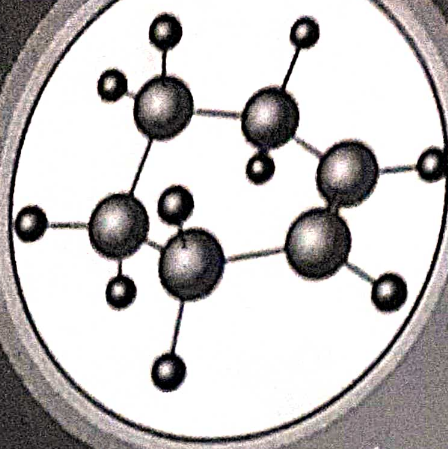
CHAPTER 2



PERIODICITY OF ELEMENTS

MODERN PERIODIC LAW

"*The physical and chemical properties of elements are the periodic function of their atomic numbers*", *i.e.*, when elements are arranged in the increasing order of their atomic numbers, similar elements are repeated after regular intervals. Based on modern periodic law, many new forms of periodic table have been suggested. The most common form out of these is **long form periodic table**. Before considering this common form of periodic table we shall discuss the cause of periodicity of elements.

ELECTRONIC BASIS OF PERIODICITY OF ELEMENTS–PERIODICITY OF ELEMENTS

The recurrence of elements with similar properties after certain regular interval when these are arranged in the increasing order of their atomic number is called **periodicity**. The properties of elements get repeated after intervals of 2, 8, 8, 18, 18 and 32.

Cause of Periodicity. Consider the electronic configuration of alkali metals.

$$_{3}\text{Li} = 1s^2\ 2s^1\ ;\ _{11}\text{Na} = (\text{Ne})^{10}\ 3s^1\ ;\ _{19}\text{K} = (\text{Ar})^{18}\ 4s^1$$

$$_{37}\text{Rb} = (\text{Kr})^{36}\ 5s^1\ ;\ _{55}\text{Cs} = (\text{Xe})^{54}\ 6s^1\ ;\ _{87}\text{Fr} = (\text{Rn})^{86}\ 7s^1$$

All these elements have one electron in their valence shell and have similar *properties*.

From the electronic configuration of these elements, we find that all elements having same number of electrons in the valence shell have similar properties. Thus, we conclude that the recurrence of similar properties is due to recurrence of similar electronic configuration. Hence, **cause of periodicity** is the **recurrence of similar electronic configuration.** The properties of elements get repeated after intervals of 2, 8, 8, 18, 18 and 32 because similar electronic configurations recur only after these intervals. The numbers 2, 8, 18 and 32 are called **magic numbers**. These numbers are useful to find elements with similar properties.

Example

EXAMPLE 1. To find out elements which resemble H-atom (At. No. 1).

SOLUTION. The elements with At. No. 3, 11, 19, 37, 87 resemble hydrogen atom. These atomic numbers are obtained as follows :

(*i*) At. No. of 'H' + 2 (Magic number) = 1 + 2 = 3, Lithium (Li)

(*ii*) At. No. of Li + 8 (Magic number) = 3 + 8 = 11, Sodium (Na).

(*iii*) At. No. of Na + 8 (Magic number) = 11 + 8 = 19, Potassium (K).

(*iv*) At. No. of K + 18 (Magic number) = 19 + 18 = 37, Rubimdium (Rb).

(*v*) At. No. of Rb + 18 (Magic number) = 37 + 18 = 55, Cesium (Cs).

(*vi*) At. No. of Cs + 32 (Magic number) = 55 + 32 = 87, Francium (Fr).

MODERN IUPAC PERIODIC TABLE-LONG OR EXTENDED FORM OF THE PERIODIC TABLE (BOHR'S TABLE)

This table is based on the modern periodic law which was discovered by Moseley (1913).

According to this law: '*The physical and chemical properties of elements are the periodic function of their atomic number, i.e.*, when elements are arranged in the increasing order of their atomic number, similar elements are repeated after regular interval.

The table 2.1 is an improved form of Mendeleeff's periodic table. This table has the following **features**.

Table 2.1 Long form of Periodic Table

1 H 1.008	Atomic number Atomic mass

Groups → Period ↓	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 0
(1)	1 H 1.008																	2 He 4.003
(2)	3 Li 6.939	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
(3)	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
(4)	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.54	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Sc 78.96	35 Br 79.91	36 Kr 83.80
(5)	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (99)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
(6)	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 181.0	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
(7)	87 Fr (223)	88 Ra (226)	89 Ac (237)	104 Rf (261)	105 Db (262)	106 Sg 263.18	107 Bh 262.12	108 Hs 265	109 Mt 266	*110 Ds 270	111 Rg 272	112 Cn 277	113 Nh 286	114 Fl 289.19	115 Mc 288.19	116 Lv 293	117 Ts 294	118 Og 294

LANTHANOIDS	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
ACTINOIDS	90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cr (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (253)	103 Lr (257)

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*The name of elements from atomic number 104 to 118 have been accepted as given below in IUPAC system. Rutherfordium ($_{104}$Rf), dubnium ($_{105}$Db), seaborgium ($_{106}$Sg), bohrium ($_{107}$Bh), hassium ($_{108}$Hs), meitnerium ($_{109}$Mt), Darmstadtium ($_{110}$Ds), Rontgenium ($_{111}$Rg) and Copernicium ($_{112}$Cn), Nihonium ($_{113}$Nh), Flerovium ($_{114}$Fl), Moscovium ($_{115}$Mc), Livermorium ($_{116}$Lv), Tennessine, ($_{117}$Ts), Oganesson ($_{118}$ Og).

1. All elements have been arranged in the increasing order of their atomic numbers.
2. Elements with similar electronic configurations have similar properties and hence, have been placed together at one place.
3. Elements with different configurations have different properties and hence have been placed at different places in the periodic table.

This periodic table consists of :

(*i*) Seven horizontal rows called periods or rows.

(*ii*) Eighteen vertical columns called groups or families.

(*iii*) Four blocks.

PERIODS

The horizontal rows from left to right in the periodic table are called periods. There are seven periods in all. The number of elements in each period correspond to the number of electrons in different major energy levels. These energy levels can be known from energy level diagram of multi electron atoms, *i.e.*, aufbau principle. Each period starts with a new principal quantum number, *n, i.e.*, filling of new main energy level.

First, second and third periods are called **short periods**. These contain 2, 8 and 8 elements respectively. Fourth, fifth sixth and seventh periods contain 18, 18, 32 and 32 elements respectively. These are called **long periods**. Seventh period is now complete and contains 32 elements. Out of these 32 elements, two elements belong to *s*-block, 6 elements belong to *p*-block, 14 elements belong to *f*-block and 10 elements belong to *d*-block (fourth transition series). These 32 elements belong to seventh period with atomic number 89 (actinium) to 118 (Oganesson).

First period contains only two elements. This period corresponds to first main energy level whose capacity is only of two electrons. Hence, only two different elements in which one and two electrons are present in first energy level are possible. H ($1s^1$), He ($1s^2$).

Second period contains eight elements. It corresponds to the second main energy level ($2s^2$ $2p^6$) whose capacity is of eight electrons and hence, eight elements occur in this period.

Third period contains eight elements. It corresponds to third main energy level ($3s^2$ $3p^6$ $3d^{10}$). It is clear from energy level diagram for multi-electron atoms (Chapter, 1) that 3*d*-orbitals are higher in energy than 4*s* orbital. Consequently, 3*d*-orbitals are filled after filling 4*s*-orbital. Hence this period involves the filling of only 3*s* and 3*p* orbitals. Therefore, it contains eight elements and not eighteen elements.

Fourth period contains eighteen elements. This period corresponds to fourth main energy level. It starts with the element which receives electron in 4*s*-orbital. After filling 4*s* orbital, the filling of 3*d* and then 4*p* takes place. It is so because energy of 3*d* sub-level is in between the 4*s* and 4*p* sub-levels. As 4*s*, 3*d* and 4*p* can have 2, 10 and 6 electrons respectively, therefore 18 elements are present in this period. The 4*d* and 4*f* sub levels are higher in energy than 5s (see multi-electron energy level diagram) and hence are filled up in the next periods.

Fifth period also contains 18 elements, ($_{37}$Rb to $_{54}$Xe) like the fourth period.

Sixth period contains 32 elements, ($_{55}$Cs to $_{86}$Rn) due to the filling of 6*s*, 4*f*, 5*d* and 6*p* orbitals. The first three elements resemble the corresponding three elements of the 5th period. The next 14 elements known as lanthanides are very much similar in their properties and these have been placed at one place along with lanthanum. The next 15 elements ($_{72}$Hf to $_{86}$Rn) are arranged in the same way as the last 15 elements of the fifth period.

Seventh period contains 32 elements, (87-118). These elements are radioactive. Upto $_{92}$U, the elements are naturally occurring and the remaining elements are artificially prepared. Hence, the elements having atomic number higher than 92 are known as **synthetic elements**.

The relationship between electron filling of orbitals and the number of elements in a period is summarised in table 2.2.

Table 2.2 Number of elements in each period and electron filling of orbitals.

Period	Starting principal quantum number	Orbitals being filled and their progressive filling	No. of electrons needed to fill the orbitals	No. of elements in the period
First	1	$1s^{1-2}$	2	2
Second	2	$2s^{1-2}\ 2p^{1-6}$	8 (*i.e.*, 2 + 6)	8
Third	3	$3s^{1-2}\ 3p^{1-6}$	8 (*i.e.*, 2 + 6)	8
Fourth	4	$4s^{1-2}\ 3d^{1-10}\ 4p^{1-6}$	18 (*i.e.*, 2 + 10 + 6)	18
Fifth	5	$5s^{1-2}\ 4d^{1-10}\ 5p^{1-6}$	18 (*i.e.*, 2 + 10 + 6)	18
Sixth	6	$6s^{1-2}\ 4f^{1-14}\ 5d^{1-10}\ 6p^{1-6}$	32 (*i.e.*, 2 + 14 + 10 + 6)	32
Seventh	7	$7s^{1-2}\ 5f^{1-14}\ 6d^{1-10}\ 7p^{1-6}$	32 (*i.e.*, 2 + 14 + 10 + 6)	32

There are 14 elements just after lanthanum ($_{57}$La) and another 14 elements just after actinium ($_{89}$Ac). These are placed in two separate rows, at the bottom of the periodic table, to avoid the undue expansion of the periodic table. The elements in the first row are called lanthanides and those in the second row are called actinides. These are also called inner transition elements because the last electron in them enters into the shell which is inner to the penultimate* shell (ante-penultimate shell).

Similarly, keeping energy level diagram in view, we can explain the capacities of 5th, 6th and seventh periods. This explanation also justifies the magic numbers.

There is a regular change in properties of the elements in a period as we move from left to right. The trend in the properties of elements can be explained on the basis of effective nuclear charge and screening constant.

EFFECTIVE NUCLEAR CHARGE AND SHIELDING EFFECT

A number of physical and chemical properties of elements show periodicity based upon the electronic configuration of elements. In considering the variation in periodic properties, it is important to find the controlling power of the nucleus of the atom on its electrons. We have to consider the manner in which electrons are affected by the nuclear charge in a poly-electronic atom. How the nuclear charge (Z) differs from effective nuclear charge (Z*) can be explained by the following discussion.

Screening or Shielding constant σ. The energy of an electron in an atom is given by the relation.

$$E_n = -\frac{2\pi^2 m e^4 Z^2}{n^2 h^2};\ E_n \propto \frac{Z^2}{n^2}$$

where n = Principal quantum number, and

Z = Actual nuclear charge (= Atomic number)

Thus, the energy of the outermost electron will increase rapidly with increase in principal quantum number.

If E_H is the energy of the hydrogen atom (13.6 eV.), the ionisation energy of other elements will be:

$E_{He} = 4E_H = 13.6 \times 4 = 54.4$ eV., $E_{obs} = 24.4$ *e*.V. [∵ for $_2$He ($1s^2$), Z = 2, n = 1 and $\frac{Z^2}{n^2} = \frac{2^2}{1^2} = 4$]

$E_{Li} = \frac{9}{4} E_H = 30.5$ eV, $E_{obs} = 5.4$ eV [$_3$Li = $1s^2\ 2s^1$, Z = 3, n = 2]

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* Penultimate shell is that shell which is before the outermost shell.

[$_4Be = 1s^2\ 2s^2, Z = 4, n = 2$]

$E_{Be} = \frac{16}{4} E_H = 54.4$ eV, $E_{obs} = 7.32$ eV

From the calculation it is found that the value of Z corresponding to E_{obs} is less than the actual nuclear charge. For example, the charge on the nucleus 2, 3 and 4 (He, Li and Be respectively) gets reduced to 1.35, 1.59 and 1.7 respectively on the outer electrons.

In lithium (Z = 3), majority of the electron density of 1*s* electron pair will be between the nucleus and outer 2*s* electrons. The net effect of the $1s^2$ electrons (in between nucleus and 2*s* electrons) is to reduce the nuclear charge by two units such that the effective nuclear charge (Z*) becomes equal to 3 – 2, *i.e.*, one. The radial probability distribution curve also shows that 2*s* orbital has "*maximum*" around the "*maximum of 1s electron.*" Thus, an electron in 2*s* orbital penetrates into 1*s* orbital. The energy of 2*s* electron will be determined by Z* (effective nuclear charge) which is somewhat less than the nuclear charge, Z.

Thus, Z* = Z – σ where σ is the screening or shielding constant

"The effect of reduction of force of attraction by the shell between the nucleus and valence electrons is called screening or shielding effect."

Penetration of orbitals

Definiton. *The extent to which an orbital of a shell interacts with the lower quantum number orbitals is called penetration of orbitals.* For example :

(*i*) The energy of 4*s*-orbital is less than that of 3*d* orbital. So the 4*s*-orbital is filled first than 3*d*. It is called as the *penetration of the 3d-orbital by the 4s-orbital.*

s-orbitals (*l* = 0) are more penetrating and are somewhat less shielded by inner-shell electrons than *p*, *d* and *f*-orbitals (*l* = 1, 2 and 3 respectively). It is because of the presence of comparatively more number of maximum near the nucleus. *s*-orbitals, thus shield the nucleus somewhat better than other orbitals. The decreasing order of shielding of different orbitals is *s* > *p* > *d* > *f*. If we now compare the radial distribution curves of 3*s*, 3*p* and 3*d*-orbitals (see chapter, 1), we find that the probable radius of these orbitals decrease in the order 3*s* > 3*p* > 3*d*. Thus 3*d*-orbitals should screen the nucleus more effectively than 3*p* and 3*s*. But it is not so. It is because

"The presence of one node and an intranodal maximum in 3p orbital and the presence of two nodes and two intranodal maximum in 3s-orbital cause them to be affected more by the nucleus as compared to 3d-orbital having no node and intranodal maximum."

Hence the energies of these orbitals are 3*d* > 3*p* > 3*s*.

Calculation of shielding constant (σ) – Slater's rules. Slater has given a number of empirical rules 'for the calculation of 'σ' which are based on the average behaviour of electrons. **For *ns* or *np* electrons the rules are :**

(*i*) Write the electronic configuration of the element and group the electrons in the order :
(1*s*), (2*s*, 2*p*), (3*s*, 3*p*), (3*d*), (4*s*, 4*p*), (4*d*), (4*f*), (5*s*, 5*p*), (5*d*, 5*f*), (6*s*, 6*p*) etc.

(*ii*) Electrons present in a group '*which are on the right to the (ns, np) group*' do not contribute to the screening constant.

(*iii*) All of the other electrons in the (*ns*, *np*) group (*i.e.*, **one electron less than the number of group** electrons) shield the valence electron to an extent of 0.35 each. **For an electron in 1s-orbital, there will be a contribution of 0.30 from other single electron in (s-orbital).**

(*iv*) All the electrons in the (*n* – 1)th shell shield the valence electron to an extent of 0.85 each.

(*v*) All the electrons in the (*n* – 2)th or lower shell shield the valence electron to an extent of 1.00 each.

Rules for calculating 'σ' when electron being shielded is in nd or nf group are :

(*a*) Rules (*i*), (*ii*) and (*iii*) are same but rules (*iv*) and (*v*) become :

(*ii*) σ for $1s^1$ (one electron less than group electrons *i.e.*, $2 - 1 = 1$) of $_{30}$Zn atom $= 1 \times 0.30 = 0.30$.

$\therefore$ Effective nuclear charge, $Z^* = Z - \sigma = 30 - 0.30 = \mathbf{29.70}$

EXAMPLE 4. Find the effective nuclear charge felt by 6s electron in tantalum atom (at. no. 73).

SOLUTION. (*i*) The electron configuration of Ta-atom is $[Kr]^{36}\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^4\ 6s^1$

(*ii*) The grouped electron configuration is $[Kr]^{36}\ (4d)^{10}\ (4f)^{14}\ (5s, 5p)^8\ (5d)^4\ (6s)^1$.

The shielding constant (σ) felt by 6s electron = 0.35 (one electron less than the number of electrons in $n = 6$) + 0.85 (number of electrons in "$n - 1$" shell *i.e.*, 5th shell) + 1.0 (number of electrons with $n < 5$)

$$= 0.35 \times 0 + 0.85 \times 12 + 1.0 \times 60 = 70.2.$$

$\therefore$ Effective nuclear chare, $Z^* = Z - \sigma = 73 - 70.2 = \mathbf{2.8}$

Applications of effective nuclear charge (Slater's rules)

Effective nuclear charge is helpful to solve many chemical problems as described below.

1. Explains why a cation is smaller in size than that of its parent atom. Let us compare the size of Be^{2+} with Be-atom.

(*i*) Various groups in $_4$Be-atom $= (1s)^2\ (2s)^2$

$\therefore$ Screening constant, σ = (Number of electrons in 2*s* groups − 1) × 0.35 + (number of electrons in inner group) × 0.85 = $1 \times 0.35 + 2 \times 0.85 = 0.35 + 1.70 = 2.05$

$\therefore$ $Z^* = Z - \sigma = 4 - 2.05 = \mathbf{1.95}.$

(*ii*) Various groups in $_4$Be^{2+} $= (1s)^2$

$\therefore$ Screening constant, σ = (Number of electrons in 1*s* group − 1) × 0.30 = $1 \times 0.30 = 0.30$

$\therefore$ $Z^* = Z - \sigma = 4 - 0.30 = \mathbf{3.70}.$

The effective nuclear charge of Be^{2+} (= 3.70) is greater than effective nuclear charge of Be-atom (= 1.95). So, the size of Be^{2+} is smaller than that of Be-atom.

2. Explains why an anion is larger in size than that of its parent atom. Let us compare the size of F$^-$ ion with that of F-atom.

(*i*) Various groups in $_9$F-atom $= (1s)^2\ (2s\ 2p)^7$

$\therefore$ Screening constant, σ = (Number of electrons in (2*s*,2*p*) group − 1) × 0.35 + (number of electrons in inner group) × 0.85 = $6 \times 0.35 + 2 \times 0.85 = 2.10 + 1.70 = \mathbf{3.80}.$

$$Z^* = Z - \sigma = 9 - 3.80 = 5.20$$

(*ii*) Various groups in $_9$F$^-$ ion $= (1s)^2\ (2s\ 2p)^8$.

$\therefore$ Screening constant, σ = (Number of electrons in 2*s*, 2*p* group) × 0.35 + (number of electrons in inner group) × 0.85 = $7 \times 0.35 + 2 \times 0.85 = 2.45 + 1.70 = \mathbf{4.15}.$

$$Z^*\ (F^-) = Z - \sigma = 9 - 4.15 = 4.85$$

The effective nuclear charge of F-atom (= 5.2) is greater than effective nuclear charge of F$^-$ ion (4.85). So, the size of F-atom is smaller than that of F$^-$ ion.

3. Explains why *ns* (say 4*s*) orbital is filled first than (*n* − 1) *d* [say, 3*d*] orbital. Let us consider the electron configuration of potassium atom, $_{19}$K. It can be assigned any one of the following two electronic configurations.

(*i*) $_{19}K = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ and (*ii*) $_{19}K = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1$

(*a*) Various groups in $_{19}$K of electron configuration, (*i*) are $(1s)^2\ (2s, 2p)^8\ (3s, 3p)^8\ (4s)^1$.

$$\begin{bmatrix}\text{Screening effect, }\sigma\\ \text{on }4s\text{ electron}\end{bmatrix} = 0.35 \times \begin{bmatrix}\text{Number of electron}\\ \text{in }4s\text{ group-1}\end{bmatrix} + \begin{bmatrix}\text{number of electrons}\\ \text{in }3s, 3p\text{ group}\\ \times\ 0.85\end{bmatrix} + \begin{bmatrix}\text{number of electrons}\\ \text{in }(2s, 2p)\text{ and group}\\ (1s)\text{ group} \times 1.0\end{bmatrix}$$

$= (0 \times 0.35) + (8 \times 0.85) + (10 \times 1.0) = 0 + 6.8 + 10 = 16.8$

∴ Effective nuclear charge, $Z^* = 19 - 16.8 =$ **2.2**

(*b*) Various groups in $_{19}$K of electron configuration, (*ii*) are $(1s)^2\ (2s, 2p)^8\ (3s, 3p)^8\ (3d)^1$.

$$\begin{bmatrix}\text{Screening effect, } \sigma \\ \text{on } 3d \text{ electron}\end{bmatrix} = \begin{bmatrix}\text{Number of electron in} \\ 3d \text{ group } (-1) \times 0.35\end{bmatrix} + \begin{bmatrix}\text{Number of electrons in the} \\ \text{left of } 3d \text{ shell} \times 1.0\end{bmatrix}$$

$$= 0 \times 0.35 + 18 \times 1 = 18$$

∴ Effective nuclear charge, $Z^* = 19 - 18 = 1$. The effective nuclear charge of $_{19}$K for electron configuration (*i*) is greater (= 2.2) than that of $_{19}$K for electron configuration, (*ii*) (= 1). So 4*s* electron is strongly held by K-nucleus than 3*d* electron. Hence 4*s* orbital is filled first than 3*d*.

4. While forming cations of transition elements, why 4*s* electrons are lost prior to 3*d* electrons. Let us consider the electron configuration of $_{25}$Mn

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$$

The electron configuration of $_{25}\text{Mn}^{+2}$ is :

(*i*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$ (*ii*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$

(*i*) Various groups in Mn^{2+} for electron configuration, (*i*) are : $(1s)^2\ (2s, 2p)^8\ (3s, 3p)^8\ (3d)^5$

∴ Screening effect, σ on 3*d* electron = (number of electrons in 3*d* group – 1) × 0.35 + (number of electrons to the left of 3*d* subshell × 1.0)

$$= 4 \times 0.35 + 18 \times 1 = 1.4 + 18 = 19.4$$

∴ Effective nuclear charge, $Z^* = 25 - 19.4 =$ **5.6**

(*ii*) Various groups in Mn^{2+} for electron configuration, (*ii*) are : $(1s)^2\ (2s, 2p)^8\ (3s, 3p)^8\ (3d)^3\ (4s)^2$

∴ Screening effect, σ on 4*s* electron = (number of electrons in 4*s* group – 1) × 0.35 + (number of electrons in $n - 1^{\text{th}}$ group) × 0.85 + (number of electrons in (*n* – 2), (*n* – 3) etc. groups) × 1.0

$$= 1 \times 0.35 + 11 \times 0.85 + 10 \times 1.0 = 0.35 + 9.35 + 10 = 19.70$$

∴ Effective nuclear charge, $Z^* = 25 - 19.70 =$ **5.3**

The effective nuclear charge on Mn^{2+} for electron configuration (*i*) (= 5.6) is greater than that on Mn^{2+} for electron configuration (*ii*), (= 5.3). Thus the electron configuration (*i*) is more stable than electron configuration, (*ii*). Hence 4*s* electrons are lost prior to 3*d* electrons.

5. It explains successive ionisation energies of elements. It explains why third ionisation energy is greater than second ionisation energy which in turn is greater than first ionisation energy. Let us compare the second ionisation energy of Al (*g*), with first ionisation energy of Al (*g*) with the help of their effective nuclear charge.

$$_{13}\text{Al}\ (1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1) + \text{IE}_1 \longrightarrow \text{Al}^+\ (1s^2\ 2p^2\ 2p^6\ 3s^2)$$

(*i*) Various groups in Al (*g*) = $(1s)^2\ (2s, 2p)^8\ (3s, 3p)^3$

∴ Screening constant, σ on 3s or 3p electron = (number of electrons in nth shell –1)×0.35 + (number of electrons in (*n*–1) shell)×0.85+(number of electrons in (*n* – 2) shell) × 1.0

$$= 2 \times 0.35 + 8 \times 0.85 + 2 \times 1 = 0.70 + 6.80 + 2 = 9.50$$

∴ Effective nuclear charge $Z^* = 13 - 9.5 =$ **3.5**

(*ii*) Various groups in Al^+ (*g*) = $(1s)^2\ (2s, 2p)^8\ (3s, 3p)^2$

∴ Screening constant, σ on 3*s* or 3*p* electron = (Number of electrons in nth shell–1)×0.35 +(number of electrons in (*n*–1) shell) × 0.85 + (number of electrons in (*n* – 2) shell) × 1.0

$$= 1 \times 0.35 + 8 \times 0.85 + 2 \times 1 = 0.35 + 6.80 + 2 = 9.15$$

∴ Effective nuclear charge, $Z^* = 13 - 9.15 =$ **3.85**

The effective nuclear charge on $Al^+(g)$ (= 3.85) is greater than the effective nuclear charge on $Al(g)$ (= 3.5), hence valence electron is strongly held by nucleus in Al^+ (g) than that of $Al(g)$. Hence high energy is needed to remove an electron from $Al^+(g)$ than $Al(g)$. In other words, second ionisation energy is greater than first ionisation energy.

Similarly, it can be shown that third ionisation energy is greater than second ionisation energy of Al (g).

6. It explains why atomic and ionic size of elements of s and p block decrease along a period. Consider elements Li and Be of second period.

(*i*) Various groups in $_3Li$ ($1s^2 2s^1$) are : $(1s)^2 (2s)^1$

Screening constant, σ on 2*s* electron = (number of electrons in 2*s* – 1) × 0.35 + (number of electrons in (n –1) shell) × 0.85 = 0 × 0.35 + 2 × 0.85 = 1.70.

∴ Effective nuclear charge, $Z^* = 3 - 1.70 =$ **1.30**

(*ii*) Various groups in $_4Be$ ($1s^2 2s^2$) are $(1s)^2 (2s)^2$

Screening constant, σ on 2*s* electron = (number of electrons in 2*s* – 1) × 0.35 + (number of electrons in (n – 1) shell) × 0.85 = 1 × 0.35 + 2 × 0.85 = 0.35 + 1.70 = **2.05.**

∴ Effective nuclear charge = 4 – 2.05 = **1.95.**

Since the effective nuclear charge in Be-atom (= 1.95) is greater than that in Li atom (= 1.30), the size of Be-atom is smaller than that of Li-atom. Similarly, it can be explained that ionic size of elements decrease along a period.

7. It also justifies the auf-bau principle according to which the electrons are filled in various orbitals in the order of their increasing energies.

Limitations of Slater rules

Various limitations of Slater rules are :

1. It is less reliable for atoms of heavier elements.
2. These rules state that all the electrons present in *s*, *p*, *d* and *f*-subshells of (n – 1) shell shield the outer n-shell electrons with equal contribution *i.e.* 1. It does not appear to be true because electrons present in *s*, *p*, *d* and *f*-subshells have different energies and donot shield the nucleus to same extent.
3. Radial distribution curves for orbitals show that *s*-orbitals penetrate more to-wards nucleus than *p*-orbitals. So, screening effect of *s*-orbitals should be more than *p*-orbital but according to Slater rules, *s* and *p* orbitals of the same shell are grouped together.

CHARACTERISTICS OF PERIODS

The main characteristics of the period are given below :

(*i*) **Electronic configuration.** The atomic number of the elements increase by one unit as one moves from left to right in a period. Thus, each element attains a new electronic configuration. (Table 2.3).

Table 2.3.

Element	Li	Be	B	C	N	O	F	Ne
Electronic configuration →	$1s^2 2s^1$	$1s^2 2s^2$	$1s^2 2s^2 2p^1$	$1s^2 2s^2 2p^2$	$1s^2 2s^2 2p^3$	$1s^2 2s^2 2p^4$	$1s^2 2s^2 2p^5$	$1s^2 2s^2 2p^6$
Period	2	2	2	2	2	2	2	2
Principal quantum No. (n) of outer shell	2	2	2	2	2	2	2	2

(*ii*) **Valency.** (*a*) The valency of an element increases from 1 to 4 and then decreases to zero with respect to hydrogen.

(*b*) The valency of an element increases from 1 to 7 with respect to oxygen, *e.g.*, in the third period (Table 2.4), we have:

Table 2.4.

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Valency w.r.t. 'H'	1	2	3	4	3	2	1	0
Hydrides	NaH	MgH_2	AlH_3	SiH_4	PH_3	H_2S	HCl	–
Valency w.r.t. 'O'	1	2	3	4	5	6	7	0
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7	–
Behaviour of oxides	Strongly Basic	Basic	Amphoteric	Feebly acidic	Acidic	More acidic	Most acidic	—

(*iii*) **Trend in properties along a period from left to right in the periodic table.** As we move from left to right in the periodic table : "the atomic number, *i.e.*, nuclear charge goes on increasing". The electrons get added in the same shell. The added electrons do not screen the nucleus appreciably. The attraction of the nucleus for the outermost electron goes on increasing. *The effective nuclear charge becomes greater than screening effect.* As a result :

(*a*) *atomic radius, ionic radius, atomic volume, i.e., atomic size, metallic character and hence basic nature of their oxides and electropositive character goes on decreasing.*

(*b*) *Ionization potential, electron affinity, electro-negativity, non-metallic character and hence acidic nature of their oxides goes on increasing.*

(*iv*) *Diagonal relationship.* Elements present in 2nd and 3rd periods show diagonal relationship with each other, *i.e.*, these resemble each other, *e.g.*, Li, Be, B resemble Mg, Al, Si respectively.

$$\begin{tikzcd}
\textit{2nd period elements :} & \text{Li} \arrow[dr] & \text{Be} \arrow[dr] & \text{B} \arrow[dr] & \text{C} \\
\textit{3rd period elements :} & \text{Na} & \text{Mg} & \text{Al} & \text{Si}
\end{tikzcd}$$

Reason. (*a*) *On moving along a period* :

(*i*) The size as well as electropositive character of elements decrease.

(*ii*) The polarizing power of the ions increases.

(*b*) *On moving down the group* :

(*i*) The size as well as electropositive character of elements increase.

(*ii*) The polarizing power of ions decreases.

(*c*) *On moving along the diagonal*, the decrease and increase of size, electropositive character and polarizing power partly cancel each other. Thus, there is a good similarity in the properties of the diagonally opposite elements.

For trends in periodic properties of periods 2, 3 and 4 elements see section, 2.24.

GROUPS*

Vertical columns in the periodic table starting from top to bottom are called groups or families.

All the elements in a group have similar electronic configuration and hence similar properties. These show a regular variation in physical properties.

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*In the new IUPAC system, group IA, IIA, IIIB, IVB, VB, VIB, VIIB, VIII, VIII, VIII, IB, IIB, IIIA, IVA, VA, VIA, VIIA and zero are called 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17 and 18 groups respectively.

Some important families are :

(*i*) Alkali metals, (IA) (*ii*) Alkaline earth metals (IIA), (*iii*) Chalcogens (VIA), (*iv*) Halogens (VIIA) (*v*) Aerogens, noble gases, inert or rare gases (zero) (*vi*) Coinage metals (IB) (*vii*) Pnictogens (VA).

There are eighteen groups in the long form of the periodic table. These are numbered as IA, IIA, IIIB, IVB, VB, VIB, VIIB, VIII, VIII, VIII, IB, IIB, IIIA, IVA, VA, VIA, VIIA, and zero.

(*i*) *Similar electronic configuration*. All the elements belonging to a particular group have similar electronic configuration, *e.g.*, Alkali metals (group IA).

Li (at. No. 3) = $1s^2\ 2s^1$; Na (at. No. 11) = $1s^2\ 2s^2\ 2p^6\ 3s^1$ and so on.

Both Li and Na have one electron in their outermost *s*-orbital.

(*ii*) *Same valency*. All the elements belonging to a particular group have same valency, *e.g.*,

(*a*) *Alkali metals (group IA)* have one electron in their outermost shell and have *valency* = 1.

(*b*) *Alkaline earth metals (group IIA)* have two electrons in their outermost shell and have *valency* = 2.

(*iii*) *Similar chemical properties*. Various elements of the same group have similar electronic configuration and hence their chemical properties are *quite similar*.

Trend in properties down the group in the periodic table. As we move down the group in the periodic table, the atomic number, *i.e.*, nuclear charge goes on increasing. The electrons get added in the new shells which screen the nucleus and the screening effect by the new shells goes on increasing. The attraction of the nucleus for the outermost electrons goes on decreasing. The screening effect becomes greater than effective nuclear charge. As a result :

(*i*) *Atomic radius, ionic radius, atomic volume, i.e. atomic size, metallic character* and hence basic nature of their oxides and electropositive character goes on increasing.

(*ii*) *Ionization potential, electron affinity, electronegativity and non-metallic character* goes on *decreasing*.

Advantage of classification of elements or merits of long form of periodic table

The elements are classified to have a better control on their studies with small effort. Following are major advantages of the long form of periodic table :

(*i*) It is based upon the atomic number which is a more fundamental property of the elements. Hence there is no problem of placing the isotopes of an element separately.

(*ii*) The position of elements in the periodic table is governed by their electronic configuration.

(*iii*) The division of elements into *s*, *p*, *d* and *f*-blocks has made the study more simple and has a logical explanation.

(*iv*) It is simple and easy to reproduce.

(*v*) The position of some elements which are misfit on the basis of atomic mass is now justified on the basis of atomic number. For example, argon (atomic mass = 39.9) preceeds potassium (atomic mass = 39.1) because argon has atomic number 18 and potassium has 19.

(*vi*) The lanthanoids and actinoids, which have properties different from other groups are placed separately at the bottom of the periodic table.

(*vii*) The properties of new elements can be predicted even before their actual discoveries.

Defects of long form of the periodic table

Although long form of the periodic table gives the best arrangement of elements, yet it suffers from the following defects:

(*i*) **Position of hydrogen.** It does not resemble fully with alkali metals but has been placed alongwith them. It also resembles halogens as well as carbon.

(*ii*) Group VIII consists of three columns instead of one.

(*iii*) Position of lanthanides and actinides is not proper in the periodic table.

(*iv*) According to electronic configuration, helium ($1s^2$) should be placed in *s*-block whereas it is placed in *p*-block.

(*v*) The designation of sub-groups as A and B has got no significance.

s, *p*, *d* AND *f*-BLOCK ELEMENTS

Types of elements on the basis of their electronic configuration (*arrangement of electrons in orbitals*).

On the basis of the electronic configuration of the atoms, the elements have been divided into three types and four blocks (*s*, *p*, *d* and *f*).

(*i*) **Representative or *s* and *p*-block elements.**

(*ii*) **Transition or *d*-block elements.**

(*iii*) **Inner transition or *f*-block elements.**

(*i*) **Representative elements.** *It includes elements which have their outermost shells incomplete.* The electron configuration of the incomplete shells is either $ns^{1 \text{ or } 2}$ or $ns^2\ np^{1 \text{ to } 6}$.

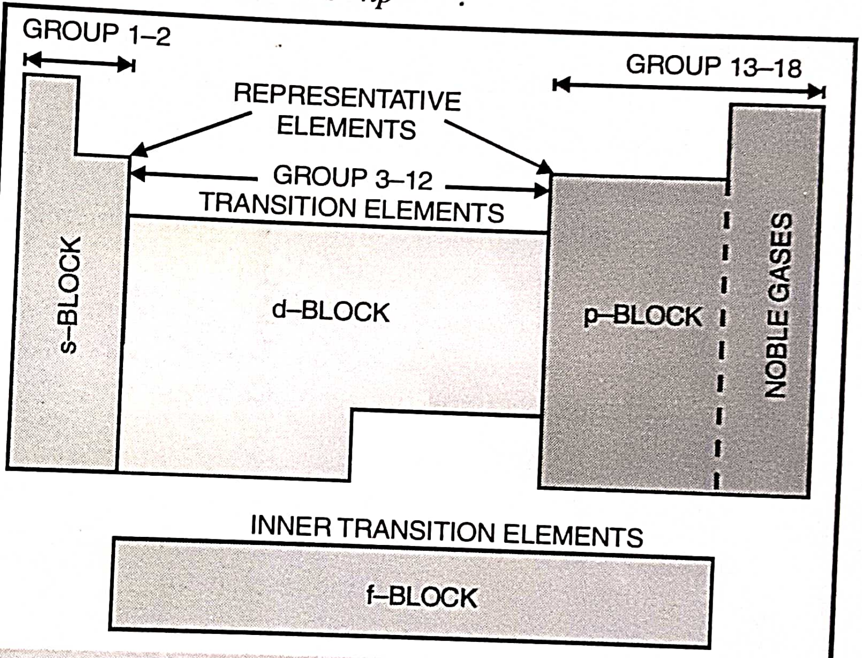


Fig. 2.1. Division of periodic table into four blocks.

The $ns^2\ np^6$ configuration is assigned to group zero and consists of noble gases. Except noble gas elements, the group number is the number of electrons in the outermost shell.

From chemical viewpoint, representative elements have been subdivided as follows fig. 2.1.

I. s-Block elements. *Those elements (except He) in which last electron enters into the s-subshell of the outermost main energy level, are called s-block elements e.g.,*

$$_{11}\text{Na} = 1s^2\ 2s^2\ 2p^6\ 3s^1$$

This block is situated on the left hand side of the periodic table. It contains 13 elements in two groups (1 and 2). Their general configuration is ns^1 (group 1 or IA) and ns^2 (group 2 or IIA), where *n* stands for the outermost shell. These are all *active* metals (except H) and show a fixed electropositive valency. Group 1 and group 2 elements are respectively called alkali metals and alkaline earth metals.

Important characterisitcs of s-block elements. With the exception of hydrogen, the *s*-block elements have the following characterisitcs :

(*i*) They are soft metals having low melting and boiling points.

(*ii*) They have low ionisation enthalpies (energies).

(*iii*) They are highly reactive and readily form univalent or bivalent positive ions by losing the valence electrons.

(*iv*) The metals and their salts impart characteristic colours to the flame. For example, sodium salts impart a golden yellow colour to the flame. Exceptions include Be and Mg metals.

(*v*) In the molten state or solution form, these are good conductors of heat and electricity.

(*vi*) Cations of *s*-block elements are diamagnetic (not-attracted by magnets) and colourless due to the absence of unpaired electrons.

(*vii*) Act as good reducing agents due to their low ionisation energies. Group 1 (IA) elements are stronger reducing agents than elements of group 2 (IIA).

(*viii*) Their hydroxides are strong bases.

(*ix*) Last elements of group 1 (francium) and of group 2 (radium) are radioactive.

II. p-block elements. These elements (except He) in which last electron enters into the p-sublevel of the outermost main energy level, are called p-block elements, *e.g.*,

$$_{17}\text{Cl} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$$

This block is situated on the right hand side of the periodic table. It contains 31 elements in six groups 13-18. Their general electronic configuration is $ns^2\ np^{1-6}$ where *n* stands for the outermost shell. Their $(n-1)$ *d* orbital along with $(n-1)\ s$, $(n-1)\ p$ and *ns* orbitals are fully filled. The differentiating electron enters in the *np* orbital.

Exceptions. If we follow the definition of representative elements strictly, we find many exceptions. For example.

(*i*) Copper and zinc families have outer shell configurations as $(n-1)\ d^{10},\ ns^{1,\,2}$.

(*ii*) Ytterbium, $_{70}\text{Yb} = [_{54}\text{Xe}]\ 4f^{14}\ 6s^2$ and (*iii*) Nobelium, $_{102}\text{No} = [_{86}\text{Rn}]\ 5f^{14}\ 7s^2$.

These should be included in the representative elements. However :

(*i*) Cu and Zn families resemble transition elements more than representative elements. Hence these are classified as **transition elements.**

(*ii*) **Yb and No resemble lanthanides and actinides respectively more than representative elements. Hence these are classified as inner transition elements. Cu and Zn families are, thus, the bridging elements between transition and representative elements.**

It includes elements of :

(*i*) IIIA, IVA, VA, VIA, VIIA ($\text{F} = 1s^2\ 2s^2\ 2p^5$) and zero group or group 18.
Includes highly electronegative elements (halogens, *chalcogens*, *viz*, O, S, Se, etc.), inert elements (noble gases), electropositive elements (Al, Pb, etc.) and metalloids (As, Sb, Bi, etc.).

(*ii*) Include elements which exist as gases (F_2, Cl_2, etc.), liquids (Br_2 etc.) and solids (Al, Sn, etc.).

Important characteristics of p-block elements

(*i*) They include both metals and non-metals. But there is a regular gradation from metallic to non-metallic character as we move from left to right.

(*ii*) They have quite high ionisation enthalpies (energies) and the values tend to increase as we move from left to right.

(*iii*) Generally, *p*-block elements form mostly covalent compounds.

(*iv*) In a period, there is gradation from reducing to oxidising properties.

(*v*) *p*-block elements are generally bad conductors of heat and electricity (except those which are metals).

(*vi*) Atomic radii decrease across a period and increase down a group.

(*vii*) Heavier elements exhibit variable valency.

(*viii*) Last elements in group 16 (chalcogens) and 17 (halogens) are polonium (P_o) and astatine (At) which are radioactive. Last element of group 18 (radon) is also radioactive.

Typical Elements. Elements of the third period are called typical elements.

Group number	IA (1)	IIA (2)	IIIA (13)	IVA (14)	VA (15)	VIA (16)	VIIA (17)
Third period elements	Na	Mg	Al	Si	P	S	Cl

The second period elements ($n = 2$) have only two shells and second shell has only s and p-orbitals. It has no d-orbitals. On the other hand, elements of third period ($n = 3$) have vacant d-orbitals and the electrons in these elements have greater mobility. Thus Li which is the first member of group IA (or 1) differs in a number of properties from other members of the family. On the other hand, sodium very much resembles potassium and other alkali metals. Thus *properties of all the elements present in each group are similar to the properties of the typical elements of that group.*

Bridge Elements (Diagonal relationship). Elements of second period are known as bridge elements. They resemble, in certain properties, with the elements of third period diagonally placed.

$$\begin{tikzcd}
\textbf{Second period} & Li \arrow[dr] & Be \arrow[dr] & B \arrow[dr] & C \arrow[dr] & N \arrow[dr] & O \arrow[dr] & F \\
\textbf{Third period} & Na & Mg & Al & Si & P & S & Cl
\end{tikzcd}$$

Thus Li has similarities with Na as well as Mg and it acts as a bridge between two groups.

III. *d*-block elements or Transition elements. It includes elements which have incompletely filled d-orbitals in their ground or combined state. The electron configuration of the incomplete shells is $(n-1)$ s^2 $(n-1)$ p^6 $(n-1)$ $d^{1 \text{ to } 10}$ ns^2 with a few irregularities. There are four transition series corresponding to the filling up of $3d$, $4d$, $5d$ and $6d$ orbitals. This block is situated in-between s and p-blocks. It includes 40 elements in four transition series. These series are :

(*a*) **First transition series.** It includes 10 elements with atomic number 21 (scandium) to 30 (zinc). The last electron enters in $3d$-orbital.

(*b*) **Second transition series.** It includes elements with atomic numbers 39 (yttrium) to 48 (cadmium). The last electron enters in $4d$ orbital.

(*c*) **Third transition series.** It includes elements with atomic number 57 (Lanthanum) 72, (Hafnium) to 80 (Mercury). The last electron enters in $5d$-orbital.

(*d*) **Fourth transition series.** It is now a complete transition series. It includes elements with atomic number 89 (actinium, Ac), 104 (rutherfordium, Rf), 105 (dubnium, Db), 106 (seaborgium, Sg), 107 (bohrium, Bh), 108 (hassium, Hs), 109 (meitnerium, Mt) 110 (dermstadtium, Ds), 111 rontgenium, Rg) and 112 Copernicium ($_{112}$Cn).

It includes the elements of IIIB (3) to VIIB (7), VIII (8, 9, 10), IB (11) and IIB (12) groups.

Group VIII consists of three vertical columns containing twelve elements in all.

If we follow the definition of transition elements strictly, we find some exceptions. For example. (*i*) Lutecium, $_{71}$Lu = $[Xe]^{54}$ $4f^{14}$ $5d^1$ $6s^2$ and (*ii*) Lawrencium, $_{103}$Lr = $[_{86}Rn]$ $5f^{14}$ $6d^1$ $7s^2$.

These should be included in the transition elements. However, their properties justify their inclusion in the inner transition elements. These elements are the bridging elements between transition and inner transition elements.

These **are called transition elements** because their properties are intermediate between those of s and p block elements. These **are called d-block elements** because their penultimate shell of electrons is being expanded from 8 to 18 by the addition of d-electrons.

METHOD TO KNOW THE NUMBER OF PERIOD, GROUP AND BLOCK TO WHICH AN ELEMENT BELONGS

Various steps to know the period, group and block of an element are given below :

(*i*) Write the electronic configuration of the element.

(*ii*) Write the groups in the following order with the sub-shell in which the valence electrons of the element concerned is filled. Do not change the configuration by considering that half-filled or fully-filled orbitals are most stable.

IA (s^1), IIA (s^2) except He, IIIB (d^1), IVB (d^2), VB (d^3), VIB (d^4), VIIB (d^5), VIII (d^6), d^7 or (d^8), IB (d^9), IIB (d^{10}), IIIA (p^1), IVA (p^2), VA (p^3), VIA (p^4), VIIA (p^5), Zero group (p^6) and $1s^2$ of helium.

Or

For *s*-block elements, group number is equal to the number of valence electrons (*ns*)

For *p*-block elements, group number is equal to 10 + number of valence electrons (*ns* and *np*)

For *d*-block elements, group number is equal to the number of electrons in (*n* – 1) *d* and *ns* subshells.

(*iii*) The name of the block is that sub-shell in which the last electron of the element is filled.

(*iv*) Number of the period is the highest value of shell which is present in the electronic configuration of element concerned.

Example

EXAMPLE 5. Find the number of period, group and block in which the element with atomic number 24 is present.

SOLUTION. (*i*) The electronic configuration of element with atomic number 24 is :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4\ 4s^2$ (unstable).

(*ii*) In the configuration, the last electron of the element is filled in *d*-subshell as $3d^4$. Thus this element belongs to *d*-block of the periodic table with group number VIB or 6 (*i.e.*, 2 e^-*s* of 4*s* + 4e^-*s* of 3*d* = 6).

(*iii*) The highest shell present in the electron configuration of this element is 4*s*. Thus the period number is 4.

ATOMIC AND IONIC PROPERTIES

Atomic and ionic radii

Except noble gas atoms, all atoms or ions are almost unstable. Also, it is impossible to isolate an atom or an ion. So, atomic and ionic radii of an element cannot be determined. So, in order to measure the atomic and ionic radii of the atom of an element, we measure their internuclear distances in crystals and in gaseous molecules. We, then derive the radii from these distances in one way or the other. Their exact calculations are, however, affected by many factors given below :

Factors on which atomic size depend

1. Hybridisation. The state of hybridisation also affects the radius of an atom. For example,

(*i*) C-atom in CH_4 is sp^3 hybridised (*s*-characer, 25%) and has atomic radius 77 pm.

(*ii*) C-atom in $H_2C = CH_2$ is sp^2 hybridised (*s*-character, 33%) and has atomic radius, 67 pm.

(*iii*) C-atom in $HC \equiv CH$ is *sp*-hybridised (*s*-character, 50%) and has atomic radius, 60 pm.

From above discussion it is clear that *greater the s-character of an atom, smaller will be the atomic radius of that atom.* There are many factors like bond order, bond type, crystal structure and oxidation number of concerned atom, on which the atomic radius of an atom depends. For example:

The multiplicity of bonds (*i.e.* double and triple covalent bonds) causes the decrease in covalent radius between any two atoms. It is because such bonds are formed by the overlapping of atomic orbitals to greater extent. Greater overlapping brings bonded atoms close to-gether. It is clear from the following table.

Bond	Radius	Bond	Radius
$N - N$ $N = N$ $N \equiv N$	70 pm 60 pm 55 pm	$C - C$ $C = C$ $C \equiv C$	77 pm 67 pm 60 pm

2. Nuclear charge. With increase in nuclear charge, the force of attraction between the nucleus and the electron cloud increases. Hence, the electron cloud moves closer to the nucleus and atomic size decreases.

3. Number of orbits. With increase in number of orbits, the distance between the nucleus and last orbit increases. Hence, atomic size increases. Similarly, with decrease in number of orbits, the atomic size decreases.

4. Bond order. Greater the bond order between similar atoms, smaller will be the bond length (= 2 × atomic radius) because overlapping of *p*-orbitals brings the combining atoms together. For example, bond lengths of $C \equiv C$ (120 pm) > $C = C$ (= 134 pm) > $C - C$ (= 154 pm)

5. Bond type *i.e.*, degree of ionic, covalent or metallic character.

6. Molecular structure. **7. Oxidation states** of the bonded neighbours.

So, we **conclude that** "*no single type of atomic radius is completely satisfactory.*" Hence we discuss here different kinds of radii.

1. Bonded radii. Such radii are of two types: (*i*) **Atomic radius** (*ii*) **Ionic radius (crystals)**

The atomic radii are further subdivided into

(*i*) **Covalent** as in covalent molecules and in the non-metals and

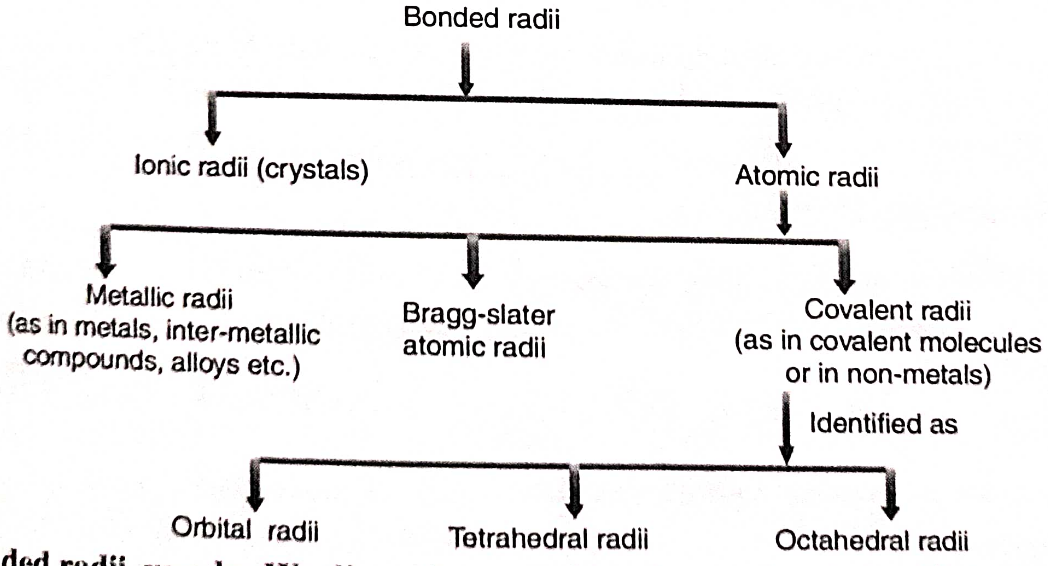
(*ii*) **Metallic** as in the metals, intermetallic compounds or in alloys.

Sometimes, the covalent radii are further identified as **tetrahedral or octahedral radii**. So, there is a need to distinguish single bond radii from double bond and triple bond radii. In case *when multiple bonding* *e.g.*, double, = or triple, ≡) is present, *the shape of the atom does not remain spherical but gets* somewhat distorted. So, in such cases, measurement of *internuclear distances* is done which, in fact, is generally done in molecules which donot have a regular polyhedron geometry *e.g.*, square planar, trigonal bipyramidal. For this purpose, we consider two **additional radii** related to atomic or covalent radii. These are :

(*i*) **Bragg-Slater atomic radii** and

(*ii*) **Orbital radii** (identified by the radial distribution functions of the outermost orbitals).

The above discussed radii can be summarised as follows:



2. Non-bonded radii. van der Waal's radii are considered as non-bonded radii. Such radii for the atoms in covalent compounds are essentially identical with the univalent or bivalent anionic radii for these atoms. Details are given below :

Van der Waal radius. (*a*) **For covalent molecules.** It is defined as "Half of the distance between the nuclei of two similar adjacent atoms belonging to two neighbouring molecules in the solid state (fig. 2.2).

(*b*) **For inert gases.** It is *defined* as 'Half of the distance between the nuclei of two adjacent non-bonded atoms at the time of their closest approach'. It may be noted that inert gas elements exist as monoatomic.

van der Waal radius is larger than the covalent radius. A covalent radius is formed by the overlapping of atomic orbitals of bonding atoms. The overlapped region becomes common to both the atoms. This common region is responsible for shortening the covalent radius. On the other hand, the van der Waal radius is only calculated for non-bonded atoms or between adjacent atoms belonging to two neighbouring molecules. In such cases, no overlapping of atomic orbitals takes place. Covalent radii of a few elements are given in Table 2.5. The atomic radii decrease along a period. However, at the end of each period, there is increase in atomic radii for noble gases. It is because in case of noble gases, the atomic radii are van der Waal radii.

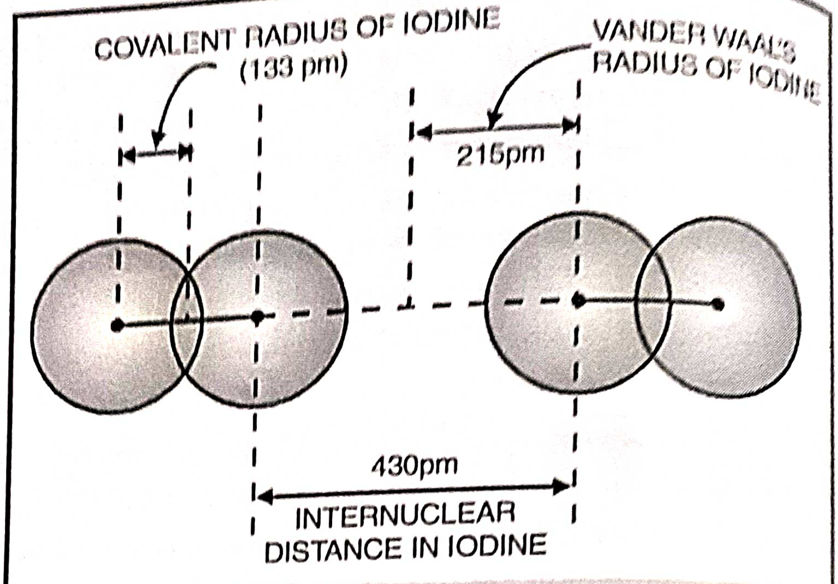


Fig. 2.2. van der Waal's radius of iodine.

Table 2.5 Covalent and van der Waal's radius in Å

Element	Covalent radius	van der Waals radius
Fluorine	0.72	1.35
Chlorine	0.99	1.80
Bromine	1.44	1.95
Iodine	1.33	2.15

METALLIC RADII (or Covalent Radii of Metallic Atoms)

We know that most of the metals donot form covalent compounds. Metallic hydrides and organometallic compounds are, however, exceptions. Radius of a metal atom can be calculated from the atomic volume of metallic phases where :

$$\text{Atomic volume of metallic phase} = \frac{\text{Atomic mass of metal atom}}{\text{Density of metal atom}}$$

Since the value of metallic radii obtained from the use of atomic volume of metallic phases, are almost same, the values of the covalent radii determined from metallic hydrides or organometallic compounds, may be called as metallic covalent radii.

3. Metallic radius. *It is defined as 'Half of the inter-nuclear distance between two adjacent atoms in a metallic bond.*

The radius helps to know the size of atoms of metallic elements. It is *measured by X-ray diffraction* method. This method indicates that metal atoms are closely packed in a metal. This close packing of atoms is called crystal lattice. This packing of atoms is different in different elements and hence different metallic radii. For example :

Metallic radius of Na and K = 1.86 Å and 2.34 Å respectively. *Metallic radius is larger than covalent radius*. The *reason is* that there is no actual overlapping of atomic orbitals in metallic bond. There is, however, overlapping of atomic orbitals in covalent bond.

The overlapping shortens the inter nuclear distance between the atoms, *e.g*,

Metallic radius of Na = 1.86 Å

Covalent radius of Na = 1.54 Å

ATOMIC RADIUS

An atom is assumed to be spherical in shape. Its size is generally measured in terms of its radius. **"Atomic radius is defined as the distance from the centre of the nucleus upto which its outermost electron is extended." It is measured in Angstrom units or picometer (1Å = 100 pm).**

Difficulties to measure exact atomic radius

(*i*) An atom is unstable. It cannot be isolated to get its radius.

(*ii*) The exact position of the outermost electron is uncertain. (Heisenberg's uncertainty principle).

(*iii*) The electron density around an atom is affected by the presence of neighbouring atoms. Thus, exact atomic radius cannot be determined. However, atoms pack up at certain definite distances in solids. This gives an idea about the approximate size of the atom.

Measurement. Atomic radii are measured by *electron diffraction* method in angstrom units (1 Å = 10^{-8} cm) or picometer units (1 Å = 100 pm).

Study of atomic radii. (*i*) **Covalent radius.**

Covalent single-bonded radius of an atom in homonuclear molecules such as H-H, F-F etc. The covalent single bond radius for homonuclear molecules is equal to one half the distance between the nuclei (internuclear distance or bond length) of two like atoms.

Mathematically, covalent single bond radius for homonuclear molecules

$$= \frac{\text{Distance between the nuclei of two like atoms forming a single covalent bond}}{2}$$

The condition for such a calculation is that the bond under consideration is covalent and has no appreciable multiple bond (*e.g.*, double, = or triple, ≡) character. Following examples are given for clarity.

(*i*) *Calculation of single covalent radius of carbon.* Bond length of C – C single bond in diamond and organic compounds containing C – C single bond = 1.54 Å ± 0.01 Å

$$\therefore \text{Covalent radius of carbon, C} = \frac{1.54\ \text{Å}}{2} = 0.77\ \text{Å}.$$

(*ii*) Bond length (or internuclear distance) AB in a H_2 molecule (fig. 2.3)

$$= \frac{74\ \text{pm}}{2} = 37\ \text{pm} = 0.37\ \text{Å}.$$

(*iii*) *Calculation of single covalent radius of silicon, Si*

Bond length of Si–Si simple bond = 2.34 Å

∴ Covalent radius of silicon, Si = 2.34 Å/2=1.17 Å.

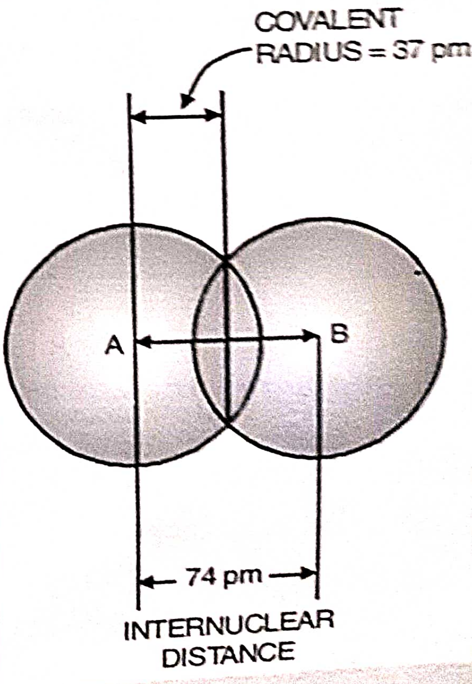


Fig. 2.3.

2. *Covalent single-bonded radius of an atom in* **heteronuclear** molecules such as Si – C $(CH_3)_3$, H – F etc. The covalent single bond radius of atom A (say) in heteronuclear molecules (say AB) is equal to the difference between their bond length (A – B) and covalent radius of one of the single bonded atom B (say). Mathematically :

Covalent radius of one single bonded atom, A in A – B molecule = Bond length of A – B single – single bond – Covalent radius of second bonded atom, B in A – B molecule

Following example is given for clarity.

Example

EXAMPLE 6. Calculate the single covalent radius of silicon, Si in Si – C$(CH_3)_3$ compound. Given, C – Si single covalent bond length =1.94 Å and C – C single covalent radius of carbon, C = 0.77 Å.

SOLUTION. Single covalent radius of silicon,

Si = Bond length of Si–C single bond – Covalent radius of single bonded C-atom = 1.94 Å–0.77 Å = 1.17 Å

Limitation of above relation (1). When two single bonded atoms differ much in their electronegativity (*i.e.*, these have increasingly ionic character) and have multiplicity in bond, the bond length cannot be calculated by simply adding their covalent radius. It is because the additivity becomes a poorer approximation in direct proportion to

(*a*) electronegativity difference between the bonded atoms (*i.e.*, increasing ionic character of bond) and

(*b*) multiplicity of bond. In order to calculate the covalent radius of single bonded atoms of above nature. **Schomaker** and **Stevensen** have given the following relation which is only empirical but not universal.

A – B bond length in Å = Covalent radius of single bonded atom, A in Å + Covalent radius of single bonded atom. B in Å – 0.09 $(x_A - x_B)$. ...(2)

where x_A and x_B are the electronegativities of atoms A and B respectively on Pauling scale. Also, value of x_A > x_B. When covalent radii are taken in picometer (pm), the relation (2) will become :

A – B bond length in pm = Covalent radius of single bonded atom, A in pm + Covalent radius of single bonded atom, B in pm – 9 $(x_A - x_B)$.

The term radius has no physical significance for multibonded atoms because their spherical shape becomes distorted.

Example

EXAMPLE 7. Calculate the C-F bond length if covalent radius of C = 0.77 Å, F = 0.72 Å ; $x_C = 2.5$, $x_F = 4.0$.

SOLUTION. Since the values of electronegativities of C and F differ much and will have some ionic character, so, we have to use Schomaker and Stevensen relation :

C – F bond length in Å = Covalent radius of C in Å + Covalent radius of F in Å – 0.09 $(x_F - x_C)$

= 0.77 Å + 0.72 Å – 0.09 (4.0 – 2.5) = 1.49 Å – 0.135 Å ≃ 1.36 Å

NOTE. 1. In case of a non-metal, the covalent radius generally coincides with its atomic radius but the covalent radius for a metal atom is usually shorter than its atomic (metallic) radius. Following examples are given for clarity.

	K	Cr	Ba	In	Pd	La
Covalent radius (Å)	2.025	1.45	1.98	1.50	1.28	1.69
Metallic radius (Å)	2.31	1.59	2.17	1.62	1.38	1.88

2. Atomic radii should be used where atoms are bonded to one another by metallic bond or a covalent bond.

3. Ionic radii should be used where we assume that the outer electron is completely removed from the electropositive atom and placed in the valence shell of the electronegative atom.

4. We cannot obtain the single bond radii of N_2 and O_2 from their bond lengths. It is because both N_2 (*i.e.*, N ≡ N) and O_2 (*i.e.*, O = O) contain multiple bonds *i.e.*, triple bond and double bond respectively. So, the radius obtained from the bond lengths of N_2 and O_2 will be triple bonded and double bonded radii respectively.

So, in order to get O – O and N – N single bond lengths, we are to take the help of compounds such as H – O – O – H (hydrogen peroxide) for oxygen and $H_2N - NH_2$ (hydrazine) for nitrogen which contain single bonds O – O and N – N respectively.

Method to calculate multiple bond lengths. In order to get a **double bond length, C = O,** a double bonded radius C = C of carbon (= 0.667 Å) is obtained from ethene ($H_2C = CH_2$) and double bonded radius (O = O) of oxygen (= 1.21 Å/2 = 0.605 Å) is obtained from O_2. Combining the double bonded radii of carbon and oxygen gives the expected bond length (0.667 Å + 0.605 Å = **1.272 Å**) for a C = O bond as compared with the observed bond length of 1.22 Å in CO_2.

Similarly, in order to calculate the **triple bond length** of C ≡ N, the triple bonded (C ≡ C) radius of C (= 60 pm) is obtained from C ≡ C bond length in ethyne (HC ≡ CH) while triple bonded (N ≡ N) radius of N (= 55 pm) is obtained from N ≡ N bond length in N_2 (*i.e.*, N ≡ N). Combining the two triple bonded radii of C and N, we get C ≡ N bond length equal to 60 pm + 55 pm = 115 pm. It is quite close to the C ≡ N bond length in $CH_3 - C \equiv N$.

In case of multiple bonded (double, triple bonds) atoms, the corresponding radii are called **multiple bond radii.**

Multiple bond lengths are shorter than single bond lengths. In the formation of multiple bonds, the *p*-orbitals of the combining atoms come close for overlapping. As a result, multiple bond lengths (double, triple) become shorter than single bond lengths. The bond length order is :

Triple bond < double bond < single bond.

The multiple bond, changes the type of hybridization and affects the bond lengths. For example, C – H bond length in HC ≡ CH (C is *sp* hybridised) is 106.5 pm, in $H_2C = CH_2$ (C is sp^2 hybridised) is 107.1 pm and in CH_4 (C is sp^3 hybridised) is 109.6 pm.

IONIC RADIUS

Ionic radius is the distance from the nucleus of that ion upto which it has its influence in an ionic bond. It is measured in angstrom units (1 Å = 10^{-8} cm). *e.g.* in $Na^+ Cl^-$, the sizes of Na^+ and Cl^- ions are 95 pm and 181 pm respectively as shown in the fig. 2.4.

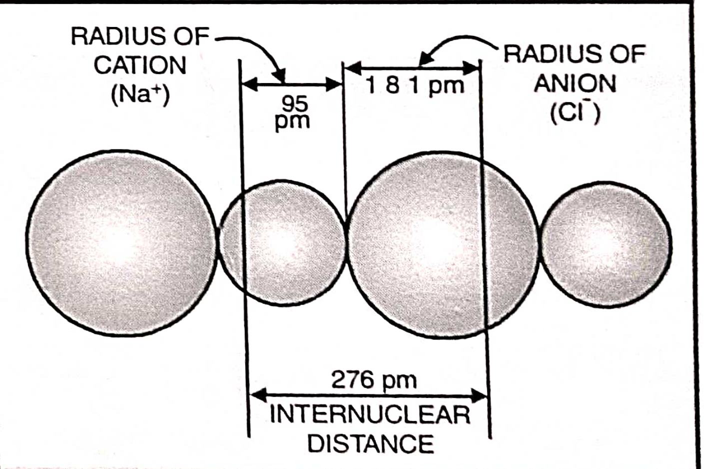


Fig. 2.4. Illustration of ionic radius.

The internuclear distance between cation and anion present in an ionic crystal can be determined by X-ray crystallography. But the radius of cation (portion of the internuclear distance contributed by the cation) and radius of anion (portion of the internuclear distance contributed by the anion) cannot be determined directly because the electrons are transparent to X-rays. So, in order to understand the concept of ionic radius (or to calculate the radius of cation and anion), following assumptions will be meaningful.

(*i*) Existence of ions in solid compounds.

(*ii*) Correct division (apportion) of the internuclear distance between cation and anion.

(*iii*) Additivity (or constancy) of the ionic radii.

Let us describe these one by one.

(*i*) **Existence of ions in solid compounds.** The indirect evidence for the existence of ions is available during the electrolysis of their molten salts as well as their aqueous solutions. But the direct evidence of their presence comes only from the electron density (ED) maps for ionic crystals (though in less number) studied by X-ray crystallography. These maps give us both the internuclear density and the electron charge density (ED) in the region surrounding the nucleus.

Such an ED is shown for NaCl in fig. 2.5. Each line in the figure represents a constant electron density (in electron nm^{-3} or electron $Å^{-3}$). The circle nearest the Na-nucleus represent 70 electrons $Å^{-3}$ and that nearest the Cl-nucleus represents 170 electrons $Å^{-3}$. It is clear from the figure that the charge density extends continuously from one atom to the other but drops off to about 0.2 electron $Å^{-3}$ (or 200 electron nm^{-3}) at the outer edges. It is even lower in the unmarked internuclear regions.

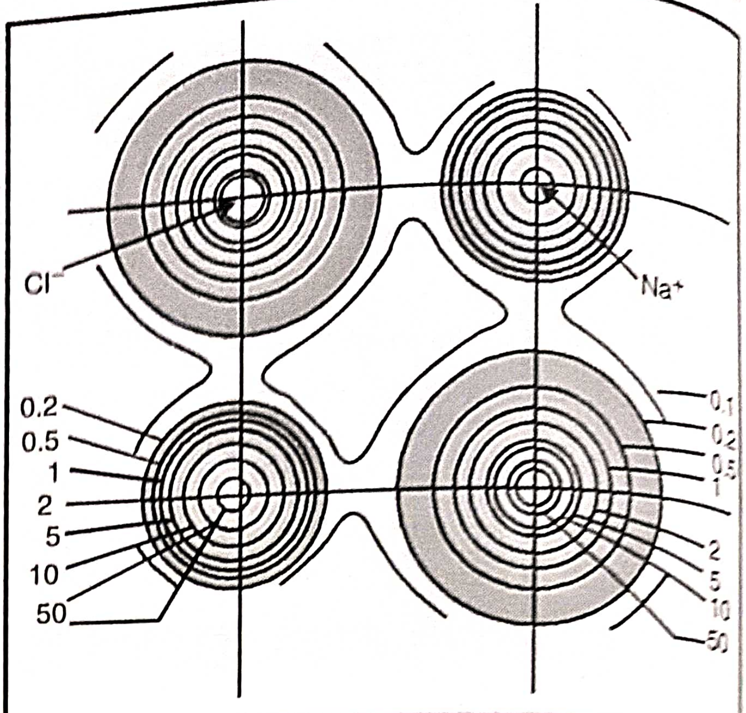


Fig. 2.5. The electron charge density (ED) map of part of cubic face of NaCl. The ED in electrons $Å^{-3}$ is constant along each of the contour lines and increase towards the nuclei of the ion (Na^+, Cl^-)

If we select an arbitrary point of low ED and integrate the ED inward from this point, we find ≃ 10.05 electrons around the Na-nucleus and ≃ 17.70 electrons around the Cl-nucleus. It is thus the direct solid state evidence of electron transfer to produce Na^+ (10 electrons) and Cl^- (18 electrons). The unaccounted ≃ 0.25 electrons (10 + 18 – 10.05 – 17.70 = 0.25) must be present in that internuclear space which was not included in the somewhat arbitrary integration. *The region of minimum ED may be considered to define a boundry* between two spherical ions (Na^+ and Cl^-) that contain most (but not all) of the charge. Using above concept, following "*electron density map radii*" have been obtained (table 2.6).

Table 2.6.

Salt of cation (pm)	Radius of anion (pm)	Radius	Salt of cation (pm)	Radius of anion (pm)	Radius
LiF	92	109	MgO	102	109
NaCl	118	164	NiO	94	115
KCl	145	170	CuCl	110	125
CaF_2	126	110	CuBr	110	136

The ED map radii fall between the metallic (or covalent) radii but closer to those of apparent radii as shown in table 2.7.

Table 2.7.

Atom radius (pm)	Atomic radius (pm)	Covalent radius	ED map radius (R) (pm)	Apparent ionic radius (r)	Difference between ED map radius and apparent ionic radius (R–r)
K	227	196	145	133	12
Na	186	154	118	95	23
Li	152	134	92	60	32
Cu^+	–	–	125	187	56

1. Size of Cation. A cation is formed by the removal of one or more electrons from the neutral gaseous atom, *e.g.*,

$$\underset{\text{Neutral atom}}{A(g)} \longrightarrow \underset{\text{Cation}}{A^+(g)} + \underset{\text{Electron}}{e^-(g)}$$

Why size of cation is smaller than that of its corresponding neutral atom ?

It is due to following reasons :

(*i*) Number of electrons in a cation are less than that in neutral atom. The magnitude of nuclear charge is, however, the same. Thus, the nucleus attracts lesser number of electrons with greater force. As a result, the size of cation decreases.

(*ii*) In certain cations, the *number of orbits* are less than that of neutral atom. However, the magnitude of nuclear charge is same in both cases. Thus, the nucleus attracts lesser number of orbits more strongly.

As a result, the size of cation decreases, *e.g.*

$${}_{11}\text{Na}\ (\underset{K}{1s^2},\ \underbrace{2s^2,\ 2p^6}_{L},\ \underset{M}{3s^1}\ ;\ \text{Na}^+\ (\underbrace{1s^2}_{K},\ \underbrace{2s^2,\ 2p^6}_{L})$$

In-Na-atom, the nucleus attracts three orbits, *i.e.*, K, L and M. In Na$^+$. ions, the nucleus attracts two orbits, *i.e.*, K and L. The nuclear attraction is, thus, more in Na$^+$-ion than Na-atom. Hence, Na$^+$-ion is smaller in size than Na-atom. Following Table 2.8 makes it clear.

Table 2.8.

	Nuclear charge	No. of e^- s	No. of orbits	Force of attraction of nucleus for e^- s	Size
Na-atom	11	11	3 ; (K, L, M)	Less	(1.54 Å) Large
Na$^+$-ion	11	10	2 (K, L)	More	(0.95 Å) Small

2. Size of anion. An anion is formed by the gain of one or more electrons by a neutral gaseous atom, *e.g.*

$$\underset{\text{Neutral atom}}{A(g)} + e^-(g) \longrightarrow \underset{\text{Anion}}{A^-(g)}$$

Why size of an anion is larger than that of its corresponding neutral atom ? It is due to the following reason:

The number of electrons is an anion is *more* than that in a neutral atom. But the magnitude of nuclear charge is same. Thus, the nucleus attracts more number of electrons with less force. As a result, the size of anion increases, *e.g.*, Size of Cl$^-$ ion is more than that of Cl-atom.

$$\underset{\text{Neutral atom}}{\text{Cl}(g)} + e^-(g) \longrightarrow \underset{\text{Anion}}{\text{Cl}^-(g)}$$

Following table 2.9 makes it clear.

Table 2.9.

	Nuclear charge	Number of electrons	Force of attraction of nucleus for e^- s	Size
Cl-atom	17	17	more	less
Cl$^-$-ion	17	18	less	more

3. Size of Iso-electronic ions. *These are such cations or anions which carry same number of electrons.* The size of such ions depends upon the effective nuclear charge*. Greater the nuclear charge of an ion, greater will be the force of attraction for same number of electrons. As a result, the size of ion decreases.

Example. N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+}, are iso-electronic ions.

The Table 2.10 explains the relative size of ions.

Table 2.10.

Ions →	N^{-3}	O^{-2}	F^-	Na^+	Mg^{2+}	Al^{3+}
Nuclear charge →	7	8	9	11	12	13
No. of e^-s →	10	10	10	10	10	10
Force of attraction of nucleus for e^-s	Minimum	goes on increasing →				Maximum
Size	Largest 1.71Å	goes on decreasing →				Smallest 0.50Å

In O^{-2} ion, eight protons attract ten electrons more strongly than seven protons attracting ten electrons in N^{-3} ion. Thus, size of O^{-2} ion is smaller than that of N^{-3}. Similarly, we can prove the following decreasing order of size of ions.

$$N^{3-} > O^{-2} > F^- > Na^+ > Mg^{2+} > Al^{+3}$$

For the same reason, it can be explained that the size of :

(*i*) $Li^+ > Be^{+2} > B^{+3}$ and (*ii*) $P^{-3} > S^{-2} > Cl^-$ ions

EXPERIMENTAL METHODS TO DETERMINE IONIC RADII

Following methods are used to determine ionic radii.

1. Lande's method. Lande (1920) assumed that :

(*i*) In case of ionic crystal having **small sized cation** (*e.g.* Li^+) and large sized anion (*e.g.*, I^-), the anions touch each other while the cation does not touch the anions (fig. 2.6).

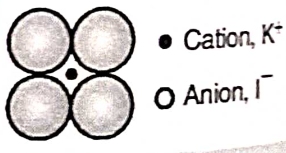


Fig. 2.6.

In such cases : Radius of anion = (Internuclear distance between two anions)/2

For example in $Li^+ I^-$ ionic crystal :

Radius of I^- = [Internuclear distance (I – I)]/2 = 426/2 = 213 pm.

(*ii*) In case of ionic crystals having **large sized cation** (*e.g.* K^+) and **large sized anion** (*e.g.* I^-), the cation touches the anions but anions donot touch each other (fig. 2.7).

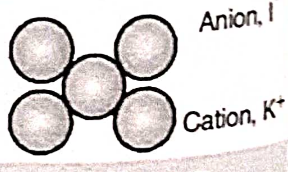


Fig. 2.7.

In such cases : Internuclear distance between the cation and anion = radius of cation + radius of anion.

For example, the inter-nuclear distance between K^+ and I^- ions in $K^+ I^-$ ionic crystal is 353 pm. If radius of I^- ion is 213 pm, the ionic radius of K^+ will be equal to 140 pm (*i.e.* 353 – 213 = 140 pm).

---

*It is better to use effective nuclear charge Z^* instead of single Z value. The value of Z^* increases regularly within a given series (see table below) because the added electrons in the same valence shell do not shield each other effectively. As a result there is steady decrease in the radii from left to right along a period. See table below.

Element	Li	Be	B	C	N	O	F
Z	3	4	5	6	7	8	9
Z^*	1.30	1.95	2.60	3.25	3.90	4.55	5.20

For example, the experimental value of internuclear distance (205 pm) between Mg^{2+} and O^{2-} in Mg-O^{2-} ionic crystal is less than the sum total (= 257.4 pm) of univalent radius of Mg^{2+} ($r_u = 81.9$ pm) and univalent radius of O^{2-} ($r_u = 175.5$ pm) *i.e.* 81.9 + 175.5 = 257.4 pm.

CONCEPT OF CRYSTAL RADIUS (R_C)

In order to remove the discrepancy in the experimental and theoretical values of internuclear distance concept of crystal radius (r_c) was introduced by Pauling.

The magnitude of r_c for an ion having valency, υ is related to uni-valent radius (r_u) as follows.

$$r_c = r_u \times \upsilon^{-2/n-1)} \quad ...(1)$$

Where *n* is the Born exponent whose value depends upon the electronic configuration of the ion. For ions having the electron configuration of helium, neon, argon, krypton and xenon, the value of *n* is 5, 7, 9, 10 and 12 respectively.

Using above relation (1), let us calculate the radius (r_c) for Mg^{2+} and O^{2-}.

For Mg^{2+} ion, $r_c = 81.9 \times (2)^{-2/(7-1)} = 62$ pm

For O^{2-} ion, $r_c = 175.5 \times (2)^{-2/(7-1)} = 140$ pm

Sum total of r_c of Mg^{2+} and O^{2-} = 62 + 140 = 202 pm

Experimental value of internuclear distance between Mg^{2+} and O^{2-} is 205 pm. This value is very near to 202 (theoretical value).

Example

EXAMPLE 8. Find the ionic radius of Cl^- ion in KCl if internuclear distance in KCl is 3.14 Å. The effective nuclear charges of K^+ and Cl^- ions are 7.40 and 5.40 respectively.

SOLUTION. Let ionic radius of $Cl^- = r^-$

Effective nuclear charge of K^+ (*a*) = 7.40

Effective nuclear charge of Cl^- (*b*) = 5.40

Inter nuclear distance (*d*) in KCl = 3.14 Å

$$\therefore \text{ Ionic radius of } Cl^- \text{-ion } (r^-) = \frac{a}{a+b} \times d = \frac{7.40}{7.40 \times 5.40} \times 3.14 = 1.81 \text{ Å}.$$

TETRAHEDRAL AND OCTAHEDRAL RADII

These are such types of covalent radii which are important for the ionic crystals and for coordination (or complex) compounds. Tetrahedral radii are smaller than octahedral radii.

Tetrahedral radii (or tetrahedral covalent radii)

This type of covalent radius is present in crystals with the diamond, sphalerite (zinc blende) and wurtzite arrangements. In such arrangements, each atom is surrounded by four other atoms (same or different atoms) tetrahedrally. If the atoms are of group 14 (*i.e.*, C, Si, Ge, Sn), these have appropriate number of valence electrons (*i.e.*, 4 *e.g.*, $^6C = (He)^2\, 2s^2\, 2p^2$) to permit the formation of tetrahedral covalent bond between each atom and its four neighbours (fig. 2.9, 2.10).

The diamond arrangement is shown by C, Si, Ge and Sn. The sphalerite or wurtzite (or both) arrangements are shown by many compounds. A comparison of observed interatomic distances in X_3 crystals [sphalerite structure (cubic)] and X_4 crystals [wurtzite structure (hexagonal)] with sums of tetrahedral radii are given in the following table 2.11.

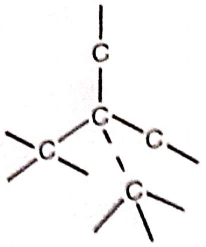


Fig. 2.9. Simple representation of carbon (C) atoms in diamond.

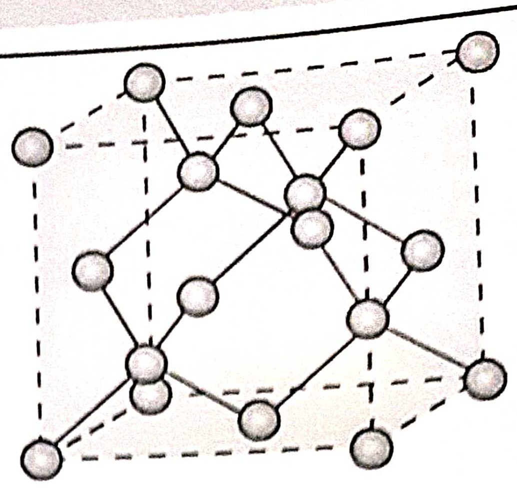


Fig. 2.10. The arrangement of the carbon atoms in the diamond crystal. Each carbon atom has four near neighbours, which are arranged about it at the corners of a regular tetrahedron.

Table 2.12. Comparison of observed interatomic distances in X_3 and X_4 crystals with sums of tetrahedral radii.

AlN	196 pm	AlP 236 pm	AlAs 244 pm	AlSb 262 pm
X_4	190 pm	X_3 236 pm	X_3 244 pm	X_3 264 pm
ZnO	197 pm	ZnS 235 pm	CdS 252 pm	HgS 252 pm
X_4	197 pm	X_3. X_4 235 pm	X_3, X_4 253 pm	X_3 252 pm
CuF	199 pm	BeO 172 pm	SiC 194 pm,	
X_3	185 pm	X_4 165 pm	X_3, X_4 189 pm	

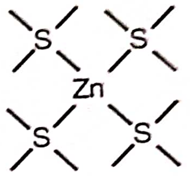


Fig. 2.11. Simple representation of sphalerite, the cubic form of zinc sulphide.

It is probable that the bonds in these crystals are covalent having some ionic character. For example, in ZnS, the structure (fig. 2.11) has formal charge '–2' on Zn and '+2' on sulphur. Probably the crystal has enough ionic character so that the actual charges of the atoms are nearly zero. In case of ZnS, it would need 50% ionic character.

Tetrahedral covalent radii of some elements are given in the following table 2.13.

Table 2.13. Tetrahedral covalent radii of some elements.

Element with tetraheral Covalent radii (in pm)	Be	B	C	N	O	F
	(106)	(88)	(77)	(70)	(66)	(64)
	Mg	Al	Si	P	S	Cl
	(140)	(126)	(117)	(110)	(104)	(99)
	Cu	Ag	Zn	Cd	Hg	
	(135)	(152)	(131)	(148)	(148)	

The table includes elements which form four covalent bonds with neighbouring atoms which surround it tetrahedrally. For example, in pyrite FeS_2 (a derivative of hydrogen disulphide, H_2S_2) each sulphur atom is surrounded tetrahedrally by one S-atom and three Fe-atoms through covalent bonds. The S–S distance (209 pm) in this crystal is very close to the value 208 pm. (104 pm + 104 pm = 208 pm) given in the above table.

(*i*) Experiments reveal that the sum total of the tetrahedral radii agree with the values found experimentally with an average deviation of 0.01 Å, e.g., in case of AlP (sphalerite cubic), the observed internuclear distance (= 236 pm) is the same as that found by adding their tetrahedral radii [Al, 126 pm + P, 110 pm = 236 pm]. In case of HgTe, the observed internuclear distance

(= 279 pm) differ from the sum of their tetrahedral radii (Hg, 148 pm + Te, 132 pm = 280 pm) by 1 pm.

(*ii*) In case of BeO, AlN, SiC and CuF, the observed bond lengths are significantly less than the sum total of their tetrahedral radii (table 2.14)

(*iii*) In case of elements of first and second row, the tetrahedral radii are the same as their single bond covalent radii as shown in the following table 2.14.

Table 2.14.

	C	N	O	Si	P	S
Element with single bond covalent radii (pm)	(77)	(70)	(66)	(117)	(110)	(104)
Tetrahedral radii (pm)	77	70	66	117	110	104

(*iv*) In case of heavier elements, a small difference between tetrahedral radii and observed radii has been observed. For example, in case of Se and Te, this difference is 3 pm and 5 pm respectively. This difference is due to the difference in the nature of bond orbitals in normal and tetrahedral covalent compounds.

Octahedral covalent radii

This type of covalent radius is present in crystals with the pyrite (FeS_2) structure or a closely related structure of arsenopyrite (or marcasite) type.

Some interatomic distances in pyrite-type crystals are given in the following table 2.15.

Table 2.15. Interatomic distances in pyrite type crystals.

Substance	**FeS_2**	**CoAsS**	**PtP_2**	**$PtAs_2$**	**$PtSb_2$**	**CoS_2**	**NiS_2**
Distance M–X (pm)	227	240, 226	238	249	267	237	242
Radius of M (pm)	123	124, 124	128	131	131	133	138

In such arrangements, each atom is surrounded by six other atoms (same or different) octahedrally.

For example : In pyrite (FeS_2), each Fe-atom is surrounded by six sulphur atoms, which are at the corners of a nearly regular **octahedron** corresponding to the formation of $3d^2\,4s\,4p^3$ hybrid bonds by iron (fig. 2.12).

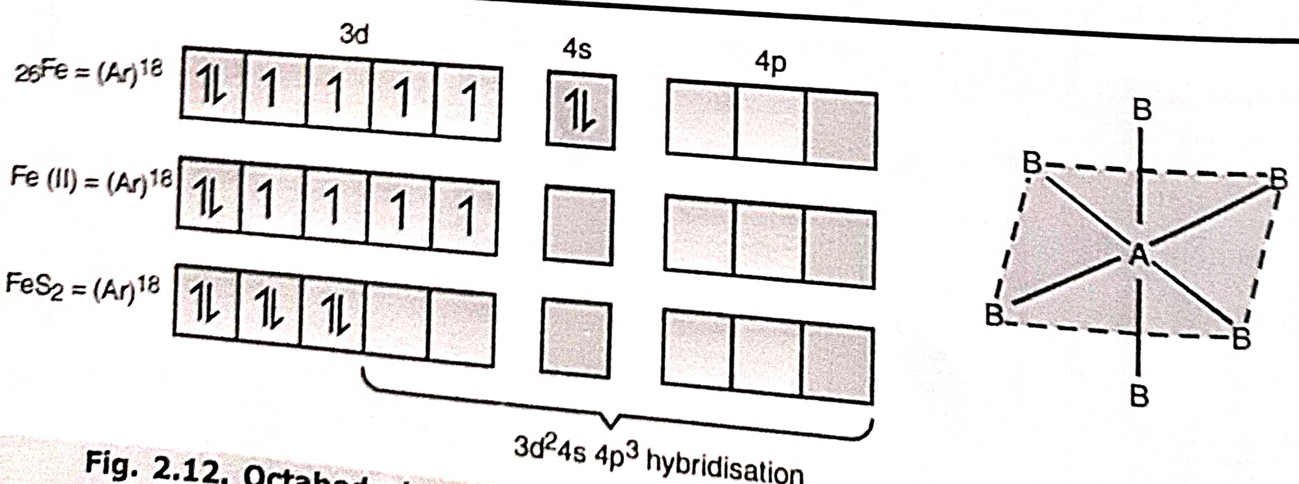


Fig. 2.12. Octahedral arrangement of central atom A with six atoms, B which are at the six corners of the octahedron.

Also, each S-atom is surrounded tetrahedrally by one S-atom and three Fe-atoms (fig. 2.13).

Here Fe–S distance = 227 pm (table 2.15)

Tetrahedral radius of S = 104 pm (table 2.16)

∴ Octahedral radius of Fe(II) = 227 – 104 = 123 pm which is same as shown in table 2.16.

Similarly, octahedral radii of elements of other transition series can be calculated.

Octahedral radii of isoelectronic species. Elements, having different oxidation states but isoelectronic (same number of electrons) and differ by one unit atomic number, have almost same value of octahedral radii. The decrease in octahedral radius by increase in one unit atomic number is nearly 1 pm.

For example, consider the following isoelectronic elements having different oxidation states (Table 2.16).

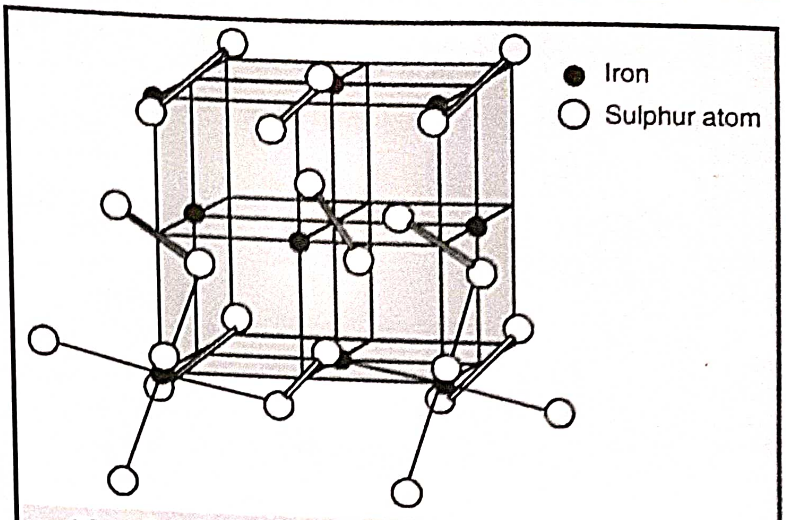


Fig. 2.13. Cubic crystal of pyrite, FeS_2. Here, each iron, Fe-atom is surrounded octahedrally by six S-atoms and each S-atom is surrounded tetrahedrally by one S-atom and three Fe-atoms.

Table 2.16.

Isoelectronic species with at. no. and oxidation state		Octahedral radius (pm)
$_{26}$Fe (II)	No. of	123
$_{27}$Co (III)	e^-s in	122
$_{28}$Ni (IV)	each = 24	121
$_{27}$Co (II)	no. of	132
$_{28}$Ni (III)	e^-s = 25	130
$_{44}$Ru (II)	no. of	133
$_{45}$Rh (III)	e^-s in	132
$_{46}$Pd (IV)	each = 42	131
$_{76}$Os (II)	e^-s in	133
$_{77}$Ir (III)	each = 74	132
$_{78}$Pt (IV)		131

Octahedral radii of Ni (II), Fe (III) and Au (IV) are 139 pm, 120 pm and 140 pm respectively.

Effect of extra electrons present in (n – 1) d subshell (if $d^2\ sp^3$ hybridisation is considered) on the value of octahedral radius. The effect of one extra electron present in the (*n* – 1) *d* subshell when $d^2\ sp^3$ hybridisation is used, is to produce an increase of 9 or 10 pm in the octahedral covalent radius for each of the central atom. *e.g.*, in CoS_2, $CoSe_2$, NiAsS, $AuSb_2$ etc. In case of Ni(II), where two extra electrons are present, total increase in octahedral radius is twice to 9 pm *i.e.*, it is 2 × 9 = 18 pm.

Effect of deficient electrons present in (n – 1) d subshell (after $d^2\ sp^3$ hybridisation) on the value of octahedral radius. As expected, there is little effect on the octahedral radius.

For example : (*i*) Octahedral radius of Fe (IV), $(Ar)^{18}\ 3d^4$ (= 120 pm) is slightly less than that of Fe(II), $(Ar)^{18}\ 3d^6$ (= 123 pm). (*ii*) Octahedral radius of Os(IV) is same (= 137 pm) in similar compounds such as K_2OsCl_6 (Os – Cl = 236 pm) and $K_2Os\ Br_6$ (Os – Br = 251 pm).