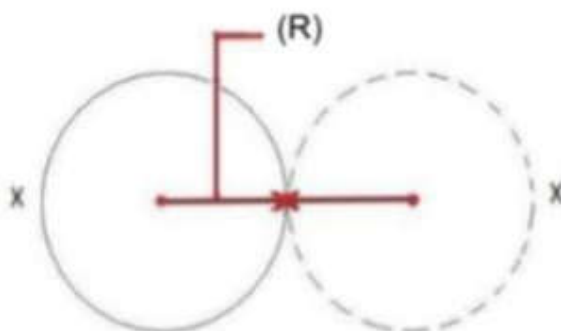


## ATOMIC RADII

The average distance between the nucleus of an atom and the

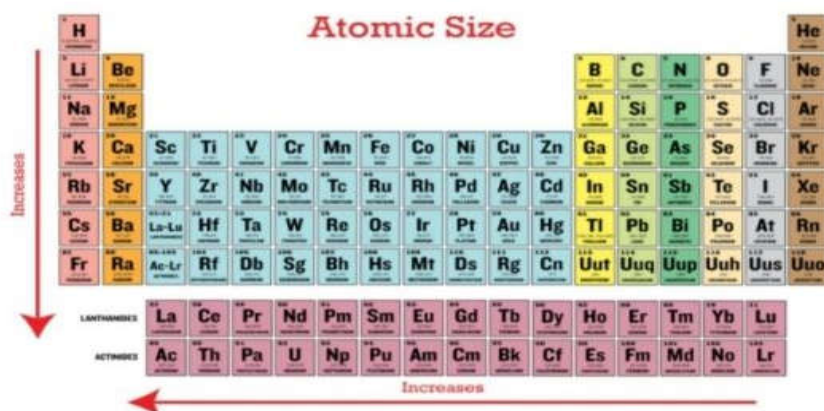


outermost orbit is called atomic radius while considering atom as spherical **R** is a radius of atom

### Measurement and units :

Atomic radii cannot be determined directly. These are measured from the distance between the centre of two adjacent atoms. It keeps all the information about elements like size, nature, behaviour towards other element, strength and weakness. However, this information is hidden inside the periodic table

Atomic radii have been measured for elements. The units for atomic radii are picometers, equal to  $10^{-12}$  meters. As an example, the inter nuclear distance between two hydrogen atoms in an  $H_2$  molecule is measured to be 74 pm.



## **VARIATION IN PERIODIC TABLE ACROSS THE GROUP**

### **SIZE OF ATOM:**

The secret of every quality lies in the subatomic particles of the atom and how these particles are arranged in an atom. Let's examine the elements of first column (group). As you go down in a column you will find the number of atomic orbitals increases it means the size of atom or the atomic radius increases. The element that is placed lower in a column has larger atomic radius /size than the element placed upper in a column

### **Atomic radii increase down the group**

It is due to two factors

#### **•INCREASE IN NO SHELL:**

In a group number of shells increases downward. Hence atomic radii increase

#### **•SHIELDING EFFECT:**





"It is the decrease in force of attraction between outermost electrons and the nucleus due to inner shell electron".

It may also consider as the repulsion due to inner electrons elements between the nucleus and outermost shell. When shell is added down the group outer electrons are less attracted by nucleus due to shielding effect of inner shall electron. These outer electrons therefore move outward and hence atomic size increases.

### **ACROSS THE PERIOD:**





Atomic radii decreases along the period from left to right .it is because positive charge on the nucleus increases in atomic number but no of shells remain same .This high positive charge on nucleus powerfully attracts electron inward resulting in the decrease of atomic radii .That is why on going toward right side in a row ,size of atom or atomic radius decreases.

Since atomic size decreases across the period / row, the elements of 1<sup>st</sup> column are largest and the elements of 17<sup>th</sup> column are the smallest .Elements of 18<sup>th</sup> column are different because they already have a complete octets in their outermost orbit .So, they called noble elements and have noble characteristics .we will discuss them separately .

Elements of 1 <sup>st</sup> column	Electronic Configuration	Number of Orbits	Size of the Atom
${}^1\text{H}$	$1s^1$	1	
${}^3\text{Li}$	$1s^2 2s^1$	2	
${}^{11}\text{Na}$	$1s^2 2s^2 2p^6 3s^1$	3	
${}^{19}\text{K}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	4	

When we observe the trend of atomic radius across the row .you will find it is not as steady we expect .It decreases across the row but when you move from “ d-block” to “p-block” there is a large contraction in size .And again after “ f- block you will see larger contraction in the size of “d-block”

**The factors responsible for the contraction of a size:**

Elements of 2 <sup>nd</sup> Row	${}^3\text{Li}$	${}^4\text{Be}$	${}^5\text{B}$	${}^6\text{C}$
Electronic Configuration	$1s^2 2s^1$	$1s^2 2s^2$	$1s^2 2s^2 2p^1$	$1s^2 2s^2 2p^2$
Number of electron	3	4	5	6
Number of Proton	3	4	5	6
Size of the Atom				

- Nuclear charge / no of protons, which pull electron toward nucleus like a magnet.
- Distance between outer electron and nucleus, which prevent them to be pulled toward the nucleus.
- Across the row nuclear charge increases and ideally the distance between outer orbit and nucleus should decrease gradually. Nothing can change the nucleus charge and the distance between nucleus and orbit. But if something happens which increase or decrease the force experienced by electron it can change trend.
- The electron of inner orbit cancels some of the nuclear charge so the electron of outer orbit experience less attraction by nucleus. This is called shielding effect. The extend of shielding caused by different sub-shell is different because every sub-shell has different shape

The order of shielding effect of different sub-shell is follow

**s>p>d>f**

## **IONIC RADII**

*“The radius of the ion while considering it spherical is called ionic radius”*

**OR**

*“The ionic radius is the distance between the nucleus and the electron in the outermost shell of an ion”*

The ionic radius is similar to but different from the atomic radius for the ionic size is dependent on the distribution of its outermost electron and inversely proportional to the effective nuclear charge experienced

## **MEASUREMENTS AND UNITS:**

It is calculated from the inter nuclear distance between a cation and a neighbouring anion in a lattice. However it is to consistently and accurately determine the proportional of the ionic bonds.

Ionic radii are typically reported in picometers (pm,  $1 \times 10^{-12}$  m) or in older literature as Angstroms (Å) where  $1 \text{ Å} = 100 \text{ pm}$ .

After comparing many compound chemist Linus Pauling assign a radius of 140 pm to  $\text{O}^{2-}$  and use this as a reference point to determine the sizes of the other ionic radii (Jensen 2010). Ionic radius is not a permanent trend of an ion, but changes depending on coordination number spin state and other variables (Shannon 1976). For given ions the

ionic radius increases with increasing coordination number and is larger in a high spin state than in a low spin state.

According to group theory, the idea of ionic radii as a measurement of spherical shapes only applies to ions that form highly symmetric crystal lattice like  $\text{Na}^+$  and  $\text{Cl}^-$ . The point group symmetric of a lattice determines whether or not the ionic radii in that lattice can be accurately measured (Johnson 1973).

### IONIC RADII OF CATION:

An atom loses one or more electron to form cation. Positive ion is smaller in size than the neutral atom from which it is formed

It is due to two reasons:

- In many atoms outermost shell is lost due to removal of one or more electron.
- In positive ions number of electrons are reduced but positive charge on nucleus remain same.

Therefore, nucleus powerfully attracts outer electron inward resulting in decrease of ionic radius.

The ionic radius of a dipositive ion is less than the monopositive ion, the ionic radius of a tripositive ion is less than the dipositive ion

Example: Atom	Atomic radius (pm)	positive ion	ionic radius (pm)
Na	157 (pm)	$\text{Na}^{1+}$	95(pm)
Be	90 (pm)	$\text{Be}^{2+}$	31(pm)

### IONIC RADII OF ANION:

- An atom gains one or more electron to form anion.
- Negative ion is always larger in size than the neutral atom.
- It is due to two reasons.
- In negative ions, number of electrons is increased but positive charge on nucleus remain same.
- Therefore, hold of nucleus on outer electron decreases resulting in the increase of ionic radius.
- In negative ion, the electron -electron repulsion increase due to increase in number of electrons in the valence shell. So ionic radius increases. The ionic radius of negative ions increases with the increase in negative charge on the ion

Example:

Atom	Atomic radius (pm)	negative ion	ionic radius (pm)
F	72 (pm)	F <sup>-</sup>	136 (pm)
O	66(pm)	O <sup>2-</sup>	140(pm)

## VARIATION IN PERIODIC TABLE

### **ALONG GROUP:**

Ionic radii of similar charged ion increased down the group. As move down a group in periodic table additional layer of electrons are being added, which naturally causes the ionic radius to increases as you move down the periodic table

### **ALONG PERIOD:**

Ionic radii of isoelectronic positive ions decrease from left to right. Similarly, ionic radii of isoelectronic negative ions also decrease from left to right

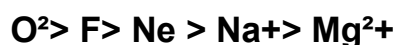
### **ISOELECTRONIC SPECIES:**

The species which have same number of electron and hence have same electronic configuration are called isoelectronic species.

Example: **O<sup>2-</sup>, F<sup>-</sup>, Ne<sup>-</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>**

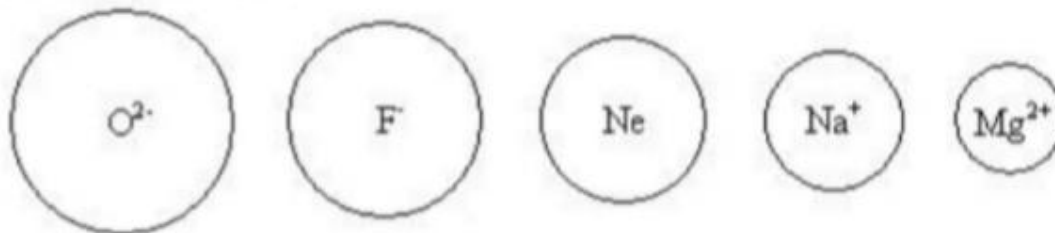
All these species have 10 electron each .However number of protons are different in their nuclei example O<sup>2-</sup> has 8 protons , F has 9 protons , Ne has 10 protons ,Na<sup>+</sup> has 11 protons and Mg<sup>2+</sup> has 12 protons , Thus Mg<sup>2+</sup> nucleus attracts its electrons powerfully hence it size is smallest while O nucleus has least attraction for its electron .hence its size is largest .Among isoelectronic species generally greater the negative charge larger the size and vice versa . grater the positive charge smaller the size and vice versa.

Hence order of size for above example is



## Isoelectronic Species

Relative ionic sizes.



All species have electron configuration:  $1s^2 2s^2 2p^6$

### Covalent radius

The covalent radius, is a measure of the size of an atom that forms part of one covalent bond. It is usually measured either in picometres (pm) or angstroms (Å), with  $1 \text{ \AA} = 100 \text{ pm}$ . In principle, the sum of the two coequal the covalent bond length between two atoms,  $R(AB) = r(A) + r(B)$ . Moreover, different radii can be introduced for single, double and triple bonds ( $r_1$ ,  $r_2$  and  $r_3$  below), in a purely operational sense. These relationships are certainly not exact because the size of an atom is not constant but depends on its chemical environment. For heteroatomic A–B bonds, ionic terms may enter. Often the polar covalent bonds are shorter than would be expected on the basis of the sum of covalent radii. Tabulated values of covalent radii are either average or idealized values, which nevertheless show a certain transferability between different situations, which makes them useful. The bond lengths  $R(AB)$  are measured by X-ray diffraction (more rarely, neutron diffraction on molecular crystals). Rotational spectroscopy can also give extremely accurate values of bond lengths. For homonuclear A–A bonds, Linus Pauling took the covalent radius to be half the single-bond length in the element, e.g.  $R(\text{H–H, in } \text{H}_2) = 74.14 \text{ pm}$  so  $r_{\text{cov}}(\text{H}) = 37.07 \text{ pm}$ : in practice, it is usual to obtain an average value from a variety of covalent compounds, although the difference is usually small. Sanderson has published a recent set of non-polar covalent radii for the main-group elements, but the availability of large collections of bond lengths, which are more transferable, from the Cambridge Crystallographic Database

has rendered covalent radii obsolete in many situations. The values in the table below are based on a statistical analysis of more than 228,000 experimental bond lengths from the Cambridge Structural Database. For carbon, values are given for the different hybridisations of the orbitals.

### **Multiple Bond Radii**

A different approach is to make a self-consistent fit for all elements in a smaller set of molecules. This was done separately for single, double, and triple bonds up to super heavy elements. Both experimental and computational data were used. The single-bond results are often similar to those of Cordero et al. When they are Radii for multiple bonds different, the coordination numbers used can be different. This is notably the case for most (d and f) transition metals. Normally one expects that  $r_1 > r_2 > r_3$ . Deviations may occur for weak multiple bonds, if the differences of the ligand are larger than the differences of R in the data used. Note that elements up to atomic number 118 (oganesson) have now been experimentally produced and that there are chemical studies on an increasing number of them. The same, self-consistent approach was used to fit tetrahedral covalent radii for 30 elements in 48 crystals with sub picometer accuracy.

### **Vander Waals Radii**

Vander Waals radii is defined as one half of the internuclear distance between the adjacent atoms belonging to nearest neighbouring molecule of the same substance in the solid state. There are some weak forces of attraction between the neutral noble gas atoms or in between various non polar molecules which is called Vander Waals Force.  $r_{VDW}$  is the shortest distance to which two non-bonded atoms can approach before repulsion between their electron clouds come into play

### **Internuclear distance between two non-bonded nearest neighbouring atoms**

Internuclear distance between two non-bonded nearest neighbouring atoms for Cl =  $3.6 \text{ \AA}$ ,  $r(\text{Cl}) = 3.6/2 \text{ \AA} = 1.80 \text{ \AA}$

The Vander Waals radii of some atoms are given below along with their covalent

Elements	N	O	F	Ne	P	S	Cl	Ar
$r_{\text{cov}}(\text{\AA})$	0.77	0.74	0.72	.....	1.10	1.04	0.99	.....



$r_{VDW}(A^\circ)$	1.50	1.40	1.35	1.31	1.80	1.90	1.80	1.74
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The Vander Waal radii are larger than the covalent radii because in the formation of covalent bond the atoms come close to each other due to the overlapping of orbital. On the other hand, Vander Waal forces existing between atoms or molecules non bonded weaker and atoms are at large distances. Hence the internuclear distances in case of atoms held by Van der Waals forces is greater than between covalently bonded atoms consequently Vander Waal covalent.