Atomic Properties : Periodic Properties

Introduction

Before proceeding to understand the topics, like chemical bonding and geometry (shape) of molecules and ions, it is necessary to have an adequate knowledge of the properties of the atoms of the elements. These properties are called **atomic properties.** These properties show a variation, when we proceed from left to right, in a period, and from top to bottom, in a group of the periodic table. These properties are, therefore, also called **periodic properties.**

The atomic properties, which we shall discuss in this chapter, are atomic and ionic radii, ionisation energies, electron affinity, eletronegativity, metallic (eletropositive) and non-metallic (electronegative) character, density, atomic volume, melting and boilong points, oxidising and reducing properties and oxidation states. These properties will be discussed in connection with main group elements.

Size of Atoms and Ions (Atomic and Ionic Radii)

Radius of an atom and of an ion

The size of an atom or an ion is represented by the magnitude of the radius of the atom (atomic radius) or ion (ionic radius). In ordinary sense, the radius of an atom or an ion is defined as the distance between the nucleus of the atom or ion and the electron cloud of the outer-most shell. If an atom or an ion is assumed to be a sphere, then atomic or ionic radius is the radius of the sphere.

In spite of the above limitations, we have three operational concepts to define the atomic and ionic radius. These are *covalent radius*, *van der Waals radius* and *ionic raidus.*

Definition of covalent radius of atom A in A_2 molecule (Homo-nuclear diatomic molecule)

Covalent radius of atom A (abbreviated as r_A) in A_2 type covalent molecule, in which two A-atoms are linked together by a single covalent bond ($A—A$ bond), is defined as half of the distance between the nuclei of the two A-atoms. Thus if d_{A-A} is the distance between the nuclei of the two A-atoms (this distance is called *bond distance* or *inter-nuclear distance* or *bond length* of A_2 molecule), then the covalent radius of atom A (*i.e.* r_A) is given by :

$$r_A = \frac{d_{A-A}}{2} \qquad \ldots(i)$$

Examples (*i*) Since the distance between the nuclei of the two H-atoms in H_2 molecule has been found to be equal to 0.74Å, covalent radius of H-atom = 0.74/2 = 0.37Å.

(*ii*) Since the inter-nuclear distances in Cl_2 and Br_2 molecules are 1.98 Å and 2.28 Å respectively, the covalent radii of Cl and Br atoms would be equal to 1.98/2 = 0.99 Å and 2.28/2 = 1.14 Å respectively.

Double-bond and triple-bond covalent radii

If the two A-atom in A_2 molecule are linked together by a double bond, $A = A$ (*e.g.*, two O-atoms in O_2 molecule are linked as $O = O$), the covalent radius of A atom is called its *double bond covalent radius*. Similarly if the two A atoms in A_2 molecule are attached together by a tripple bond, $A \equiv A$ (*e.g.*, two N-atoms in N_2 molecule are attached together as $N \equiv N$), the covalent radius of A atom is called its *tripple bond covalent radius*. Double and triple bone covalent radii of some elements are given below :

Double bond covalent radii (Å) :	$B = B$,	$C = C$,	$N = N$	$O = O$
	0.76	0.67	0.60	0.55
Triple bond covalent radii (Å) :	$B \equiv B$,	$C \equiv C$,	$Si \equiv Si$,	$N \equiv N$
	0.68	0.60	1.07	0.55

Relation between single bond, double bond and triple bond covalent radii of an atom

It may be seen from the above values, that double and triple bond covalent radii of the atom of a given element are shorter than its single bond covalent radius. This is because of the fact that in the formation of a single covalent bond, only sigma orbitals overlap, while in the formation of a double or a triple bond, sigma as well as pi orbitals overlap. The additional overlapping of pi orbitals bring the two atoms closer to each other and hence bond length in reduced. The reduction in bond length reduces the double bond and triple bond covalent radius. We can conclude from this discussion that the magnitude of covalent radius of a given element decreases with the increase of the multiplicity or bond order of the bonds between the atoms, *i.e.*, these radii of a given element decrease in the order : single bond covalent radius > double bond covalent radius > triple bond covalent radius.

Factors affecting the magnitude of covalent radii of elements

The following factors are important :

1. **Effective nuclear charge (Z_{eff}).** With the increase in the magnitude of Z_{eff} felt by the electron of the outer-most shell, the force of attraction between the nucleus and the outer-most shell electron increases and hence the electron cloud of the element moves closer to the nucleus. This ultimately results in that the covalent radius of the atom of the element decreases. This factor has been used to explain why the covalent radii generally decrease, as we move from left to right, in a given period of main group elements (See the variation of covalent radii of main group elements in a period).

2. **Number of shells or principle quantum number.** Principal quantum number of an element represents the total number of shells present in that element. With the increase in the number of shells or principal quantum number, the outer-most shell electron(s) in the atom gets farther and farther away from the nucleus and hence the covalent radius increases. This factor has been used to explain why the covalent radii of the elements increase, as we move from top to bottom, in a given group of main group elements (See the variation of covalent radii of main group elements in a group).

3. **Multiplicity of the bonds between the atoms.** We have already seen that the magnitude of covalent radius decreases with the increase of the multiplicity of the bonds between the atoms. The reason for this has already been given.

Variation of covalent radii in main group elements

(*a*) **Variation in a period.** Generally speaking, the covalent radii decrease, in moving from left to right in a given period of the main group elements. This variation can be explained by considering, as an example, the covalent radii of the elements of 2*nd* period, as given in Table 5.2. In this table, the value of effective nuclear harge (Z_{eff}) felt by $2s^1$ electron (L-shell electron) in Li$_3$ and Be$_4$ and $2p^1$ electron (L-shell electron) in B$_5$, C$_6$, N$_7$, O$_8$, F$_9$ and Ne$_{10}$ has also been given. These values have been calculated with the help of Slater'*s* rules. This table shows that, as we proceed from Li$_3$ to F$_9$, the magnitude of Z_{eff} felt by L-shell electron goes on increasing and hence L-shell electrons (also K-shell electrons) are pulled closer and closer to the nucleus. Consequently the covalent radii of these elements go on decreasing, in moving from Li$_3$ to F$_9$. When we reach Ne$_{10}$, its Z_{eff} increases and hence its size should be smaller than that of F$_9$. But actually the size of Ne$_{10}$ is greater than that of F$_9$. The larger size of Ne$_{10}$, as compared to that of F$_9$, has been explained as follows. Since the forces holding the atoms together in noble gases (*i.e.* inter-atomic forces) are only van der Waals forces, which are very weak forces, the radii of the atoms of noble gases are in fact van der Waals radii, which are larger than the covalent radii of the atoms of halogens. Thus Ne$_{10}$ has bigger size than F$_9$.

Table 5.2 : *Covalent radii of the elements of 2nd period.* The radius of Ne$_{10}$ is its van der Waals radius.

Elements of 2*nd* period	Li$_3$	Be$_4$	B$_5$	C$_6$	N$_7$	O$_8$	F$_9$	Ne$_{10}$
Covalent radii (Å)	1.23	0.85	0.52	0.77	0.75	0.73	0.72	1.31
Electronic configuration	$1s^2, 2s^1$	$1s^2, 2s^2$	$1s^2, 2s^2 p^1$	$1s^2, 2s^2 p^2$	$1s^2, 2s^2 p^3$	$1s^2, 2s^2 p^4$	$1s^2, 2s^2 p^5$	$1s^2, 2s^2 p^6$
Z_{eff} felt by the outermost shell electron shown in bracket.	1.30 ($2s^1$)	1.95 ($2s^1$)	2.60 ($2p^1$)	3.25 ($2p^1$)	3.90 ($2p^1$)	4.55 ($2p^1$)	5.20 ($2p^1$)	5.85 ($2p^1$)

(*b*) **Variation in a group.** The covalent radii increase, in moving from top to bottom, in a given group of the main group elements. This variation can be explained by considering, as an example, the covalent radii of the elements of group IA as given below :

Elements of group IA :	Li	Na	K	Rb	Cs
Covalent radii (Å) :	1.23	1.54	2.03	2.16	2.35
Number of shells :	2	3	4	5	6
Z_{eff} felt by ns^1 electron :	increasing →				

As we proceed from Li to Cs, the number of shells or principal quantum number and Z_{eff} felt by ns^1 electron, both increase. The increase in the number of shells tends to increase the covalent radii while the increase in Z_{eff} tends to decrease the covalent radii. The effect caused by the increase of Z_{eff} is cancelled by the effect caused by the increae in the number of shells and hence the effect in the increase in the number of shells on covalent radii dominates. This results in that the covalent radii go on increasing, as we move down the group.

Definition of ionic radius

Ionic radius is the radius of an ion (cation or anion) in an ionic crystal. It may be defined as the distance between the nucleus of the ion and the point upto which the nucleus exerts its attractive force on the electron cloud of the ion. This definition shows that beyond the distance equal to the ionic radius the nucleus will not exert any attractive force on the electron cloud. Ionic radii of some ions (cations and anions) are given in Table 5.1.

Variation of ionic radii of iso-electronic ions

Iso-electronic ions are the cations or anions of different atoms. These ions have the same number of electrons and same electronic configuration. Examples of iso-electronic ions are C^{-4}, N^{3-}, O^{-2}, F^-, Na^+, Mg^{2+}. Al^{3+}, Si^{4+}, P^{5+}, S^{6+}, Cl^{7+} etc. Each of these ions has 10 electrons and the electronic configuration of each ion is $1s^2$, $2s^2p^6$.

The size of iso-electronic ions decreases with the increase in their nuclear charge (nuclear charge is equal to the atomic number with plus sign). This is because of the fact that with the increase in the nuclear charge, the force of attraction between the nucleus and the same number of electrons increases and hence the size of iso-electronic ions decreases. This fact is supported by the values of the size of the above iso-electronic ions as given below.

(a) Atomic and ionic radii

Key points: Atomic radii increase down a group and, within the s and p blocks, decrease from left to right across a period. The lanthanide contraction results in a decrease in atomic radius for elements following the f block. All monatomic anions are larger than their parent atoms and all monatomic cations are smaller.

Variation of ionic radii in main group elements

(*a*) **Variation in a period.** Since the size of the atoms of the elements decreaes as we move from left to right in a given period, the cations and anions of the elements also decrease in size in the same direction (See Table 5.1).

(*b*) **Variation in a group.** Since the size of the atom of the elements increases as we move down a group of main group elements, the cations and anions derived from these elements also increase in size in the same direction (See Table 5.1).

It may be noted from Table 5.1 that the increase in ionic radii amongst the first two pairs of ions is larger than that in the pairs of the last two elements. For example the increase in the radii of the pairs of alkai metal cation is given as $Na^+ - Li^+$ pair = 0.95 – 0.60 = 0.35, $K^+ - Na^+$ pair = 1.33 – 0.95 = 0.38, $Rb^+ - K^+$ pair = 1.48 – 1.33 = 0.15, and $Cs^+ - Rb^+$ pair = 1.69 – 1.48 = 0.21: These values show that the increase in cationic radius is quite large, as we move from Li^+ to Na^+ and from Na^+ to K^+, but the increase is not so large, as we move from K^+ to Rb^+ and from Rb^+ to Cs^+. This behaviour is because of the presence of ten elements of 1*st* transition series (Sc_{21} to Zn_{30}) between K^+ and Rb^+ ions. As these transistion series elements enter between K^+ and Rb^+ ion, their increasing nuclear charge tends to cause the contraction in the size of the atoms and ions, which follow them. Thus, the ions which follow the transition series elements have smaller size.

Table 5.1: *Single bond covalent radii and ionic radii (Å) of the atoms of main group elements. The figures given in bracket are the van der Waal's radii (1Å = 100 pm).*

Period number	I A	II A	III A	IV A	V A	VI A	VII A	Zero
1	H 0.37 2.08 (–1) (1.2)							He (0.93)
2	Li 1.23 0.68 (+1)	Be 0.90 0.31 (+2)	B 0.85 0.20 (+3)	C 0.77 0.15 (+4) 2.60 (–4)	N 0.75 0.11 (+5) 1.71 (–3) (1.5)	O 0.73 0.09 (+6) 1.42 (–2) (1.40)	F 0.72 1.36 (–1) (1.35)	Ne (1.31)
3	Na 1.54 0.95 (+1)	Mg 1.36 0.65 (+2)	Al 1.43 0.50 (+3)	Si 1.11 0.41 (+4) 2.71 (–1)	P 1.06 0.34 (+5) 2.12 (–3) (1.85)	S 1.02 0.29 (+6) 1.84 (–2) (1.80)	Cl 0.99 0.26 (+7) 1.81 (–1) (1.80)	Ar (1.75)
4	K 2.03 1.33 (+1)	Ca 1.74 0.99 (+2)	Ga 1.35 0.62 (+3) 1.13 (+1)	Ge 1.22 0.53 (+4) 0.93 (+2)	As 1.20 0.47 (+5) 2.22 (– 3) (2.00)	Se 1.16 0.42 (+6) 1.98 (–2) (1.90)	Br 1.14 0.39 (+7) 1.95 (–1) (1.95)	Kr (1.89)
5	Rb 2.16 1.48 (+1)	Sr 1.91 1.13 (+2)	In 1.67 0.81 (+3) 1.32 (+1)	Sn 1.41 0.71 (+4) 1.12 (+2)	Sb 1.40 0.62 (+5) 2.45 (–3) (2.20)	Te 1.36 0.56 (+6) 2.21 (–2) (2.10)	I 1.33 0.50 (+7) 2.16 (–1) (2.15)	Xe (2.09)
6	Cs 2.35 1.69 (+1)	Ba 1.98 1.35 (+2)	Tl 1.70 0.95 (+3) 1.40 (+1)	Pb 1.47 0.84 (+4) 1.20 (+2)	Bi 1.46 0.74 (+5) 1.20 (+3)	Po 1.46 — —	At —	Rn (2.14)

(*i*) *The radii of various species having the same nuclear charge but different oxidation states decrease with the increase in the oxidation number of the species.* Thus since the oxidation number of the given species increases as –1 → 0 → + 1, their sizes are in the order $I^- > I^\circ > I^+$. This order is based on the fact that with the increase in the oxidation number of the species, the number of electrons decreases and hence their size also decreases.

The above discussion shows that if we are given two or more cations of the same element, then the size of these cations will decrease with the increase in their positive oxidation number. Thus Pb^{4+} ion is smaller in size than Pb^{2+} (Pb^{2+} = 1.20 Å and Pb^{4+} = 0.84 Å).

Similarly, if we are given two or more anions of the same element (e.g. M^-, M^{2-}, M^{3-} etc.), then the size of these anions will increase with the increase in their negative oxidation number. Hence the sizes of M^-, M^{2-} and M^{3-} anions are in the order $M^- < M^{2-} < M^{3-}$.

(*ii*) *An anion is larger in size than its parent atom.* This conclusion is also explained by saying that, since the anion has greater number of electrons than its parent atom, it is larger in size than its parent atom.

(*iii*) *A cation is smaller in size than its parent atom.* This is because of the reason that the cation has smaller number of electrons and hence is smaller in size than its parent atom.

Variation of ionic radii of iso-electronic ions

Iso-electronic ions are the cations or **anions** of different atoms. These ions have the same number of electrons and same electronic configuration. Examples of iso-electronic ions are C^{-4}, N^{3-}, O^{-2}, F^-, Na^+, Mg^{2+}. Al^{3+}, Si^{4+}, P^{5+}, S^{6+}, Cl^{7+} etc. Each of these ions has 10 electrons and the electronic configuration of each ion is $1s^2, 2s^2p^6$.

Iso electronic ions	*Number of electrons and electronic configuration*	*Nuclear charge (= + Z)*	*Size of the ions (Å)*
C^{-4}	10 ($1s^2$, $2s^2p^6$)	+ 6	2.60
N^{-3}	10 ($1s^2$, $2s^2p^6$)	+ 7	1.71
O^{-2}	10 ($1s^2$, $2s^2p^6$)	+ 8	1.42
F^-	10 ($1s^2$, $2s^2p^6$)	+ 9	1.36
Na^+	10 ($1s^2$, $2s^2p^6$)	+ 11	0.95
Mg^{2+}	10 ($1s^2$, $2s^2p^6$)	+ 12	0.65
Al^{3+}	10 ($1s^2$, $2s^2p^6$)	+ 13	0.50
Si^{4+}	10 ($1s^2$, $2s^2p^6$)	+ 14	0.41
P^{5+}	10 ($1s^2$, $2s^2p^6$)	+ 15	0.34
S^{6+}	10 ($1s^2$, $2s^2p^6$)	+ 16	0.29
Cl^{7+}	10 ($1s^2$, $2s^2p^6$)	+ 17	0.26

2.3.1 Ionization Energy

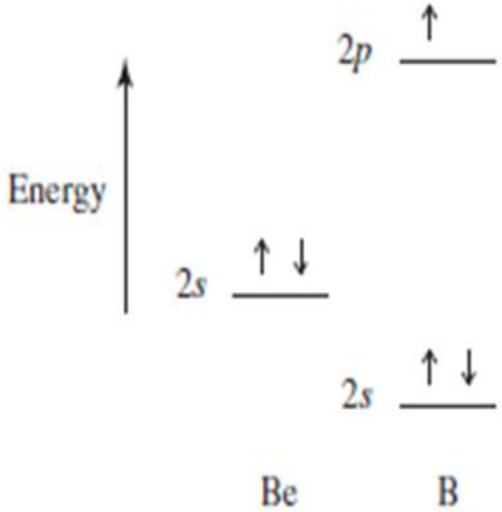
The ionization energy, also known as the *ionization potential*, is the energy required to remove an electron from a gaseous atom or ion:

$$A^{n+}(g) \longrightarrow A^{(n+1)+}(g) + e^- \qquad \text{ionization energy } (IE) = \Delta U$$

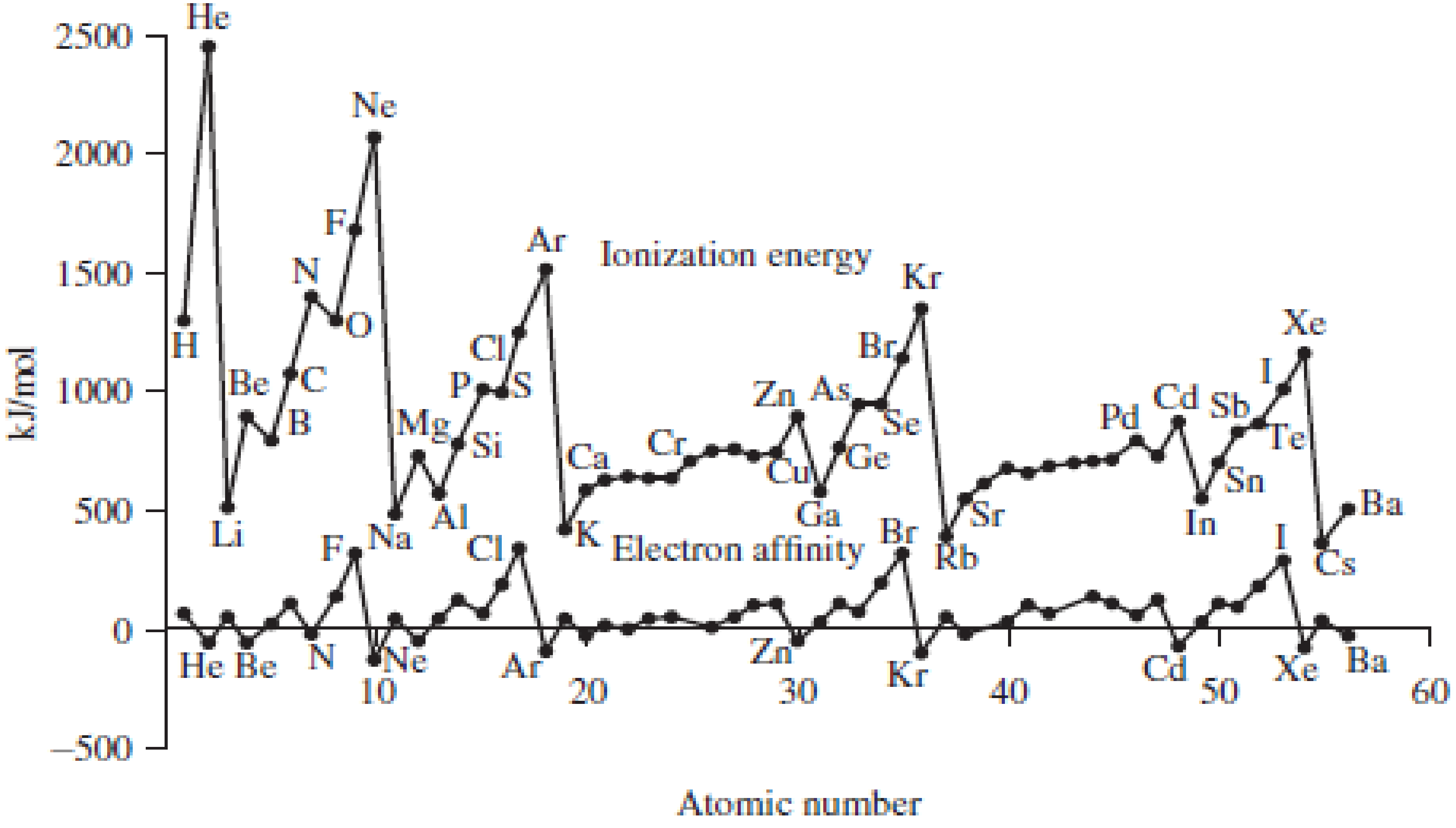
where $n = 0$ (first ionization energy), $n = 1$ (second ionization energy), and so on.

As would be expected from the effects of shielding, the ionization energy varies with different nuclei and different numbers of electrons. Trends for the first ionization energies of the early elements in the periodic table are shown in Figure 2.13. The general trend across a period is an increase in ionization energy as the nuclear charge increases. However, the experimental values show a break in the trend in the second period at boron and again at oxygen. Because boron is the first atom to have an electron in a higher energy 2*p* orbital that is shielded somewhat by the 2*s* electrons, boron's 2*p* electron is more easily lost than the 2*s* electrons of beryllium; boron has the lower ionization energy.

$$IP = \frac{2\pi^2 m Z^2 e^4}{n^2 h^2}$$



At the fourth 2*p* electron, at oxygen, a similar decrease in ionization energy occurs. Here, the fourth electron shares an orbital with one of the three previous 2*p* electrons



($\underline{\ \uparrow\downarrow\ }\ \underline{\ \uparrow\ }\ \underline{\ \uparrow\ }$), and the repulsion between the paired electrons (Π_c) reduces the energy necessary to remove an electron from oxygen; oxygen has a lower ionization energy than nitrogen, which has the 2*p* configuration $\underline{\ \uparrow\ }\ \underline{\ \uparrow\ }\ \underline{\ \uparrow\ }$.

Similar patterns appear in the other periods, for example Na through Ar and K through Kr, omitting the transition metals. The transition metals have less dramatic differences in ionization energies, with the effects of shielding and increasing nuclear charge more nearly in balance.

Much larger decreases in ionization energy occur at the start of each new period, because the change to the next major quantum number requires that the new *s* electron have a much higher energy. The maxima at the noble gases decrease with increasing Z, because the outer electrons are farther from the nucleus in the heavier elements. Overall, the trends are toward higher ionization energy from left to right in the periodic table (the major change) and lower ionization energy from top to bottom (a minor change). The differences described in the previous paragraph are superimposed on these more general changes.

Factors affecting the magnitude of ionisation energy

Following are the important factors which affect the magnitude of ionisation energy of the elements.

1. Nuclear charge. For the species having different charges, the force of attraction between the nucleus and the outer-most shell electron increases with the increase of nucleus charge and ence more energy is required to remove the outer-most shell electron from the atom. Thus with the increase of nuclear charge, the magnitude of ionisation energy also increases. This factor has been used to explain the following :

(*a*) Ionisation potential of Li^+ ion ($1s^2$) is greater than that of He-atom ($1s^2$) [Li^+ = 7298.1

KJ/mole, He = 2372.3 KJ/mole], although the electron to be removed belongs to the same orbital (*viz.* 1*s* orbital) in both the species. Greater value of ionisation potential for Li^+ ion is explained as follows. Both the species have different nuclear charges (Li^+ = 3, He = 2), but the number of electrons in both the species is the same (Li^+ = 3 – 1 = 2, He = 2). Due to greater nuclelar charge on Li+ ion, the force of attraction between the nucleus and the outer-most shell electron cloud increases and hence the value of ionisation potential also increases.

(*b*) With a few exceptions, the ionisation potentials of representative elements increase on proceeding from left to right in a period. For explanation see "Variation of IE values in main group elements" discussed on page 116.

2. Size of the atom or ion. Greater is the size of an atom or an ion, more far is the outer-most shell electron from the nucleus and hence lesser is the force of attraction between the nucleus and the outer-most shell electron and lesser amount of energy will be required to remove the outer-most shell electron. Consequently lesser will be the ionisation energy of the atom or its ion. Thus the magnitude of ionisation energy of an atom or an ion is inversely proportional to its size. This factor has been used to explain the following :

(*a*) The magnitude of 1*st* (IE_1), 2*nd* (IE_2), 3rd (IE_3) etc. ionisation potentials of an element, M(*g*) are in the order : $IE_1 < IE_2 < IE_3 <$ .... Since the size of M(*g*), $M^+(g)$ $M^{2+}(g)$ etc. is in the order : M(g) > $M^+(g)$ >$M^{2+}(g)$ > ...., the ionisation potentials of these species should be in the reverse order *i.e.* $IE_1 < IE_2 < IE_3 <$..... .

(*b*) On proceeding from top to bottom in a group of the representative elements of the periodic table, ionisation potential values decrease. For explanation, see page 117.

3. Principal quantum number (*n*). Greater is the value of *n* for the valence-shell electron of an atom, farther away this electron will be from the nucleus and hence lesser will be the force of attraction between the nucleus and the valence-shell electron. This means that lesser amount of energy will be required to remove the valence-shell electron. Thus with the increase of the principal quantum number (*n*) of the orbital from which the electron is to be removed, the magnitude of the ionisation energy decreases. This factor has been used to explain the following :

(*a*) For Mg-atom ($1s^2$, $2s^2p^6$, $3s^2$) the value of IE_3 is much greater than those of IE_1 and IE_2 both as shown in bracket (IE_1 = 737.7, IE_2 = 1450.7, IE_3 = 7732.8 KJ/mole). This can be explained as follows. IE_1 and IE_2 are ionisation energies required to remove an electron from 3s-orbital which has higher value of *n* (= 3) while IE_3 is the ionisation energy required to remove an electron from 2*p*-orbital which has a lower value of *n* (= 2). With the decrease of the value of principal quantum number of the orbital from which the electron is to be removed, the value of ionisation potential increases. Consequently the value of IE_3 is much greater than those of IE_1 and IE_2 both.

(*b*) IE_3 value for Be-atom ($1s^2$, $2s^2$) is much greater than IE_3 value of B-atom ($1s^2$. $2s^2p^1$) (IE for Be = 14848.7 KJ/mole, IE_3 for B-atom = 3659.8 KJ/mole). IE_3 for Be-atom is the energy required to remove an electron from 1*s*-orbital which has a lower value of *n* (=1) while IE_3 for B-atom is the energy required to remove an electron from 2*s* orbital which has a higher value of *n* (=2). With the increase of the value of *n* of the orbital from which the electron is to be removed, the value of IE_3 decreases. Thus IE_3 for B-atom is much lower than IE_3 for Be-atom.

4. Shielding effect. We have already said that, due to shielding effect produced by intervening electrons, the force of attraction between the nucleus and the outer-most shell electron decreases and hence the ionisation energy also decreases. Thus with the increase of shielding effect, the magnitude of ionisation energy decreases. This factor has also been used to explain why a large decrease in the values of ionisation potential is observed, when we pass from a noble gas to an alkali metal. In alkali metals the electron to be removed from *ns* orbital is effectively screened or shielded by the electrons present in $(n-1)$ *th* shell, while in noble gases (ns^2p^6) the electron to be

removed from *np* orbitals is *not effectively* shielded by the remaining five electrons residing in *np* orbitals. Due to greater shielding effect in alkali metals, ionisation potentials of alkali metals become smaller than those of noble gases.

5. Energy of the orbital from which the electron is to be removed. The relative order of energy of *s*, *p*, *d* and *f* orbitals of a given *nth* shell is as $ns < np < nd < nf$. This order implies that the relative ease with which the electron residing in these orbitals can be removed will be as $ns < np < nd < nf$. This order clearly indicates that to remove an electron from *f*-orbital of a given shell will be the easiest while to remove the same from *s-orbital* belonging to the same shell will be the most difficult, *i.e.* the amount of energy required to remove an electron from *f*-orbital is minimum while that required to remove an electron from *s*-orbital is maximum. In other words, other factors remaining the same, the ionisation energies of an electron in *s*, *p*, *d* and *f*-orbitals are in the order : $ns > np > nd > nf$.

Variation of IE values in main group elements

(*a*) **Variation in a period.** On proceeding from left to right in a period of main group elements of the periodic table, the nuclear charge increases by +1 at each next element. The increase in the nuclear charge increases the electrostatic force of attraction between the nucleus and the valence-shell electron and hence the magnitude of IE increases. Thus, on proceeding from left to right, the IE values, in general, increase with the successive increase in the magnitude of nuclear charge. Consequently, if we consider the IE values of the elements of 2*nd* period, these should increase from Li to Ne, *i.e.* the order should be Li < Be < B < C < N < O < F < Ne. The experimental values, as given in Table 5.3, however, show that the actual order is Li < B < Be < C < O < N < F < Ne. This order can be explained as follows : since the completely-filled 2*s* orbital in Be atom (Be = $2s^2$) is more stable than $2s^2p^1$ configuration of the next element *viz.*, B -atom (B = $2s^2p^1$) and half-filled 2*p* orbitals of N-atom (N = $2s^2p^3$) are more stable than $2s^2p^4$ configuration of the next element *viz.*, O-atom (O = $2s^2p^4$), both these elements (*i.e.* Be and N) have greater IE values than B and O-atoms respectively. Thus the actual order of IE values of the elements of 2*nd* period becomes Li < Be > B < C < N > O < F < Ne or Li < B < Be < C < O < N < F < Ne.

Similarly, it can be shown that the actual order of IE values of the elements of 3*rd* period is : Na <Al < Mg < Si < S < P < Cl < Ar. Greater values of Mg and P as compared to those of Al and S respectively have been explained in the same manner in which these values of Be and N as compared to B and O respectively have been explained.

It may be seen that in each period, alkali metals have the lowest IE values while the noble gases have the highest IE values. The highest values for noble gases can be explained on the basis of the fact that greater amount of energy is required to remove an electron from the highly stable 8-electron configuration (ns^2p^6 configuration).

(*b*) **Variation in a group.** On descending a group, IE values of the elements go on decreasing. The following two explanations have been suggested :

(*i*) On proceeding down the group, the size of the atoms and nuclear charge, both increase simultaneously. The increase in size of the atoms tends to decrease the magnitude of ionisation energies, while the increase in nuclear charge tends to increase the magnitude of ionisation energies. It appears that the increase in the size of atoms dominates the increase in the nuclear charge and hence ultimately IE values of the elements gradually go on decreasing down the group.

(*ii*) As we move down a group, the number of inner-shell electrons (*i.e.* intervening electrons) increases and hence the magnitude of shielding effect caused by these electrons on the valence-shell electron increases. With the increase of the magnitude of shielding effect, the ionisation energy decreases.

العمر هيا وهو وجود (E) أي علاقة عددية ثابتة في كل مدار

$$E_n = \frac{-2\pi^2 \overset{\text{Kg g}}{m} \overset{4.8\times10^{-10}\ \text{e.s.u}}{e^4} \overset{\text{العدد الذري}}{Z^2}}{\underset{\text{رقم الغلاف}}{n^2}\ \underset{\text{J.sec}\ \ \text{erg.s}}{h^2}}$$

$$\Delta E = E_{n_2} - E_{n_1}$$

$$\Delta E = \frac{2\pi^2 e^4 m Z^2}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{when } n_2 = \infty$$

$$\therefore \Delta E = \frac{2\pi^2 m e^4 Z^2}{h^2 n_1^2} = \text{I.P.} \quad (\text{جهد تأين})$$

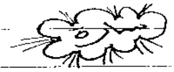
$n=1,\ Z=1$

$$\underset{\text{للهيدروجين}}{IP_H} = \frac{2\pi^2 m e^4}{h^2} \quad (\text{for hydrogen Atom})$$

* element or ion isoelectronic with H Lik $_2He^+$ and $_3Li^{2+}$

$$\underset{_3Li^{2+}\text{ and }_2He^{+}}{IP} = IP_H \times Z^2 = \frac{2\pi^2 m e^4}{h^2} \times Z^2$$

* when $n \neq 1$ and $Z \neq 1$



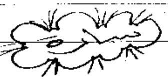
$$IP = IP_H \times \frac{Z^2}{n^2} \Big]$$ for 1 electron atom or ion

ولأننا (e) لا يعقل Z حيث عند تعدد الالكترونات تبدأ عملية الحجب لذلك
يجب استبدال Z^* لدراسة الحجب وكذلك لانه مضبوط اكثر

* for more than one electron → Shelding effect

$Z^* = Z - S$

$$IP_{\text{Polyelectron}} = IP_H \times \frac{Z^{*2}}{n^2}$$



$IP_H = 13.6\ \text{eV} = 2.169 \times 10^{-11}\ \text{erg}$

$1\ \text{erg} = 6.24 \times 10^{11}\ \text{e.V}$

Calcalate the ionization Potential for hydrogen atom.

$H_{(g)} \longrightarrow H^+ + e \qquad \Delta E = IP$

$$IP = \frac{2\pi^2 m Z^2 e^4}{n^2 h^2}$$

$$= \frac{2(3.141)^2 (9.1085 \times 10^{-28}\,g \times (1)^2 \times (4.8032 \times 10^{-10})^4}{(1)^2 \times (6.62 \times 10^{-27}\,erg \cdot sec)^2}$$

$= 2.1799 \times 10^{-11}\,erg$

$= 2.1799 \times 10^{-11}\,erg \times 6.24145 \times 10^{11}\,ev.erg^{-1}$

$= 13.6\,eV$

Ex/ Calculate the first and second ionization potential (IP_1) of Lithium

Sol^n.

$_3Li: (1s^2) 2s^1)$

or $S = 0 \times 0.35 + 2 \times 0.85$

σ

$\sigma = 1.7$

$Z^* = Z - \sigma$

$= 3 - 1.7$

$= 1.3$

$$IP_1 = IP_H \times \frac{(Z^*)^2}{n^2}$$

$$= 13.6 \text{ ev} \times \frac{(1.3)^2}{(2)^2}$$

$= 5.746$ ev

Electron Affinity

What is electron affinity (EA) ?

Electron affinity (EA) of an element is defined as the amount of energy released when an electron is added to the valence-shell of an isolated gaseous atom of that element, to convert the atom into gaseous uni-negative ion (anion). Thus :

(*i*) $X^{\circ}(g) + e^- \rightarrow X^-(g)$, ΔH = Energy released = EA of X-atom (*Exothermic process*) ...(*i*)

The addition of an electron to an atom is thus an exothermic process. Since EA is the energy involved in adding an electron to an atom, it is also called *enthalpy of electron attachment*. Again, since EA is the energy released, it should be represented with a negative sign, according to our usual thermodynamic convention, but it is unfortunate that EA values are normally represented with a positive sign. EA, defined as above, is called *first electron affinity* (EA_1), since it is related with the addition of only one electron to a neutral gaseous atom. Since $(EA)_1$ represents the energy released, $(EA)_1$ is also called *exothermic electron affinity*.

Factors affecting the magnitude of electron affinity.

Important factors, which affect the magnitudes of electron affinity values of elements, are discussed below :

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1. Size of the atom. In case of smaller atoms, the attraction of the nucleus, for the electron to be added, is stronger. Thus, smaller is the size of the atom, greater is its electron affinity. (See electron affinity values of halogens).

2. Nuclear charge. Greater is the magnitude of nuclear charge of elements (along a period), stronger is the attraction of its nucleus for the electron to be added. Thus, with the increase in the magnitude of nuclear charge, electron affinity also increases.

3. Electronic configuration of the atom. How are the values of EA of elements affected by the electronic configuration of the atoms of the elements, can be explained by considering the following examples :

(*a*) *EA values of the elements of groups II A and II B.* The atoms of the elements of group II A have completely-filled ns orbital (ns^2 configuration) and those of the elements of group IIB have completely-filled $(n-1)\,d$ and ns orbitals [$(n-1)\,d^{10}.\ ns^2$ configuration] and hence the atoms of the elements of both these groups, either do not accept the electron being added to them or have a very little tendency to accept the electron. When they donot accept the electron, they show zero EA values.Even if they accept the electron, they do not liberate energy; rather they absorb some energy in the process of adding the electron to them, *i.e.* they have negative (*i.e.* endothermic) values of electron affinity. The elements of group IIA have completely-filed ns^2 orbitals and hence are reluctant to accept an electron. Therefore, they have negative (*i.e.* less than zero) electron affinity values. Similarly, since Zn, Cd and Hg have completely-filled ns and $(n-1)\,d$ orbitals [$(n-1)\,d^{10}$ ns^2 configuration], they show reluctance to accept an electron and hence have negative EA values (Zn = – 47 KJ/mole, Cd = – 32, Hg = – 61).

(*b*) *EA values of nitrogen and phosphorus.* EA values of N and P atoms are very low. This is because of the presence of half-filled *np* orbitals in their valence-shell ($N = 2s^2p^3$, $P = 3s^2p^3$). These half-filled orbitals, being very stable, have very little tendency to accept any extra electron to be added to them. Thus, EA values of N and P are very small.

(*c*) *EA values of noble gases.* Noble gases have stable ns^2p^6 configuration (helium has $1s^2$ configuration) and hence the atoms of these gases, either donot accept any extra electron, or have a very little tendency to accept the electron. Consequently these elements have either close to zero or slightly negative (corresponding to the endothermic process) EA values.

Variation of electron affinity in main group elements of the periodic table

(*a*) **Variation in a period.** On moving from alkali metals to halogens in a period, the size of the atoms decreases and the nuclear charge increases. Both these factors increase the force of attraction between the nucleus and the electron being added and hence the atom has a greater tendency to attract the electron towards itself. Thus *the electron affinity values go on increasing (generally) when we move from alkali metals to halogens*. From this it follows that in each period, alkali metals which lie to the extreme left of the periodic table, have the lowest values of electron affinity and the halogens which lie at the extreme right of the periodic table, have the highest values of electron affinity. Their highest values are because of the fact that, on gaining an extra electron, the halogen atoms attain the stable noble gas configuration (ns^2p^6 configuration).

(*b*) **Variation in a group.** On moving down a group, both the size of the atom and the nuclear charge increase. The increase in atomic size tends to decrease the electron affinity values, while the increase in nuclear charge tends to increase the electron affinity values. The net result is that the effect produced by the progressive increase of the atomic size outweighs the effect produced by the progressive increase in nuclear charge and *consequently the electron affinity goes on decreasing, as we move from top to bottom in a group*. The decrease in electron affinity values in a group is evident from the values (*i*) for the elements of group IA (H > Li > Na > K> Rb > C*s*) (*ii*) for the elements namely S, Se, Te and Po (S > Se > Te > Po — group VI A) and (*iii*) for the elements *viz* Cl, Br, I, At (Cl > Br > I > At - Group VII A). It may be noted that the electron affinity value of O is less than that of S (O < S) in group VI A and similarly the electron affinity value of F is less than that of Cl (F < Cl) in group VIIA. Thus the actual order of electron affinity values for

(d) Electronegativity

Key points: The electronegativity of an element is the power of an atom of the element to attract electrons when it is part of a compound; there is a general increase in electronegativity across a period and a general decrease down a group.

The electronegativity, χ (chi), of an element is the power of an atom of the element to attract electrons to itself when it is part of a compound. If an atom has a strong tendency to acquire electrons, it is said to be highly electronegative (like the elements close to fluorine). Electronegativity is a very useful concept in chemistry and has numerous applications, which include a rationalization of bond energies and the types of reactions that substances undergo and the prediction of the polarities of bonds and molecules (Chapter 2).

Periodic trends in electronegativity can be related to the size of the atoms and electron configuration. If an atom is small and has an almost closed shell of electrons, then it is more likely to attract an electron to itself than a large atom with few valence electrons. Consequently, the electronegativities of the elements typically increase left to right across a period and decrease down a group.

Table 1.7 Pauling χ_P, Mulliken, χ_M, and Allred–Rochow, χ_{AR}, electronegativities

H							**He**
2.20							5.5
3.06							
2.20							
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
0.98	1.57	2.04	2.55	3.04	3.44	3.98	
1.28	1.99	1.83	2.67	3.08	3.22	4.43	4.60
0.97	1.47	2.01	2.50	3.07	3.50	4.10	5.10
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
0.93	1.31	1.61	1.90	2.19	2.58	3.16	
1.21	1.63	1.37	2.03	2.39	2.65	3.54	3.36
1.01	1.23	1.47	1.74	2.06	2.44	2.83	3.30
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
0.82	1.00	1.81	2.01	2.18	2.55	2.96	3.0
1.03	1.30	1.34	1.95	2.26	2.51	3.24	2.98
0.91	1.04	1.82	2.02	2.20	2.48	2.74	3.10
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
0.82	0.95	1.78	1.96	2.05	2.10	2.66	2.6
0.99	1.21	1.30	1.83	2.06	2.34	2.88	2.59
0.89	0.99	1.49	1.72	1.82	2.01	2.21	2.40
Cs	**Ba**	**Tl**	**Pb**	**Bi**			
0.79	0.89	2.04	2.33	2.02			

Factors affecting the magnitude of electronegativity

Important factors which influence the magnitude of electronegativity of elements are discussed below :

1. Size of the atom. Smaller atom has greater tendency to attract the shared electron pair towards itself and hence has greater electronegativity than a smaller atom. This factor has been used to explain the variation of electronegativity values of elements in a group and in a period of the periodic table (see below).

2. Oxidation state of the element. We know that if an atom shows many positive oxidation

states, the size of the atom decreases with the increase in its oxidation state. Thus the size of Fe, Fe^{+2}, and Fe^{+3} is in the order : $Fe > Fe^{+2} > Fe^{+2}$.

Again, it is also known that smaller is the size of an atom or an ion, greater is its electronegativity. Thus the electronegativity of an element which shows many oxidation states is directly proportional to the magnitude of its positive oxidation state. Consequently the electronegativity of the above species is in the increasing order : Fe (= 1.80) < Fe^{+2} (= 1.83) < Fe^{+3} (= 1.96). Another example to show the variation of electronegativity of an atom with the change in its oxidation state is $\overset{+1}{\text{HClO}}$ — $\overset{+5}{\text{HClO}_3}$ pair. Since Cl-atom is in higher oxidation state in $HClO_3$ (Cl = +5) than in HClO (Cl = + 1), Cl-atom in $HClO_3$ shows more electronegativity (*i.e.* electron pair-attracting power) than in HClO.

Due to the fact that an anion is larger in size than its parental atom, the anion has less tendency to attract the shared electron pair towards itself and hence has lower value of electronegativity, *e.g.*, F^- ion has lower electronegativity than F atom (F^- = 0.8, F = 4.0).

3. Effective nuclear charge of the element. We have already seen that according to Allred-Rochow's formula, the electronegativity of an element is proportional to the magnitude of effective nuclear charge at the periphery of the atom of that element (Z_{eff}). Thus with the increase in the magnitude of Z_{eff} of an element, the electronegativity of that element also increases. This factor has been used to explain the variation of electronegativity of elements in a group and in a period (see below).

4. Electropositive character of elements. Electropositive character of an element is opposite of its electronegative character, *i.e.*, the elements which are highly electropositive are weakly electronegative. In other words, the elements which are highly electropositive have low values of electronegativity (*e.g.* alkali metals). Similarly, the elements which have very weak electropositive character (*i.e.* non-metallic character) have very high values of electronegativity (*e.g.* halogens). In general we can say that the electronegativity of an element is inversely proportional to its eletropositive character. This factor has been used to explain the variation of electronegativity of elements in a group and in a period of the periodic table (see below).