Quadrant II – Transcript and Related Materials

Programme: **Bachelor of Science (T. Y. B. Sc.)**

Subject: **Chemistry**

Paper Code: **CHC 106**

Paper Title: **Inorganic Chemistry - Section A**

Unit: **1 - Periodicity of Elements**

Module Name: **Atomic Radii and Ionic Radii – PART 1**

Module No: **01**

Name of the Presenter: **Ms. Janesline Fernandes**

Notes

Atomic Radius :

      Atomic radius is the distance from the centre of the nucleus to the outermost shell of electrons*.* The absolute size of an atom is difficult to define because,

   I) An atom does not have well defined boundary   and

   II) It is not possible to isolate an atom in its free state and measure its radius

Thus Atomic radius depends upon, the way an atom bonds with another atom and atomic radius of an element varies in different types of molecules. Atomic Radius is measured either in Picometres (pm) or Angstroms (Å) units (1 Å = 100 pm)

Operational Concepts of Atomic Radius

Atomic Radius and Different Types are Covalent Radius, Ionic radius, van der Waals Radius and Metallic Radius.

I. **Covalent Radius** is the radius of an atom which is covalently bonded to another atom. The sum of the covalent radii of the two atoms is equal to the internuclear distance(d) (covalent bond length) between two atoms. Covalent radius of an atom is calculated by measuring the Internuclear distance by X-ray diffraction or Spectroscopy studies. Covalent Radius varies in different types of Covalent Molecules

$$r_A = \tfrac{1}{2}\,[d_{A-A}] \qquad r_A = \tfrac{1}{2}\,[d_{A-B}] \qquad\qquad r_{(AB)} = r_{(A)} + r_{(B)}$$

i. Covalent Radius in Homonuclear Diatomic Molecules is given by the relation

r_{cov} = ½ [Internuclear distance between two similar atoms covalently bonded in a molecule]

ii. Covalent Radius in Heteronuclear Diatomic Molecules.

For molecules of AB type: (If electronegativity difference is very less) the Bond length is given as $d_{(A-B)} = r_{(A)} + r_{(B)}$ and

Covalent radii is given as $r_B = d_{(A-B)} - r_{(A)}$

When covalent radii of different atoms are added, the resulting value agrees with the experimental determined internuclear distance of that molecule. (If electronegativity difference is very less) Example: HCl molecule

iii. Covalent Radius in Heteronuclear Diatomic Molecules with different Electronegativities

Polarity develops in the bond because of different electronegativities. Consider a covalent bond between A – B. If A is more electronegative than B, the electrostatic force of attraction would be shifted nearer to A, resulting in the accumulation of excess negative charge on A and excess positive charge on B. This results in additional electrostatic attraction between A and B which brings A and B more closer to each other. And the bond between A and B gets shortened. The greater the electronegativity difference between A & B, the shorter will be the internuclear distance and smaller will be covalent radii of atoms A and B.

Schomaker & Stevenson Formula to calculate the Internuclear distance is given by

$d_{A-B} = r_A + r_B - 0.09 (\chi_A - \chi_B)$ where χ = electronegativity difference)

iv. Covalent Radius in Diatomic Molecules formed by Multiple Bond

One half of Internuclear distance of these molecules will correspond to Multiple bond covalent radii . The covalent radius of an element forming a double /triple bond is shorter than a single bond covalent radius of the same element. This is because in a double /triple bond, in addition to the overlap of sigma orbitals there is also overlap of pi orbitals. This results in the two atoms coming more closer thereby reducing the bond length and thus decrease in the covalent radius. The magnitude of covalent radius decreases with increase in the multiplicity or bond order of the element. The order is : Single bond > Double bond > Triple bond.

v. Covalent Radius and Hybridisation

Covalent atomic radius is also affected by hybridisation of the atom. With increases in *s*-character, the electron pair between C and H comes closer to the nucleus resulting in greater attraction, therefore covalent radius decreases

Periodic Trends in Size :

1. **Variation of atomic / covalent radii in a Period:**

As atomic number increases from left to right, the addition of electrons takes place in the same principal shell. The magnitude of nuclear charge also increases. With increase in nuclear charge (Z_{eff}) felt by valence electrons, force of attraction between nucleus and valence electrons increases. Thus the atomic / covalent radii decreases from left to right in a given Period.

2. **Variation of atomic / covalent radii in a Group:**

As we move down the group, the extra electrons are added to the next higher shell (principal quantum number increases). The nuclear charge also increases. The effect of increase in principal quantum number is more pronounced than the effect of increased nuclear charge. Consequently the distance of outermost electrons from the nucleus gradually increases down the group. Thus covalent radius increases from top to bottom in a Group. For example, Alkali metals (Group IA) occupy the maximum size and Halogens (Group VIIA) occupy the minimum size.