Quadrant II – Transcript

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

Hello everyone, welcome to this module in Inorganic chemistry -Section A. The paper code of is CHC- 106. And the title of the Unit 1 is Periodicity of Elements, Atomic radii and Ionic radii -Part one.

I am Miss Janesline Fernandes, Associate professor at Saint Xavier's College, Mapusa, Goa.

The outline of the study is atomic radius and its types, covalent radius and variation of covalent radii in the periodic table.

The learning outcomes- A student will be able to know the description of the atomic radius, insights into operational concepts of atomic radius. Understand the covalent radius and illustrate the variation in size of elements in the periodic table.

We shall begin with the atomic radius, and we can define atomic radius as the distance from the center of the nucleus to the outermost shell of the electrons.

As we can see in figure one, this is the atomic radius in an element.

The absolute size of an atom is difficult to define., Because an atom does not have a well defined boundary and it is not possible to isolate an atom in its free state and measure its radius.

Thus the atomic radius depends upon the way an atom bonds with another atom.

Thus, atomic radius of an element varies in different types of molecules.

Here we will see the operational concepts of atomic radius and it's different types depending upon in which molecule it is determined.

The different radius are covalent radius in covalent molecules. Then we have the Wonder World's radius. Then Ionic radius in ionic molecules and metallic radius existing in metals.

The atomic radius is measured either in picometers (pm), or Angstrom units, and the relation is 1A is equal 200 PM.

We begin with covalent radius, which is abbreviated as r_{cov}. Covalent radius is defined as 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 between the two atoms.

As we can see in Figure 3, the covalent internuclear distance between the two nuclei of hydrogen atoms is marked over here, and the covalent radius or internuclear distance is given as.

There are covalent radii of atom A plus covalent radius of the next atom A.

If the molecules is of A-B type, then internuclear distance is given as atomic radius of atom A plus atomic radius of atom B.
The covalent radius of an atom is calculated from measuring the internuclear distance by X ray diffraction, or spectroscopy studies.

Covalent radius varies in different types of covalent molecules and the different covalent molecules are homonuclear diatomic molecules, Heteronuclear diatomic molecules, molecules with appreciable Electro negativity difference, molecules formed by multiple bonds and molecules with different hybridization.

We start with covalent radius in homonuclear diatomic molecules. The relation to calculate the covalent radius in homonuclear diatomic molecules is given as r_{cov} is equal to half internuclear distance between two similar atoms covalently bonded in a molecule. For molecules of A_2 type, the internuclear distance is given as covalent radius of atom A plus covalent radius of the next atom A and thus, covalent radii can be calculated as r_A is equal to half Internuclear distance, The covalent radii of some of the homonuclear diatomic molecules is calculated and presented in table one. And we can see the covalent radius for hydrogen, fluorine and chlorine is 37, 64 and 99 picometers respectively.

We next move to covalent radius in the heteronuclear diatomic molecule of the type AB.

Now here we use this formula if the electronegativity difference is very less and the calculation is internuclear distance between the nuclei of atoms A & B is equal to the radius of atom A plus covalent radius of atom B. Thus, covalent radii of any one of the atoms can be calculated by using the internuclear distance from the radius.

Of the other atom, we have calculated here the radius of or the internuclear distance of HCL molecule; which is covalent radius of hydrogen plus chlorine, which is equal to 136 picometers.

In the diagram we see how hydrogen and chlorine with side overlap due to electro negativity difference is shown in the diagram and the covalent radii decreases in hydrogen and chlorine.

Covalent radius in heteronuclear diatomic molecules having appreciable Electronegativity difference. Consider molecule AB having appreciable electronegativity difference. Hence a polarity develops in the bond A-B because of different electronegativities.

There is increased electrostatic attraction between A and B, which brings A and B more closer to each other. Thus the bond between A and B gets shortened and

Covalent radii further decreases, As we can see here in the diagram, there are two molecules, one is non polar covalent bonding and the other one is polar covalent bonding where there is appreciable difference in electronegativity and thus the covalent bonding decreases in size.

Greater the electronegativity difference, the shorter will be the internuclear distance, and smaller will be the covalent radii.

When molecules have high electronegativity difference, the formula to calculate covalent radii is given by Schomaker and Stevenson formula which is internuclear distance between A and B is equal to covalent radius of atom A plus B minus 0.09 into electronegativity difference between A and B.

In the following table we see there are different electronegative molecules or molecules having different electronegativities. And the electronegativity difference is shown in this column.

We can see here as the difference is larger, the internuclear distance is much smaller, and when the difference of electronegativity is much smaller, the experimental internuclear distance is very large.

Covalent radius in diatomic molecules formed by Multiple bonds.

It is given as half the multiple bond distance.

In a molecule having double, triple covalent bond, in addition to the overlap of sigma orbitals there is also overlap of pi orbitals. The two atoms thus come more closer, thereby reducing the bond length. Therefore the covalent radius of an element forming multiple bonds, is shorter than a single bond covalent radius of the same element**.**

The magnitude of covalent radius decreases with increasing the bond order of the element, and the order is single bond has a longer covalent radii and then comes the double bond and the triple bond has the shortest covalent radii. As we can see in the given 2 tables, when the bond length is double bond, the covalent radius is larger and when the bond is triple bond, the covalent radius decreases.

Covalent radius and Hybridisation.

Covalent radius is also affected by the hybridization of the atom with increase in S character. The electron pair between carbon and hydrogen comes more closer to the nucleus, resulting in greater attraction and therefore covalent radius decreases. As we can see in this table with the S character increased to 50% , the covalent radii of carbon becomes 70, whereas when S character is 25%, the radius of carbon is 77 pm.

We shall now see the periodic trends in size of covalent radii. First we will take up variation in covalent radii across a period as the atomic number increases from left to right. The addition of electrons takes place in the same principle shell. The magnitude of nuclear charge also increases with increasing nuclear charge felt by the valence electrons.

The force of attraction between the nucleus and valence electron increases as we can see in the following diagram . In figure 7, the element sodium which has atomic number 11, and argon which has atomic number 18. The size decreases from sodium to argon.

These are the periodic trends of the second period from lithium to fluorine and we can see the covalent radius again decreasing.

Covalent radius across a Group

As we move down the group, the extra electrons are added to the next higher shell, that is principle 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. And we can see this in this diagram.

The following two tables show the covalent radii of alkali metals, Group One A and Group 7A, and we can see there is increase in the covalent radius. Thus, alkaline metals have maximum size, and halogens have the minimum size.

For further reading on this topic, one can use the following references.

Thank you.