Periodic Classification of Elements
Atomic& Ionic Radii

ATOMIC RADII

It refers to the distance between the centre of nucleus of atom to its outer most shell of electrons. Since absolute value of atomic size cannot be determined, it is expressed in terms of the operational definitions such as **ionic radius, covalent radius, vander waal's radius and metallic radius.**

The absolute value of atomic radius cannot be determined because :

(i) It is not possible to locate the exact position of electrons in an atom as an orbital has no sharp boundaries.

(ii) It is not possible to isolate an individual atom for its size determination.

(iii) In a group of atoms, the probability distribution of electrons is influenced by the presence of neighbouring atoms. Thus, size of an atom may change in going from one environment to other.

However, the value of atomic radii are derived from bond length measured by various techniques such as **X-ray diffraction, electron diffraction, infra-red spectroscopy, nuclear magnetic resonance spectroscopy etc.**

(a) Variation of atomic radii in a period:

Atomic radii (in picometer) of 2nd and 3rd period elements are given in the table given below. In a period, atomic radius generally decreases from left to right with increase in atomic number

2nd period

Li	Be	B	C	N	O	F
152	111	88	77	74	66	42

3rd period

Na	Mg	Al	Si	P	S	Cl
190	145	118	111	98	88	79

In a period there is a gradual increase in the nuclear charge with increase in atomic number. Since valence electrons are added in the same shell and the electron in the same shell do not screen each other from the nucleus, the increase in nuclear charge is not neutralised by the extra valence electron. As a result effective nuclear charge increases therefore valence electrons are more and more strongly attracted towards nucleus. This gradually decrease atomic radii.

Variation of atomic radii in a group:

Atomic radii increases in a group from top to bottom. This can be seen from the data of atomic radii in picometers given for groups 1 and 17 elements below.

Element (group 1)	Atomic Radius	Element (group 2)	Atomic Radius
Li	155	F	72
Na	190	Cl	99
K	235	Br	114
Rb	248	I	133

In moving down the group the nuclear charge increases with increase in atomic number. However, while going down in a group from one atom to another the number of inner shells also increases, although the number of electrons in the outermost shell remains the same. The effect of increase in the size of the electron cloud (due to increase in number of shells) is more pronounced than the effect of increased nuclear charge. Thus, the distance of outermost electron from the nucleus increases as we move down a group. For example, in lithium the valence electron is present in 2nd shell while in sodium it is present in 3rd shell. Also, the number of filled shells between valence electron and nucleus increases. Thus in group 1 Li (2, 1) has one filled shell between its nucleus and valence electron while Na (2, 8, 1) has two filled shells between them. Both the factors decrease the force of attraction between nucleus and valence electron. Therefore, atomic size increases on moving down a group.

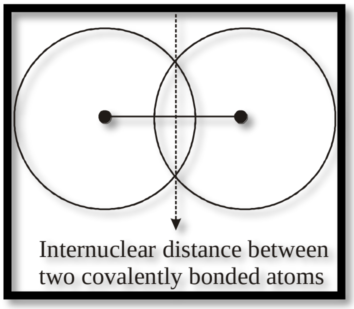
Factors influencing atomic radius:

(a) Multiplicity of bond . Covalent radii depends on the multiplicity of bonds. e.g.

	Bond length	Radius of carbon atom
$H_3C—CH_3$	154 pm	$\frac{154}{2} = 77$ pm
$H_2C = CH_2$	134 pm	$\frac{134}{2} = 67$ pm
$HC \equiv CH$	120 pm	$\frac{120}{2} = 60$ pm

(b) Percentage of ionic character : Covalent radius of H in HCl, HBr, and HI are different.

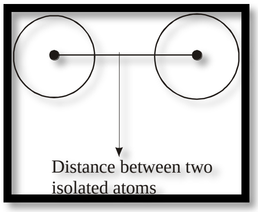
(i) Covalent radius : It is defined as half of the distance between two successive nuclei of two covalent bonded like atoms in a molecule. If the bond length in between the two atoms is say A-A = d, then

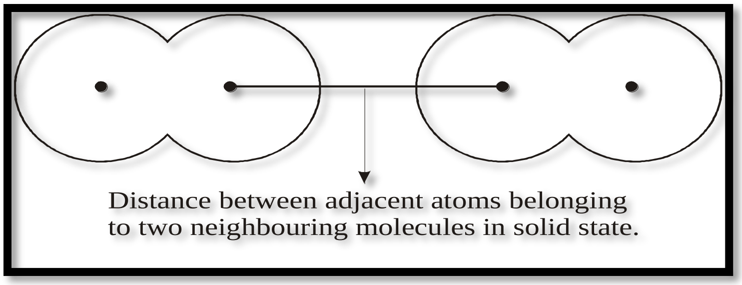


$$d_{AA} = r_A + r_B$$
$$r_A = d_{\frac{A-A}{2}}$$

Covalent radius (r_{cov}) = ½[Internuclear distance between two covalently bonded like atoms] = ½d

(ii) Vander Wall's radius ($r_{v,waat}$) . It is defined as one half of the distance between the nuclei of two non bonded isolated atoms or two adjacent atoms belonging to two neighbouring molecules of an element in the solid state.





In general, vander waals radius > Covalent radius of an atom.

(iii) Metallic radius : It is defined as half the distance between two successive nuclei of two adjacent metal atoms in the metallic closed packed crystal lattice.

(iv) Ionic Radius : Ionic radius may be defined as the effective distance from the nucleus of the ion to the point upto which it has an influence in the ionic bond.

When an atom changes into ion, its size changes appreciably.

(a) **The radius of cation is smaller than that of the parent atom.**

(b) **The radius of anion is larger than that of parent atom.**

(c) **The ions having same number of electrons but different magnitude of nuclear charge are called iso-electronic ions.**

For example, each one of sulphides (S^{2-}), chloride (Cl^{-}), Potassium (K^{+}), and Calcium (Ca^{2+}) ion has eighteen electrons but they have nuclear charge of +16, +17, +19 and +20 respectively.

Within the series of iso-electronic ions, size of the ions decreases with the increase in the magnitude of nuclear charge. For example, N^{3-}, O^{2-}, F^{-}, Na^{+}, Mg^{2+}, Al^{3+} are iso-electronic and have 10 electrons each. The size of these ions are in the order.

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

NOTE: For isoelectronic Z/e ratio determine atomic radius.

$$\frac{Z}{e} \propto \frac{1}{\text{Atomic Radius}}$$

The ionic radii of these ions are given in Table below:

Ionic Radii of Some Iso-electronic Ions

Atoms	N^{3-}	O^{2-}	F^{-}	Na^{+}	Mg^{2+}	Al^{3+}
Nuclear Charge	+7	+8	+9	+11	+12	+13
Size (pm)	1.71	1.40	1.26	0.95	0.65	0.50

$$\text{Atomic Radius} \propto \frac{1}{\text{Effective Nuclear Charge}}$$

Atomic Radius ∝ No. of shell

Atomic Radius ∝ Screnning Effect

Atomic Size ∝ Magnitude of –ve charge

$$\text{Atomic Size} \propto \frac{1}{\text{Bond Order}} \quad \text{Atomic Radius} \propto$$

$$\frac{1}{\text{Magnitude of positive Charge}}$$