table. Values of ionisation energies of elements are given in Table 2.4.

Table 2.4: Ionisation energies of elements in  $\text{kJ mol}^{-1}$

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	
<b>H</b> 1312																	<b>He</b> 2372	
<b>Li</b> 520	<b>Be</b> 900												<b>B</b> 800	<b>C</b> 1086	<b>N</b> 1403	<b>O</b> 1314	<b>F</b> 1681	<b>Ne</b> 2081
<b>Na</b> 495	<b>Mg</b> 738												<b>Al</b> 577	<b>Si</b> 787	<b>P</b> 1060	<b>S</b> 1000	<b>Cl</b> 1255	<b>Ar</b> 1520
<b>K</b> 418	<b>Ca</b> 590	<b>Sc</b> 633	<b>Ti</b> 659	<b>V</b> 650	<b>Cr</b> 653	<b>Mn</b> 717	<b>Fe</b> 762	<b>Co</b> 759	<b>Ni</b> 736	<b>Cu</b> 745	<b>Zn</b> 906	<b>Ga</b> 579	<b>Ge</b> 760	<b>As</b> 946	<b>Se</b> 941	<b>Br</b> 1142	<b>Kr</b> 1350	
<b>Rb</b> 403	<b>Sr</b> 549	<b>Y</b> 615	<b>Zr</b> 659	<b>Nb</b> 664	<b>Mo</b> 688	<b>Tc</b> 697	<b>Ru</b> 711	<b>Rh</b> 720	<b>Pd</b> 804	<b>Ag</b> 731	<b>Cd</b> 867	<b>In</b> 558	<b>Sn</b> 707	<b>Sb</b> 833	<b>Te</b> 869	<b>I</b> 1007	<b>Xe</b> 1170	
<b>Cs</b> 374	<b>Ba</b> 502	<b>La</b> 541	<b>Hf</b> 674	<b>Ta</b> 745	<b>W</b> 770	<b>Re</b> 761	<b>Os</b> 837	<b>Ir</b> 879	<b>Pt</b> 870	<b>Au</b> 890	<b>Hg</b> 1006	<b>Tl</b> 589	<b>Pb</b> 715	<b>Bi</b> 703	<b>Po</b> 813	<b>At</b> 912	<b>Rn</b> 1037	
			<b>Ce</b> 540	<b>Pr</b> 527	<b>Nd</b> 527	<b>Pm</b> 540	<b>Sm</b> 540	<b>Eu</b> 547	<b>Gd</b> 594	<b>Tb</b> 577	<b>Dy</b> 573	<b>Ho</b> 582	<b>Er</b> 586	<b>Tm</b> 561	<b>Yb</b> 598	<b>Lu</b> 594		

However, the variation of ionisation energy in a particular group or period, is best shown by plotting ionisation energies against atomic number. Fig. 2.5 shows the plot of first ionisation energies of the elements of first six periods against their atomic numbers. As is evident from the figure, the first ionisation energy generally increases from alkali metals to noble gases

across any row of the periodic table. But the increase is not perfectly regular. We will consider this aspect a little later.

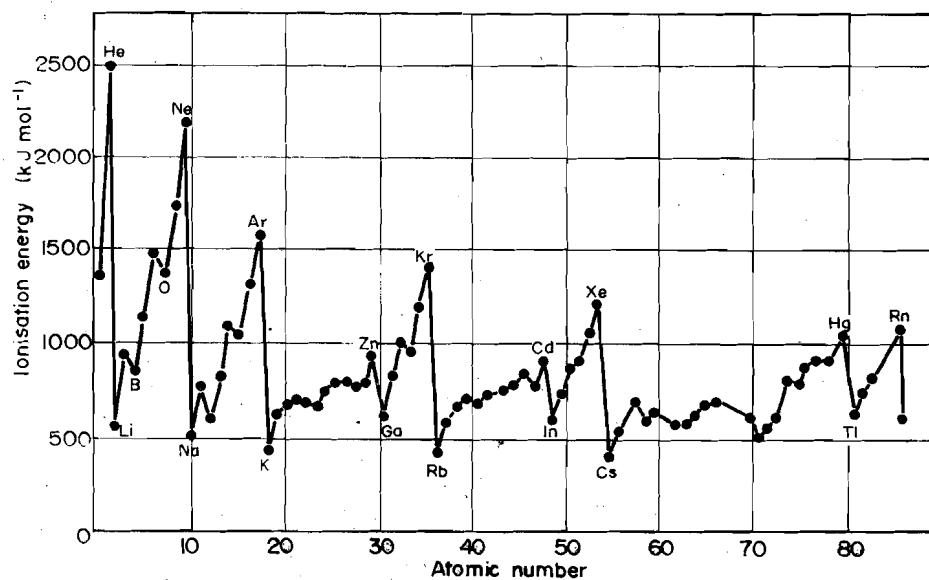


Fig. 2.5: Variation of ionisation energy with atomic number

You have studied in Sub-section 2.2.6 that across any row of the periodic table, the effective nuclear charge steadily increases and the atomic radii decrease. These two effects reinforce each other to increase the ionisation energy across a period. Thus, the ionisation energies of the alkali metals are the lowest and those of the noble gases are the highest in their respective periods. But as pointed out earlier, the increase is not smooth and some anomalies are observed. For example, in the elements of period 2, inspite of increase in  $Z^*$  and decrease in  $r$ , the first ionisation energies of B and O are lower than those of Be and N, respectively. However, these anomalies in the trend in ionisation energy can be explained by electronic structures of these elements.

In case of beryllium, the electron is removed from the filled  $2s$  subshell, whereas in boron, the electron is removed from the singly occupied  $2p$  subshell. The  $2p$  subshell is higher in energy than the  $2s$ . So, the  $2p$  electron of boron is more easily removed than a  $2s$  electron of beryllium. When we come to nitrogen, we find that we have a half filled  $2p$  subshell (electronic configuration  $1s^2 2s^2 2p^3$ ), while in oxygen the  $2p$  subshell is occupied by four electrons. The fourth electron in this  $2p$  subshell is in an orbital already occupied by another electron. So, it experiences considerable repulsion. As a result, this electron is more easily removed than one of the electrons from a singly occupied orbital in nitrogen atom. Thus, the ionisation energy of oxygen becomes less than that of nitrogen. Similar anomalies are observed in elements of period 3, where the first ionisation energies of magnesium and phosphorus are higher than those of aluminium and sulphur, respectively.

You have studied in Sub-section 2.2.6, that across a transition series, the increase in effective nuclear charge and consequent decrease in atomic radius is small. Therefore, increase in their first ionisation energies is also small. But following the transition elements, the first ionisation energy drops abruptly in gallium, indium and thallium. This again is due to the removal of an electron from the singly occupied  $np$  orbitals which are of relatively higher energy than the  $ns$  orbitals of Zn, Cd and Hg.

### 2.3.3 Trends in Ionisation Energy Down the Groups

In Sub-section 2.2.6, you have already studied that on moving down a group of  $s$ -and  $p$ -block elements in the periodic table, effective nuclear charge remains almost steady. But there is a general increase in the atomic radius due to increase in the value of the principal quantum number,  $n$ . Thus, the dominant factor in determining the ionisation energies of the elements on moving down the groups, is their atomic radius rather than the effective nuclear charge. Therefore, as expected, the first ionisation energies decrease down the groups in case of the main group elements in the periodic table. But in the case of transition elements opposite trends are observed. Thus, the first ionisation energies of the corresponding elements of  $3d$  and  $4d$  series are almost similar but these are smaller than the first ionisation

energies of the elements of *5d* series. Certainly, the higher values of ionisation energies of the *5d* transition elements are consistent with the relatively smaller size of their atoms.

### 2.3.4 Trends in Successive Ionisation Energies

We have already defined successive ionisation energies, i.e., second, third, etc. Values of eight successive ionisation energies of first twenty elements are listed in Table 2.5.

**Table 2.5: Successive ionisation energies (kJ mol<sup>-1</sup>) of first 20 elements**

	First	Second	Third	Fourth	Fifth	Sixth	Seventh	Eighth
H	1 312							
He	2 372	5 250						
Li	520	7 297	11 810					
Be	900	1 757	14 850	21 000				
B	800	2 427	3 658	25 024	32 824			
C	1 086	2 352	4 619	6 220	37 820	47 280		
N	1 403	2 858	4 578	7 473	9 443	53 270	64 360	
O	1 314	3 391	5 300	7 469	10 983	13 326	71 330	84 050
F	1 681	3 381	6 046	8 418	11 017	15 163	17 870	92 000
Ne	2 081	3 964	6 150	9 376	12 200	15 230	—	—
Na	495	4 563	6 912	9 540	13 350	16 732	20 110	25 490
Mg	738	1 450	7 730	10 550	13 625	18 035	21 735	25 660
Al	577	1 816	2 745	11 575	14 850	18 370	23 350	27 460
Si	787	1 577	3 230	4 355	16 090	19 795	23 770	29 250
P	1 060	1 869	2 908	4 954	6 272	21 270	25 413	29 840
S	1 000	2 258	3 381	4 565	6 995	8 494	27 112	31 720
Cl	1 255	2 297	3 849	5 163	6 540	9 330	11 029	33 600
Ar	1 520	2 665	3 947	5 770	7 238	8 810	11 965	13 840
K	418	3.069	4 439	5 875	7 950	9 619	11 384	14 950
Ca	590	1 146	4 941	6 464	8 142	10 500	12 350	13 830

It is evident from the values in the Table that the successive ionisation energies of an element inevitably become larger because the removal of successive electrons leaves a higher charge on the nucleus to hold the remaining electrons. It is also clear from the Table that the difference between successive ionisation energies of the same element is not constant. Big jumps occur whenever an electron from a subshell of lower principal quantum number is removed for the first time. For example, for alkali metals the second ionisation energies are much higher than the first; for alkaline earth metals the third ionisation energies are much larger than the second and for the halogens the eighth ionisation energies are much greater than the seventh. These cannot be explained on the basis of increase in nuclear charge alone. The stabilities of closed shell configurations similar to those of noble gases are more important in these cases.

In this section so far you have studied that the ionisation energy generally increases across a period and decreases down the group in the periodic table. Accordingly, the tendency to form cation, i.e., metallic character decreases across a period and increases down the group. For example, in period 3 metallic character decreases from Na to Cl whereas in the elements of Group 14, C is a nonmetal, Si and Ge are semimetals or metalloids whereas Sn and Pb are metals.

#### SAQ 6

a) Which of the atoms having following electronic configurations will have the highest first ionisation energy and why?

- i) [Ne] 3s<sup>2</sup> 3p<sup>2</sup>
  - ii) [Ne] 3s<sup>2</sup> 3p<sup>3</sup>
  - iii) [Ne] 3s<sup>2</sup> 3p<sup>4</sup>
  - iv) [He] 2s<sup>2</sup> 2p<sup>3</sup>
  - v) [Ar] 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>3</sup>.
- .....  
.....  
.....

b) The order of increasing ionisation energy for the atoms N, Ne, Na and P is

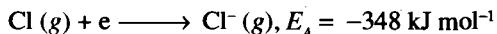
- i) Na < P < N < Ne
  - ii) N < Ne < Na < P
  - iii) N < Na < Ne < P
  - iv) Na < N < P < Ne
- .....

## 2.4 ELECTRON AFFINITY

Electron affinity of an atom is a measure of its ability to accept an electron to form an anion. It is defined as the energy released or absorbed, when an electron is added to a gaseous atom in its ground state. It can be represented by the following equation in which  $E_A$  represents the electron affinity of X:

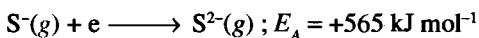
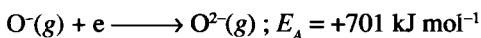


When one mole of chlorine atoms pick up one mole of electrons, 348 kJ energy is released. So, the electron affinity of chlorine is  $-348 \text{ kJ mol}^{-1}$ :

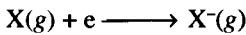


But in the reverse process of removal of an electron from the chloride ion to form a chlorine atom, obviously an equal amount of energy has to be supplied. So, the electron affinity can also be expressed as the ionisation energy of the anion. Thus, the electron affinity of chlorine atom is clearly the ionisation energy of the chloride ion. Electron affinities are difficult to measure and accurate values are not known for all elements. Values for the representative elements are given in Table 2.6.

In the preceding section, you have studied that for removing an electron from isolated neutral atoms in the gaseous state, energy is required to overcome the attractive force of the nucleus. Therefore, the reverse process of the addition of an electron to the neutral atom should release energy. Thus, the electron affinities of most elements are negative, but a few elements are known to have positive values for electron affinity which means that the electron must be forced on to the neutral atom to form an anion. For example, nitrogen, alkaline earth metals and noble gases have positive values. All second and higher electron affinities also have large positive values. This is not surprising, since the second and the subsequent electrons must be forced on against the negative charge of the anion. For example:



Here, we will like to point out that a little confusion regarding the sign convention of the electron affinity generally prevails. But we are following the standard thermodynamic convention, according to which the negative value means an exothermic process, i.e., the reaction



is exothermic. Also by high electron affinity we mean to say that the value of electron affinity is large and negative.

Table 2.6: Electron affinities of some elements in  $\text{kJ mol}^{-1}$

1	2	13	14	15	16	17	18
H							
-73							
Li	Be	B	C	N	O	F	He
-60	$\approx +100$	-27	-122	+9	-141	-328	+54
Na	Mg	Al	Si	P	S	Cl	Ne
-53	$\approx +30$	-44	-134	-72	-200	-348	+99
K	Ca	Ga	Ge	As	Se	Br	
-48	-	-30	-120	-77	-195	-325	
Rb	Sr	In	Sn	Sb	Te	I	
-47	-	-30	-121	-101	-190	-295	
Cs	Ba	Tl	Pb	Bi	Po	At	
-45	-	-30	-110	-110	-183	-270	

### 2.4.1 Factors Affecting Electron Affinity

Factors affecting electron affinities are generally the same which affect the ionisation energies. These factors are:

**Atomic radius:** When an electron adds on to any atom, the nucleus of the atom holds it by an electrostatic force of attraction, which depends upon the effective nuclear charge and size of the atom. The smaller is the size of the atom, the greater will be the force of attraction of

the nucleus for the extra electron and, therefore, higher will be the electron affinity of the atom, that is more energy will be released in picking up an electron.

**Effective nuclear charge:** The higher the effective nuclear charge, greater the force of attraction exerted by the nucleus on the added electron and hence, higher will be the electron affinity of the atom.

**Electronic configuration:** Electronic configuration of the atom also plays an important role in determining the magnitude and sign of electron affinity. Halogens can achieve a stable noble gas configuration by accepting just one electron. Therefore, they have large negative (exothermic) electron affinities. On the other hand, the noble gases with closed shell  $ns^2np^6$  configuration, beryllium and magnesium with  $ns^2$  (stable due to filled subshell) and nitrogen having  $ns^2np^3$  (stable due to half filled p subshell) configuration strongly resist the addition of any electron. Therefore, the electron affinities of these elements are either zero or have small positive values.

### 2.4.2 Periodicity in Electron Affinity

In this section you have so far studied the definition of electron affinity and have considered the factors that affect it. In this sub-section you will now learn how the electron affinity varies in the periodic table.

**Trends across periods:** On moving from left to right in a period, size of the atoms decreases and effective nuclear charge increases. Both these factors favour an increase in the force of attraction exerted by the nucleus on the extra electron. Consequently, the electron affinity generally increases across a period, though irregularly. Thus, electron affinities of alkali metals have small negative values indicating their reluctance to form an anion. On the other hand, electron affinities of halogens in a period are the highest negative values which is reflected in their ability to form anions most readily. As explained earlier, the electron affinities of noble gases, beryllium, magnesium and nitrogen have small positive values.

**Trends across groups:** You have learnt in Sub-section 2.2.6 that on moving down a group of s-and p-block elements in the periodic table, the effective nuclear charge remains almost steady, but there is a general increase in atomic radius due to increase in the value of the principal quantum number,  $n$ . As a result, the electron affinity generally decreases down any group in the periodic table, as is evident from the values listed in Table 2.6. Values of electron affinities of second row nonmetals, i.e., B, C, N, O, F are, however, against the general trend, being smaller than those of corresponding elements, i.e., Al, Si, P, S, Cl of period 3. This is apparently an indirect result of the small size of the atoms of these elements, i.e., B, C, N, O, F. Thus, the crowding of electrons in the smaller outer shell of an atom of an element of period 2 makes mutual repulsion of electrons substantially greater than that in the relatively larger outer shell of an atom of an element of period 3. Therefore, even though, an electron added to an atom of an element of period 2 is closer to the nucleus than the one added to an atom of an element of period 3, greater inter-electronic repulsion in a smaller shell leads to a lower electron affinity.

#### SAQ 7

State which of the following statements are true or false. Write 'T' if true and 'F' if false.

- Values of second electron affinities are always positive.
- Electron affinity of nitrogen is much lower than that of its neighbouring elements, carbon and oxygen.
- Electron affinity of fluorine is higher than that of chlorine.
- Electron affinities of noble gases are zero..
- Electron affinities of elements of period 3 are lower than those of the corresponding elements of period 2.

## 2.5 ELECTRONEGATIVITY

In the Sections 2.3 and 2.4 you have studied ionisation energies and electron affinities of isolated gaseous atoms. These quantities are a measure of the tendency of isolated atoms to lose or gain electrons. In the present section, you will learn about electronegativity of an element, which is a measure of the power of an atom in a molecule to attract shared

electrons to itself. Unlike ionisation energy and electron affinity, it is not a directly measurable physical quantity, but rather a theoretical concept for which several numerical scales have been developed. In this section we shall discuss three of them, namely Pauling's, Allred-Rochow's and Mulliken's scales which are comparatively more important.

### 2.5.1 Pauling Electronegativity Scale

As you know, in homonuclear diatomic molecules like  $A_2$  and  $B_2$ , the electron pair is equally shared between the bonded atoms. But in a heteronuclear diatomic molecule of the AB type, the situation is quite different. In the process of formation of bond between A and B, atom A slowly starts stripping off its electron and thereby it is becoming a partially cationic species. As the positive charge develops on A, its tendency to attract electrons increases. An analogous process also takes place on B. Thus, both the atoms A and B start attracting the electron pair towards themselves. They continue doing so until the tendencies of both the atoms in the bonded state to attract the electron pair towards themselves balance. If one of the atoms, say B, has higher tendency to attract the electron pair towards itself compared to that of the other atom, say A, the electron pair will spend more time on B than on A. Partial charges will thus be generated on A and B. This tendency of attracting the electron pair towards itself by an atom in a molecule has been termed as electronegativity of the element.

This concept was first developed by Pauling. He defined it on the basis of the patterns discernible in the single bond energies of elements, which were derived from the thermochemical data. He realised that bond energy,  $E_{A-B}$ , between two unlike atoms A and B is greater than  $\sqrt{E_{A-A} \cdot E_{B-B}}$  where  $E_{A-A}$  and  $E_{B-B}$  are bond energies of A-A and B-B homonuclear bonds. He assigned the cause of this excess bond energy,  $E_{A-B} - \sqrt{E_{A-A} \cdot E_{B-B}}$ , to the electrostatic attraction between partially charged atoms ( $A^{\delta+} - B^{\delta-}$ ) in the molecule. Partial charges on the atoms are separated due to difference in electron attracting tendencies of A and B, i.e., the difference in the electronegativities of A and B. He was able to correlate the difference in electronegativities of two atoms, with the excess bond energy and derived a relationship

$$E_{A-B} - \sqrt{E_{A-A} \cdot E_{B-B}} = 96.49 (X_A - X_B)^2$$

where  $X_A$  and  $X_B$  designate electronegativities of the elements A and B, respectively and are assumed to be the same for all molecules containing A and B. You can write this relationship as

$$\Delta X_{AB}^2 = (X_A - X_B)^2 = \frac{E_{A-B} - \sqrt{E_{A-A} \cdot E_{B-B}}}{96.49}$$

$$\text{or } \Delta X_{AB} = \sqrt{\frac{E_{A-B} - \sqrt{E_{A-A} \cdot E_{B-B}}}{96.49}}$$

Knowing bond energies, it is thus possible to calculate the difference between the electronegativities of the two elements. This formula, however, gives the difference in the electronegativities and not the absolute value assigned to a particular element. As the largest electronegativity difference on this scale between the most electronegative element fluorine and the most electropositive element caesium came out to be 3.3, Pauling assigned arbitrarily a whole number value 4.0 for fluorine so that values of electronegativity of all elements remain positive. In Table 2.7, the values of electronegativity of different elements are represented in bold face as calculated by Pauling using the above formula for differences in electronegativity.

### 2.5.2 Mulliken - Jaffe Electronegativity Scale

Mulliken defined electronegativity as the mean value of first ionisation energy and first electron affinity. Both quantities are given a positive value if loss of electron involves absorption of energy and gain of electron involves release of energy. Thus, electronegativity  $X_A$  of atom A is given by the following relationship:

$$X_A = \frac{(I)_A + (E_A)_A}{2}$$

According to this relationship, a very electronegative element has a very high ionisation energy. So, it will be difficult to remove its electrons. It also has a very high electron affinity. Hence, a very stable species results when electrons are added. On the other hand, an element of low electronegativity will have a low ionisation energy and low electron affinity. So, it loses electrons readily, and has little tendency to pick them up. Unfortunately, it is

**Table 2.7: Electronegativity values of elements.**

very difficult to measure electron affinity for all elements. Therefore, this method also is not universally applicable. The electronegativity values on Mulliken's scale are about 2.8 times those of Pauling's values. The trends in the variation of electronegativities are, however, the same.

### **2.5.3 Allred-Rochow Electronegativity Scale**

According to Allred and Rochow, electronegativity is equated to the force of attraction between an atom and an electron separated by a distance equal to the covalent radius of the atom. The force of attraction is expressed according to Coulomb's law as,

$$F = \frac{Z^* e^2}{r^2}$$

where  $Z^*$  is the Slater's effective nuclear charge,  $e$  the electronic charge and  $r$  the covalent radius. A plot of Pauling electronegativities against  $Z^*/r^2$  gives an approximately straight line. Values of the slope and intercept indicate that on the Pauling scale, Allred-Rochow electronegativities are given by the numerical relationship,

$$X_A = 3590 \frac{Z^*}{r^2} + 0.744, \text{ where value of } r \text{ is in pm.}$$

This method has an advantage in that it can be applied to a comparatively larger number of elements. Electronegativities of elements on Allred-Rochow scale have been listed in Table 2.7.

**Electronegativity** is a measure of the attraction that an atom has for electrons in a bond it has formed with another atom. The ability of an atom to attract electrons depends upon the charge on the atom and the hybridisation of the atom. An atom which has acquired a positive

charge will tend to attract electrons to it more readily than will a neutral atom. In turn, a negatively charged atom will attract electrons less than a neutral atom. Hybridisation also affects electronegativity because of the lower energy and hence, greater electron attracting power of *s*-orbitals. Thus, hybrid orbitals having greater *s*-character possess higher electronegativity. An atom in *sp* hybridised state will be more electronegative than the same atom in *sp*<sup>2</sup> hybridised state which in turn will be more electronegative than the same atom in *sp*<sup>3</sup> hybridised state. Thus, the carbon atom in CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> has different values of electronegativity. So, you can say that electronegativity is not a constant quantity. All the electronegativity scales give average values of electronegativities of elements in different bonding environments.

So far, you have studied different definitions of electronegativity for which three numerical scales have been proposed. All these scales, give relative values of electronegativity which are useful in making quantitative comparisons between elements. Electronegativities can be used to predict the nature of the bonding that a compound will have. The larger the difference between the electronegativities of two elements, the more polar will be the bond between these elements. An electronegativity difference of about 1.7 corresponds to a partial ionic character of about 50%. So, a bond can be considered predominantly ionic, if the difference in the electronegativities of the bonded atoms is more than 1.7. On the contrary, a difference in the range of 0.4 to 1.7 results in a covalent bond with partial ionic character or polar covalent bond.

#### 2.5.4 Periodicity in Electronegativity

Electronegativity values of elements show a fairly discernible periodic trend throughout the periodic table. The trend is similar to that of ionisation energies. Thus, as expected electronegativity of elements increases sharply across a row of *s*-and *p*-block elements, since the effective nuclear charge of these elements is increasing sharply for example, from lithium to fluorine. However, across a series of transition elements, the increase in electronegativity is much smaller. This is because the additional electron is being added to an inner shell which provides relatively good shielding for the outer electron from the nucleus.

On moving down a group of representative elements, for example, in the lithium group, there is a general decrease in electronegativity. The decrease is relatively small except between the first two elements. The much greater electronegativity of lithium row elements correlates well with their small size. As expected, the elements of period 4 from gallium onwards, i.e., Ga, Ge, As, Se and Br have greater electronegativities than would be expected by extrapolation from values for the first two elements in the respective groups. This is due to the insertion of transition elements, because of which, the effective nuclear charge of these elements is greater than that if the transition elements were not there. Similarly, the presence of the lanthanide elements is responsible for greater electronegativities of the elements of 5*d* series than would be expected by extrapolation from values of the elements of 3*d* and 4*d* series.

#### SAQ 8

- a) Explain the difference between electron affinity and electronegativity.

.....  
.....  
.....

- b) Arrange the following elements in the order of increasing electronegativity:

Be, Li, C, B, O, F, N

.....  
.....  
.....

- c) Name the least and most electronegative elements in the periodic table.

.....

- 10 Explain why the electronegativity values of noble gases are zero while those of halogens are the highest in each period.

- 11 Which element has the higher electronegativity in the following pairs:

## 2.6 SUMMARY

In this unit you have studied that properties like atomic radii, ionisation energy, electron affinity and electronegativity are called atomic properties because they depend on the nature of individual atoms of the elements. These atomic properties are related to the electronic configuration of the atoms of elements. These vary in a more or less regular way that is to say exhibit periodicity as we go across a period of the periodic table. Therefore, these atomic properties are also called periodic properties.

Atomic radius is a measure of the size of an atom. Atomic radius depends on two factors: i) principal quantum number,  $n$  and ii) effective nuclear charge,  $Z^*$ . Atomic radius increases with increase in principal quantum when we go down a group. It decreases with increase in effective nuclear charge when we move across a period in the periodic table.

Ionisation energy is the energy required to remove an electron from a neutral gaseous atom producing a gaseous unipositive ion. Ionisation energy increases as we go across a period. There are some notable irregularities in this trend which can be explained in the light of the electronic configuration of the elements. Ionisation energy also decreases regularly as we go down a group of normal elements.

Electron affinity is a measure of the tendency of an atom or ion to acquire an electron. Most electron affinities are negative, but some are positive. A negative electron affinity means that energy is released when an atom or ion picks up an electron. As a general trend, electron affinity increases (i.e., becomes more negative) as we go across a period from left to right upto the halogens, and decrease as we go down a group of normal elements. Second and higher electron affinities are always positive because addition of an electron to an anion is difficult due to repulsion between anion and the electron being added.

Electronegativity is defined as the power of an atom in a molecule to attract electrons to itself. The most electronegative of all the elements is F; on Pauling scale its electronegativity is set at 4.0. Metals have electronegativities less than 2. The least electronegative elements are Cs and Fr, with their electronegativity of 0.7. Electronegativity increases as we go across a period from left to right, and decreases as we go down a group of normal elements in the periodic table. However, in a series of transition or inner-transition elements, value of electronegativity changes only gradually.

## 2.7 TERMINAL QUESTIONS

- 1 a) How does atomic size vary in a group and in a period? Give reasons for the variation.  
b) Arrange H, H<sup>+</sup> and H<sup>-</sup> in order of increasing atomic radius.
- 2 What are isoelectronic ions? How does their size vary with the change of atomic number?
- 3 Which is the larger member of each of the following pairs of ions?  
i) Tl<sup>+</sup> or Tl<sup>3+</sup> ii) N<sup>3-</sup> or F<sup>-</sup> iii) O<sup>2-</sup> or S<sup>2-</sup> iv) Na<sup>+</sup> or K<sup>+</sup> v) Ca<sup>2+</sup> or Zn<sup>2+</sup>
- 4 Why is the second ionisation energy of sodium higher than that of magnesium?
- 5 Among the elements Li, K, Ca, S and Ne, which ones have the lowest and highest first ionisation energy?
- 6 Among the elements of the second period, i.e., Li, Be, B, C, N, O, F, pick out:
  - i) the element with the highest first ionisation energy
  - ii) the element with the highest electronegativity
  - iii) the element with the largest atomic radius
  - iv) the most reactive nonmetal
  - v) the most reactive metal
- 7 Alkali metals and coinage metals have the same outer electronic configuration. Then, why are the alkali metals more reactive than coinage metals?
- 8 Explain why the second electron affinity values are always positive.
- 9 Explain why is the electron affinity of nitrogen much lower than that of its neighbouring elements oxygen and carbon.

- 4 The second ionisation energy of sodium is higher than that of magnesium because for removal of a second electron from the former, the stable core of 8 electrons is to be disrupted. Therefore, more energy has to be supplied. In the latter case,

10 Explain why the electronegativity values of noble gases are zero while those of halogens are the highest in each period.

Periodicity

11 Predict which element has the higher electronegativity in the following pairs:

- i) Na or Mg
- ii) O or S
- iii) C or N
- iv) F or Cl

12 Which one of the following elements has the highest electronegativity?

- a) Cl, Br, F, I
- b) O, S, C, Mg

## 2.8 ANSWERS

### Self Assessment Questions

1 Distance between two fluorine atoms in  $F_2$  molecule will be twice the covalent radius of fluorine atom.

2 a) i) covalent ii) van der Waals iii) metallic iv) Ionic  
b) larger  
c) cation, anion  
d) larger

3 In the elements of period 2, i.e., from Li to Ne the value of effective nuclear charge increases by 0.65 units whereas in the elements of 3d series it increases by 0.15 units from one element to another. In other words in the elements of period 2, it increases more steeply.

4 a) i) Na ii)  $Br^-$  iii) I iv)  $S^-$  v)  $Cl^-$  vi) Li  
b)  $N^{3-} > O^{2-} > F^- > Ne > Na^+ > Mg^{2+} > Al^{3+} > Si^{4+}$

5 Second ionisation energy of an element is always higher than the first because the second electron is to be removed from a cation having a comparatively higher effective nuclear charge than a neutral atom.

6 a) Atom having  $[He]2s^2 2p^3$  configuration will have the highest first ionisation energy because this is the smallest atom having exactly half filled p subshell.

b) i)  $Na < P < N < Ne$

7 a) True b) True c) False d) False

8 a) Electron affinity is the energy change in acquiring an electron by an isolated atom or ion, whereas electronegativity is a measure of power of an atom to attract the electron pair in a bond to itself.

b)  $Li < Be < B < C < N < O < F$

c) Caesium and francium are the least electronegative elements, whereas fluorine is the most electronegative element in the periodic table.

### Terminal Questions

1 a) Atomic size generally decreases across a period and increases down a group in the periodic table. Across a period as the atomic number increases, effective nuclear charge also increases, whereas the number of shells remains the same. As a result of this, the electrons are pulled in and the size of the atom decreases. On the other hand, when we move down a group, the effective nuclear charge remains almost the same, but the number of shells increases from one element to the next in the group. Therefore, the electrons become farther from the nucleus and the size generally increases.

b)  $H^+ < H < H^-$

2 Ions having equal number of electrons are called isoelectronic ions. In a series of isoelectronic ions, size decreases from anion to cation. The higher is the charge on the anion, the larger is its size. For a cation, the higher the charge, the smaller is its size.

3 i)  $Tl^+$  ii)  $N^{3-}$  iii)  $S^{2-}$  iv)  $K^+$  v)  $Ca^{2+}$

- 4 The second ionisation energy of sodium is higher than that of magnesium because for removal of a second electron from the former, the stable core of 8 electrons is to be disrupted. Therefore, more energy has to be supplied. In the latter case, removal of second electron leaves behind a stable core.
- 5 Among the elements, Li, K, Ca, S and Ne, K and Ne have the lowest and the highest first ionisation energies.
- 6 i) F ii) F iii) Li iv) F v) Li
- 7 Alkali metals and coinage metals have the same outer electronic configuration, but the coinage metals have higher effective nuclear charge and smaller atomic radius than those of the corresponding alkali metals. Due to this, the ionisation energies of coinage metals are much higher than those of the alkali metals. Therefore, the alkali metals are more reactive than the coinage metals.
- 8 When an electron is added to an anion, electron is repelled by the anion. Therefore, to overcome this repulsion, energy has to be supplied. So, the second electron affinities are always positive values.
- 9 Electronic configuration of nitrogen is  $1s^22s^22p^3$  which is stable due to half filled  $p$  subshell. It therefore, resists the addition of electron, thereby its electron affinity is around zero. On the other hand, addition of an electron to carbon, changes its configuration to  $1s^22s^22p^3$ , which is more stable than that of the neutral carbon atom,  $1s^22s^22p^2$ . Similarly, addition of an electron to oxygen changes its configuration to  $1s^22s^22p^5$  bringing it nearer to the configuration  $1s^22s^22p^6$  of the next higher inert gas Ne. Therefore, the electron affinities of carbon and oxygen are higher (more negative values) than that of nitrogen.
- 10 Since noble gases have a stable electronic configuration, they have no tendency to attract the bond pair to themselves. Therefore, their electronegativity is zero. On the other hand, halogens are only one electron short of noble gas configuration. So, they have a very high tendency of attracting the bond pair to themselves. Therefore, their electronegativity values are the highest in the respective periods.
- 11 i) Mg ii) O iii) N iv) F
- 12 a) F b) O