

Atomic, Ionic and Van der Waals' Radii.

The radius of an atom is the distance between the centre of its nucleus and electrons in the last orbit. However, according to quantum mechanics, there is no certainty about the exact position of electrons at any time. Theoretically, an electron, at one time, may be very close to the nucleus while at other time it may be far away from the nucleus. In spite of these limitations we need to have some operational definition of the term atomic radius. There are three operational concepts of atomic radius.

- (1) If the bonding is covalent, the radius is called a covalent radius.
- (2) If the two atoms are not bonded by a chemical bond (as in noble gases) the radius is called van der Waal's radius.
- (3) If the bonding is ionic, the radius is called ionic radius.

(1) **Covalent radius: It is half of the distance between the nuclei of two like atoms bonded together by a single bond.** Thus covalent radius of carbon in a compound having C – C single bond can be determined by dividing the bond length by 2, i.e.

$$r_c = \frac{C-C}{2} \quad \therefore C-C = 2r_c \quad \text{or} \quad r_c + r_c$$

Where, r_c is the single bond covalent radii (SBCR) of carbon. However, if atoms forming the covalent bond are different i.e., one is more electronegative than the other then the atomic radius is determined

by the relation, $A-B = r_A + r_B - 0.009(\chi_A - \chi_B)$, where χ_A and χ_B are electronegativities of the atoms A and B respectively. This relation was given by **Stevenson** in 1941.

In a given period, **atomic radius generally decreases from left to right** and thus in any period, alkali metal is the largest and halogen is the smallest atom. For example, in second period elements the covalent radii decrease from Li to F.

${}_3\text{Li}$	${}_4\text{Be}$	${}_5\text{B}$	${}_6\text{C}$	${}_7\text{N}$	${}_8\text{O}$	${}_9\text{F}$	${}_{10}\text{Ne}$
1.23	0.89	0.80	0.77	0.74	0.74	0.72	1.6

The decrease in size along a period is due to the effect of successive increasing nuclear charge without addition of a new shell, i.e., in each element of a given period a new electron is added in the same principal quantum number. For example, in the second period the nuclear charge

increases from + 3 in Li to + 9 in F. The increased nuclear charge attracts the electrons more strongly to the nucleus and thus decreases the size of the atom. In case of noble gases, the atomic radii are only the van der Waal's radii which are naturally higher than the covalent radii of other elements.

In a given group, **Atomic radius generally increases as one moves from top to bottom**, e.g., in group 1 atomic size increases steadily from lithium to cesium, i.e. $r_{Cs} > r_{Rb} > r_K > r_{Na} > r_{Li}$

The increase in size on descending a group is due to addition of extra shell (i.e., the number of principal quantum number increases) which outweighs the effect of increased nuclear charge. Remember that He and Fr are smallest and largest atom respectively.

(2) Ionic radius: It is the effective distance from the nucleus of an ion upto which it has its influence on its electron cloud.

A cation (formed by the removal of one or more electrons from an atom) is always much smaller than the corresponding atom. Further, more the number of electrons removed smaller will be the size of the resulting positive ion. For example, $r_{Fe} > r_{Fe^{2+}} > r_{Fe^{3+}}$. This is due to following

$$1.26 \quad 0.76 \quad 0.64$$

two factors

(i) A cation formed by the loss of electrons may result in the complete disappearance of the outer shell and since the remaining inner shells do not extend so far in space, the cation is much smaller than the metal atom. For example, Sodium atom (Na) → Sodium ion (Na⁺)
(2, 8, 1) (2, 8)

(ii) Whenever a cation is formed, the ratio of nuclear charge to the number of electrons (Z/e ratio) is increased with the result the effective nuclear charge is increased and the electrons are pulled towards the nucleus. Consequently, the cation becomes smaller. An anion (formed by gain of one or more electrons to the atom) is always larger than the corresponding atom. For example, Atomic radius of I = 1.23; Ionic radii of I⁻ = 2.16

This is again due to following two factors: (a) Since in the formation of an anion, one or more electrons are added, the electron cloud expands and the ionic size increases. (b) In the formation

of anion, the effective nuclear charge decreases with the result the electrons get away from the nucleus and thus the anion becomes larger than the corresponding atom.

In any particular group, **the ions of elements increase in size on moving from top to bottom.**

In case of isoelectronic ions (ions having same number of electrons but different nuclear charge); the greater the nuclear charge, the greater is the attraction for electrons and smaller is ionic radius. Hence size of such ions decreases from top to bottom as shown in the given table,

Variation of Radii of Iso-electronic Ions (Atom)

Ion / Atom	At. number (Nuclear charge)	No. of electrons in the ion	Z/e ratio	Ionic (atomic) radii
C ⁴⁻	6	10	0.6	2.60
N ³⁻	7	10	0.7	1.71
O ²⁻	8	10	0.8	1.40
F ⁻	9	10	0.9	1.36
Ne	10	10	1.0	1.12
Na ⁺	11	10	1.1	0.95
Mg ²⁺	12	10	1.2	0.65
Al ³⁺	13	10	1.3	0.50
Si ⁴⁺	14	10	1.4	0.41
P ⁵⁺	15	10	1.5	0.34
S ⁶⁺	16	10	1.6	0.29
Cl ⁷⁺	17	10	1.7	0.26

(3) Van der Waal's radius: It is one-half of the distance between the nuclei of two adjacent atoms belonging to two neighboring molecules of an element in the solid state.

The covalent radius is always smaller than the corresponding van der Waal's radius. This is because of the fact that in the formation of a chemical bond, the two atoms have to come closer to each other. This also explains why covalent bonds are much stronger than the van der Waal's forces. It is important to note that since the noble gases ordinarily do not form any covalent bond, in crystals of noble gases, no chemical forces are operating between the atoms. Hence the

van der Waal's forces are the only attractive forces in these cases. In other words, **the van der Waal's radii constitute the atomic radii of noble gases** and since van der Waal's radii are larger than covalent radii, **atomic radii of noble gases are largest in their respective periods** (anomaly).