

# PERIODICITY IN ATOMIC PROPERTIES

## Moseley Experiment

In a discharge tube, when the anticathode is bombarded with high energy electrons, it generates X-ray. It is observed that the frequency of the X-ray (line spectrum) is independent of the energy of the incident electron beam but is a characteristic property of the anticathode used.

**Law:** The square roots of the frequencies ( $\nu$ ) of the X-ray is directly proportional with atomic number  $Z$ .

$$\sqrt{\nu} = aZ$$

Where,  $a$  = is proportionality constant and  $Z$  = atomic number.

When  $Z$  was replaced by the atomic weight, no such relationship was obtained.

### Importance:

- i) **Correction of Mendeleev's periodic table:** (From this experiment it was concluded that the atomic number ( $Z$ ) is the inherent property of the elements which control the physical and chemical properties of the elements. Thus all physical and chemical properties of the elements are the function of atomic number.)
- ii) **Discovery of new element:** (The atomic number can be easily calculated from the experimentally determined X-ray frequencies. If it is found new then a new element is discovered. In this way, technetium ( $Z = 43$ ), promethium ( $Z = 61$ ), rhenium ( $Z = 75$ ) have been discovered and identified.
- iii) **Identification of lanthanides:** The members of the lanthanide series are chemically so similar that they cannot be easily differentiated as different element. In this case, this experiment is helpful to identify and determine their atomic number.

## Classification of elements on the basis of electron ( $e^-$ ) configurations of valence shell of atoms.

On the basis of valence shell  $e^-$  configuration the elements are classified as follows –

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1	H																		He
2	Li	Be											B	C	N	O	F		Ne
3	Na	Mg											Al	Si	P	S	Cl		Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br		Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I		Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At		Rn
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt										

### i) Inert Gas Element:

(Elements with completely filled 's' and 'p' sub-shells (except He), having valence shell  $e^-$  configuration as  $ns^2p^6$  (He,  $1s^2$ ), are called inert gas element.)

They have completely filled octets and are very reluctant towards chemical reaction, hence termed 'inert'. Their valence shell is taken to be zero (0) and they are placed in the '0'-group [group-18 in modern P.T.]

*aiti*

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
																		He
																		Ne
																		Ar
																		Kr
																		Xe
																		Rn

### ) Representative Elements:

(Elements with incompletely filled valence shell, having general  $e^-$  configuration  $ns^{1-2}np^{0-5}$  are called **representative or ideal elements**.)

They may be metals, nonmetals or metalloids and may form ionic or covalent compounds. A chemical property of elements in atomic property is mainly characteristic of the elements. They occupy IA(1), IIA(2), IIIA – VIIA(13 – 17) group in the P.T. These are abbreviated as elements of **R-series**.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	
Li	Be											B	C	N	O	F	
Na	Mg											Al	Si	P	S	Cl	
K	Ca											Ga	Ge	As	Se	Br	
Rb	Sr											In	Sn	Sb	Te	I	
Cs	Ba											Tl	Pb	Bi	Po	At	
Fr	Ra																

### ii) Transition Element:

(Elements with incompletely filled inner d-sub-shell, having general  $e^-$  configuration of the valence shell as  $(n-1)d^{1-9}ns^{1-2}$  are called **transition elements**.)

Each T-series contains 10 elements, except 4<sup>th</sup> series, only seven [Ac(89), Rf(104), Db(105), Sg(106), Bh(107), Hs(108), Mt(109)]. These elements are placed in group-IIIB-VIIB(3-7), VIII(8-10), IB(11) & IIB(12) in the P.T.

This class of elements is abbreviated as **T-series**. There are four T-series involving 3d, 4d, 5d & 6d sub-shell.

### The T.E. has following characteristics –

- ⊕ They all are hard metals having high melting point (M.P) and boiling point (B.P.).
- ⊕ They exhibit striking resemblance to one another in their physical characteristics.
- ⊕ They are all good conductor of heat and electricity.
- ⊕ They exhibit variable oxidation state.
- ⊕ Due to presence of odd d-electron show paramagnetic properties.
- ⊕ They all form coloured compound and complexes.
- ⊕ They can form alloys.
- ⊕ Almost all of them (except Cu, Ag, Au, Pd, Pt) dissolve in mineral acid.

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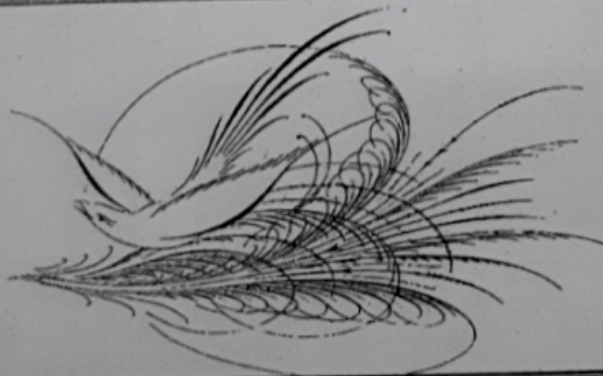
- According to this definition, members of Cu (group-IB/group-11), having complete d-sub-shell ( $3d^{10} 4s^1$ ), should not be included in this class. But it is also included as transition element (T.E.) due to following reason—
  - Its different properties are resembles with other T.E.
  - The most stable oxidation state of Cu is +2 which has incomplete d-subshell.
- According to this definition, members of Zn-family (group-IIB/group-12), having complete d-sub-shell, should not be included in this class. But it is also included as transition element (T.E.) due to following reason—
  - Its different properties are resembles with other T.E.
  - To complete the sequence of the periodic table (P.T.).

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1																		
2																		
3																		
4			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn						
5			Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd						
6			La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg						
7			Ac	Rf	Db	Sg	Bh	Hs	Mt									

**iv) Inner Transition Element:** Elements with incomplete  $(n-2)f$  sub-shell, having general e-configuration of valence shell as  $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$  are called **inner transition elements.**

They have incomplete inner d sub-shell; hence show same characteristics of T.E. But the e-entire into  $(n-2)f$  sub-shell, thus termed inner transition element. Two sub-series corresponding to  $4f$  (following La) called Lanthanides &  $5f$  (following Ac) called Actinides. Elements beyond U(92) are called trans uranic / man-made / synthetic elements. The chemical properties of the elements in a particular series are in a very similar. These elements find no place in the P.T. and are placed in two separate series below the P.T.)

Lanthanides	Ce <sub>58</sub>	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu <sub>71</sub>
Actinides	Th <sub>90</sub>	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr <sub>103</sub>



### Block classification of elements

$e^-$  are fed one by one to the different sub-shell of an atom obeying Pauli exclusion principle, Hund's rule and Aufbau principle. The last  $e^-$  fed in the process is called differentiating  $e^-$ . On the basis of occupancy of  $e^-$  the elements are classified into four blocks. This is called block classification of elements. Such blocks are:

**i) 's'-Block Elements:** Elements in which the differentiating e<sup>-</sup> occupies the 's' sub-shell of the valence shell (ns), are called s-block elements. The elements have their valence shell e<sup>-</sup> configuration ns<sup>1-2</sup> and these are placed in group IA(1) and IIA(2) in the P.T.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1	H																		
2	Li	Be																	
3	Na	Mg																	
4	K	Ca																	
5	Rb	Sr																	
6	Cs	Ba																	
7	Fr	Ra																	

**ii) 'p'-Block Element:** (Element in which the differentiating e<sup>-</sup> occupies into the valence shell 'p' sub-shell (np), are called p-block elements. These element have their valence shell e<sup>-</sup> configuration ns<sup>2</sup>np<sup>1-6</sup> and are placed in groups IIIA - VIIA(13 - 17) and 0(18) in the P.T.)

The s and p-block elements constitute the R-element and inert gas element.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1																			
2													B	C	N	O	F		
3													Al	Si	P	S	Cl		
4													Ga	Ge	As	Se	Br		
5													In	Sn	Sb	Te	I		
6													Tl	Pb	Bi	Po	At		
7																			

**iii) 'd'-Block Element:** Elements in which the ns sub-shell remain filled while the differentiating e<sup>-</sup> occupies the inner 'd' sub-shell i.e. (n-1)d sub-shell are called d-block element. These elements have their valence shell e<sup>-</sup> configuration as )

$$( (n-1)s^2p^6d^{1-10}ns^{1-2} )$$

They are placed in groups IIIB-VIIB(3-7), VIII(8-10), IB(11) and IIB(12) of the P.T.

These are the transition elements.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1																			
2																			
3																			
4		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn								
5		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd								
6		La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg								
7		Ac	Rf	Db	Sg	Bh	Hs	Mt											

**iv) 'f'-Block Element:** Elements in which the differentiating e<sup>-</sup> occupies the still inner 'f' sub-shell i.e. (n-2)f, while the (n-1)d sub-shell remains incomplete or vacant and ns complete, are called f-block element. They have valence shell e<sup>-</sup> configuration as )

$$( (n-2)f^{1-14}(n-1)d^{0-1}ns^2 )$$

They are placed separately in two series below the P.T. these are inner-transition elements.

Lanthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinides	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

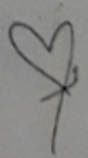
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## :: Naming of Super Heavy Elements ::

a) The digits expressing the atomic number of an element are serially represented by using the following numerical roots -

0	1	2	3	4	5	6	7	8	9
nil	un	bi	tri	quad	pent	hex	sept	oct	enn

b) The successive roots are put together and name is ended by 'ium'.

c) To avoid repetition of some letters, the following procedure is adopted -  
 $bi + ium = bium$        $tri + ium = triumenn + nil = ennium$

## Slater's rules for screening effect

(The inner  $e^-$  cores in an atom act as a screen or shield between the nucleus and outer electron, as a result the outer  $e^-$  experience only a part of the total nuclear charge. This effect of reducing the nuclear charge by the inner  $e^-$  cores towards the outer  $e^-$  is called **screening or shielding effect**.)

The amount of nuclear charge reaching the outer  $e^-$  is called **effective nuclear charge (ENC)**.

The amount of nuclear charge reduced by the inner  $e^-$  cores is called **screening or shielding constant (S)**. Slater proposed a set of rules to calculate ENC [ $Z^*$  or  $Z_{eff}$ ], where—

$$Z^* = Z - S$$

- $Z^*$  = ENC.  
 $Z$  = actual nuclear charge.  
 $S$  = shielding constant (sum of the shielding contribution).

## RULES

- The  $e^-$  of the atoms are divided into groups like—  
 $(1s), (2s 2p), (3s 3p), (3d), (4s 4p), (4d), (4f), (5s 5p), (5d) \dots \dots \dots etc.$
- Electrons in groups on the right of the one under consideration: Zero,
- Each other  $e^-$  in the same group for  $(ns np)$  shield: **0.35 each.**  
 [Except for  $1s$ , 0.30 each].
- All  $e^-$  in the  $(n - 1)$  shell shield: **0.85 each.**
- All  $e^-$  in the  $< (n - 1)$  shell shield: **1.00 each.**
- For  $nd / nf e^-$  rules a, b & c remain same, but rules d & e become:  
 All  $e^-$  lying to the left of the  $nd/nf$  group shield: **1.00 each.**

### Quick view:

$Z^*$ for 2 <sup>nd</sup> period element	$= 0.65 + 0.65 \times n$
$Z^*$ for 3 <sup>rd</sup> period element	$= 1.55 + 0.65 \times n$
$Z^*$ for 4 <sup>th</sup> period element beyond d-block element	$= 3.05 + 0.65 \times n$
$Z^*$ for 3d block element	$= 2.85 + 0.15 \times n$

$n = \text{no. of } e^- \text{ in that group.}$

**PROBLEMS:**

Calculate shielding or screen constant and the ENC of the following e<sup>-</sup> :-

- i) The first valence e<sup>-</sup> in Ca (Z=20),
- ii) The first valence e<sup>-</sup> in Mn (Z=25),
- iii) A 3d e<sup>-</sup> in Mn,
- iv) A 4s e<sup>-</sup> in Zn (Z=30),
- v) ENC at the periphery of Br Atom (Z=35).

[Ans: i) 17.15, 2.85; ii) 21.4, 3.6; iii) 19.4, 5.6; iv) 25.65, 4.35 v) 27.75, 7.25]

Ans: i) The e<sup>-</sup> configuration of Ca (20) is -  $(1s)^2(2s2p)^8(3s3p)^8(4s)^2$

Electrons in the groups to the right contribute		= 0.00
1 other electron in the (3s3p) group contribute	1 × 0.35	= 0.35
8 electrons in the (n - 1) group contribute	8 × 0.85	= 6.80
10 electrons in the < (n - 2) group contribute	10 × 1.00	= 10.00
<b>Total (S)</b>		<b>= 17.15</b>

$$\therefore ENC (Z^*) = Z - S = 20 - 17.15 = 2.85$$

**Alternative Path:**

Electronic configuration: Ca(20):  $(1s)^2(2s2p)^8(3s3p)^8(4s)^2$

Shell	< (n - 1)	(n - 1)	(n)	> n	Total (S)
Contribute	(10 × 1.00 = 10.00)	+(8 × 0.85 = 6.80)	+(1 × 0.35 = 0.35)	+0.00	= 17.15

$$\therefore ENC (Z^*) = Z - S = 20 - 17.15 = 2.85$$

ii) Electronic configuration: Mn(25):  $(1s)^2(2s2p)^8(3s3p)^8(3d)^5(4s)^2$

Shell	< (n - 1)	(n - 1)	(n)	> n	Total (S)
Contribute	(10 × 1.00 = 10.00)	+(13 × 0.85 = 11.05)	+(1 × 0.35 = 0.35)	+0.00	= 21.4

$$\therefore ENC (Z^*) = Z - S = 25 - 24.4 = 3.6$$

iii) Electronic configuration: Mn(25):  $(1s)^2(2s2p)^8(3s3p)^8(3d)^5(4s)^2$

Shell	< (nd)	(nd)	> n	Total (S)
Contribute	(18 × 1.00 = 18.00)	+(4 × 0.35 = 1.4)	+0.00	= 19.4

$$\therefore ENC (Z^*) = Z - S = 25 - 19.4 = 5.6$$

iv) Electronic configuration: Zn(30):  $(1s)^2(2s2p)^8(3s3p)^8(3d)^{10}(4s)^2$

Shell	< (n - 1)	(n - 1)	(n)	> n	Total (S)
Contribute	(10 × 1.00 = 10.00)	+(18 × 0.85 = 15.3)	+(1 × 0.35 = 0.35)	+0.00	= 25.65

$$\therefore ENC (Z^*) = Z - S = 30 - 25.65 = 4.35$$

v) Electronic configuration: Br(35):  $(1s)^2(2s2p)^8(3s3p)^8(3d)^{10}(4s4p)^7$

Shell	< (n - 1)	(n - 1)	(n)	> n	Total (S)
Contribute	(10 × 1.00 = 10.00)	+(18 × 0.85 = 15.3)	+(7 × 0.35 = 2.45)	+0.00	= 27.75

$$\therefore ENC (Z^*) = Z - S = 35 - 27.75 = 7.25$$

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## Relativistic Effect

We can think of the electron as a particle that is accelerated when the electron is revolves in higher quantum shell. The radial velocity approaches the speed of light as the nuclear charge approaches  $Z = 137.036$ . For Hg ( $Z = 80$ ), the 1s electrons move at  $80/137 = 0.58$  times of the speed of light.

According to Einstein's theory of relativity, the mass 'm' of a particle over its rest mass,  $m_0$ , when its velocity,  $u$ , approaches the speed of light,  $c$  -

$$m = \frac{m_0}{\sqrt{1 - \frac{u^2}{c^2}}} = 1.2m_0$$

Hence, the mass of 1s electron is about 1.2 times of its rest mass. But according to Bohr's theory radius of a orbit is inversely proportional to the mass of the electron.

$$r_n = \frac{n^2 h^2}{4\pi^2 m Z e^2}$$

So, we expect the radius of the 1s orbital to be about 20% less than the expected orbital size. This is **relativistic contraction**. This effect is present to a lesser extent among p - orbitals and nearly absent among d- and f- orbitals. The s- and p- orbitals are so contracted that they can effectively shield d- & f- orbitals. Thus, d- & f- orbitals experience lesser nuclear charge and expansion occurs. This is **relativistic expansion**. Thus for heavier congeners relative contraction of s- & p- and relative expansion of d- & f- orbital occur.



## Atomic Radius

According to particle mechanics, the distance between the nucleus and the outermost e- of an atom is termed atomic radius. While According to wave mechanics, it is the distance between the nucleus and the maximum e- density of the outermost e- cloud.

But it is not possible to isolate an atom and measure distance. We can determine the inter-nuclear distance when an atom in contact with other atoms and individual atomic radii can be calculated their form. Various types of atomic radii are defined. The most important of which is the covalent radii.

### Covalent Radii:

Half of the distance between the nuclei of two like atom forming a covalent bond in a diatomic molecule is called the covalent radius ( $r_{cov}$ ) of the atom.

$$d_{H-H} \text{ in } H_2 = 74 \text{ pm} \\ \therefore r_H = \frac{1}{2} \times 74 = 37 \text{ pm}$$

$$d_{Cl-Cl} \text{ in } Cl_2 = 199 \text{ pm} \\ \therefore r_{Cl} = \frac{1}{2} \times 199 = 99.5 \text{ pm}$$

These radius value are additive in nature. When two atoms are joined by a single covalent bond and their electro negativity (EN) values differ little.

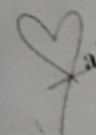
$$r_A + r_B = d_{A-B}$$

When EN difference between A and B ( $\chi_A$  and  $\chi_B$ ) is high, the experimental bond length becomes shorter than calculated value. In such cases correction terms are introduced (Schomaker-Stevenson) as -

$$d_{A-B} = r_A + r_B - 9(\chi_A - \chi_B)$$

Multiple bonds between two atoms is called multiple bond radii. Order of such bond lengths and consequently covalent radii is -

Single Bond > Double Bond > triple Bond.



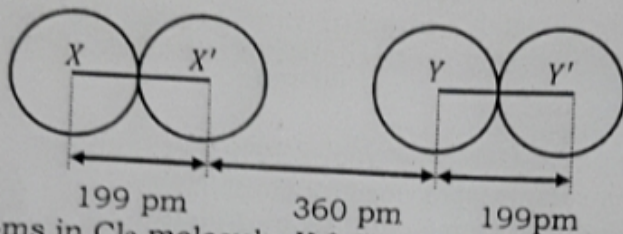
**Van der Waal's Radii:**

Half the distance between two non bonded atoms of two adjacent molecules is called non-bonded or van der Waal's radii. This type of radius is applied to nonmetallic elements.

**Features:**

- (i) Generally, covalent radius is smaller than van der Waal's radius because, in the formation of chemical bond, the atoms have to come close to each other.
- (ii) Values of radii are obtained from X-ray studies of various elements in the solid state.

**Example:** Let us consider two Cl<sub>2</sub> molecules. When the molecules come in contact, they will stick together by a weak attractive force, called van der Waal's force. This type of force arises without bond formation.



X & X' are two Cl atoms in Cl<sub>2</sub> molecule. Y & Y' are two Cl atoms in another Cl<sub>2</sub> molecule.

$$d_{X-X'} = d_{Y-Y'} = 199 \text{ pm.}$$

$$r_{\text{cov}} = \frac{1}{2} \times 199 = 99.5 \text{ pm.}$$

$$\text{Van der Waal's radius of Cl-atom} = \frac{1}{2}(d_{X'-Y}) = \frac{1}{2} \times 360 = 180 \text{ pm.}$$

Solid Ar consists Ar atoms at a distance of 380 pm. Hence van der Waal's radius of Ar =  $\frac{1}{2} \times 380 = 190 \text{ pm}$  but, when such atom link to highly EN atoms, their van der Waal's radius may decrease. Contractions of e- cloud of the less EN atom by the more EN atom occur. E.g. van der Waal's radius of Xe in XeF<sub>4</sub> is 170 pm, while that of solid Xe is 220 pm.

In this case no bond is formed, hence much less attractive force and longer radii.

**Bragg-Slater's Radii:**

The univalent cations of highly electropositive (like alkali metals) are smaller by 85 pm while, the univalent anions of highly electronegative atoms (like halogens) are larger by 85 pm than the corresponding atomic radii.

Hence sum of the ionic radii of such ions in an ionic crystal will be equal to the sum of their atomic radii. i.e,

$$r_{M^+} + r_{X^-} = r_M + r_X$$

Such radii are called Bragg-Slater radii and often in close agreement with experimental values. ✓

**Metallic Radii:**

In metal crystal the metal atoms are closely packed. The number of intermediate neighbors of an atom in a metal crystal is called its co-ordination number (CN). One-half of the distance between the atoms of a metal in the metallic close packed crystal lattice in which the metal exhibits a CN of 12 is called **metallic or crystal radii**.

Metallic radii are 10-15% longer than single bond covalent radii, but, less than van der Waal's radii. In covalent bonding, the bonding e- are localized between two atoms creating the stronger attraction and shorter distance. But, in metal crystal the e- are delocalized throughout the crystal, decreasing the attractive force and increasing the metallic radii than covalent radii.

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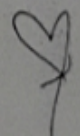
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**Ionic Radii:**

The distance between the nucleus and the point of which the outermost  $e^-$  density is maximum, is called the ionic radius.

~ X-ray diffraction patterns from ionic crystals provide knowledge about spacing of ions in crystal. But there is no way to divide this distance into cationic and anionic radii. Several indirect methods have been proposed to determine the radii of ions.

**Comparison between Atomic & Ionic Radii**

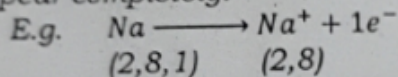
The cation has same number of proton but less number of  $e^-$  than the parent atom while anion has larger number of  $e^-$ . Hence ENC of cation is greater while that of anion is lesser than the parent atom. Consequently, the outermost  $e^-$  cloud is drawn closer in a cation. While away in an anion i.e.)

$$r_{M^{n+}} < r_M \qquad r_{X^{n-}} > r_X$$

Thus cations are smaller while anions are larger than the parent atom. The radius of cation decreases with increase of its charge while the radius of anion increases with increase of its charge.

**▲ A cation is smaller than the parent atom due to following factors:**

a) A cation is formed by the loss of one or more  $e^-$ . In this process outer shell may disappear completely.



b) When cation is formed, ENC increases than the parent atom and therefore  $e^-$  is attracted more towards the nucleus. Consequently, cations become smaller.

**▲ An anion is bigger than the parent atom due to following factor:**

a) On addition of extra  $e^-$ , repulsion between electrons increases. As a result expansion of  $e^-$  cloud occurs.

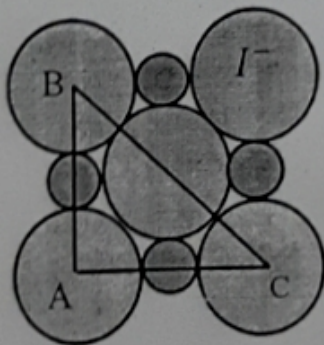
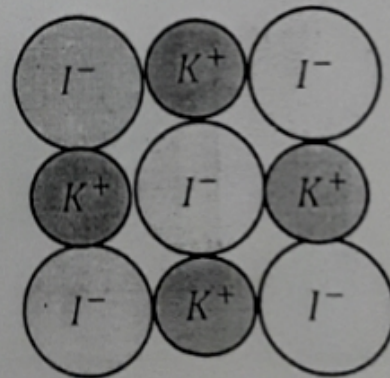
b) When anion is formed, ENC decreases than the parent atom and therefore  $e^-$  cloud getting away from the nucleus. Consequently, anions become bigger.

**Methods of Experimental Determination of Ionic Radii:**

Several methods are employed to determine the ionic radii. Here only three are given:

**Lande's Method:**

In ionic crystals containing very large anions and small cations (LiI), cation-anion as well as, anion-anion contact occurs. While crystal containing somewhat larger cations (KI), only cation-anion contact is possible.

LiI-crystalKI-crystal

Lande (1920) started with the crystal LiI in which the size of anion is much larger compared to that of tiny cation,  $Li^+$ . Thus -

$$BC^2 = AB^2 + AC^2$$

But,

$$AB = AC = 2(r_{Li^+} + r_{I^-}) = 2d_{Li^+ + I^-}$$

The inter-ionic distance in an ionic crystal can be determined experimentally i.e.  $d_{Li^+ + I^-}$  is determined. Hence AB and AC have consequently BC.

But,  $BC = 4r_{I^-}$

$$\therefore r_{I^-} = \frac{1}{4}BC \quad \text{and } r_{I^-} \text{ is obtained.}$$

Now,  $r_{Li^+} = [(d_{Li^+ + I^-}) - (r_{I^-})]$  and  $r_{Li^+}$  is also obtained.

In  $K^+I^-$  crystals the anions are not in contact but cation-anion contact occurs. The radius of  $I^-$  determined previously in  $Li^+I^-$  crystal. This value can be used and subtracted from experimentally determined  $d_{K^+ + I^-}$  distance and  $r_{K^+}$  is obtained.

$$r_{K^+} = [(d_{K^+ + I^-}) - (r_{I^-})]$$

By continuing this process, ionic radii for the other ions have been determined.

### Bragg's Method:

Bragg in 1927 assumed that in silicates cations are smaller & anions are larger & the large sized anions touch with one another. Thus, half of the internuclear distance of the adjacent oxide ions ( $O^{2-}$ ) is the radius of  $O^{2-}$ . Thus

$$r_{O^{2-}} = \frac{1}{2}R_{O-O} = \frac{1}{2} \times 270 \text{ pm} = 135 \text{ pm}$$

By using this value, Bragg & West computed the ionic radii for more than 80 ions.

### Pauling's Method:

This method is based on the following three assumptions:-

a) This method is applicable to ionic crystal containing only **iso-electronic ions**.  
E.g.  $Na^+F^-$ ,  $K^+Cl^-$ ,  $Rb^+Br^-$ ,  $Cs^+I^-$  etc.

b) In an ionic crystal, closest contact between cation and anion is occurs i.e.

$$d_{A^+ - B^-} = r_{A^+} + r_{B^-}$$

[Where 'd' & 'r' terms are distance & radii respectively.]

c) Ionic radii are inversely proportional to their respective ENC. i.e.

$$r_{A^+} \propto \frac{1}{Z_{A^+}^*} \quad r_{B^-} \propto \frac{1}{Z_{B^-}^*}$$

$$\therefore \frac{r_{A^+}}{r_{B^-}} = \frac{Z_{B^-}^*}{Z_{A^+}^*}$$

$d_{A^+ - B^-}$  can be determined experimentally and the ENC that is  $Z^*$  value can be calculated from Slater's Rule. Hence ionic radii can be calculated by Pauling's method.

**Q:** The inter-ionic distance in  $NaF$  crystal is 231 pm. Calculate the radii of  $Na^+$  and  $F^-$  ions.

**A:** The inter-ionic distance in  $Na^+F^-$  crystal is -

$$d_{Na^+ - F^-} = r_{Na^+} + r_{F^-} = 231 \text{ pm} \dots \dots \dots (i)$$

$Na^+$  &  $F^-$  are iso-electronic ions with  $e^-$  configuration  $(1s)^2(2s2p)^8$

From Slater's rule,

$$\text{Screening constant } s = (8 \times 0.35) + (2 \times 0.85) = 4.5$$

$$\therefore Z_{Na^+}^* = 11 - 4.5 = 6.5 \quad \text{and} \quad \therefore Z_{F^-}^* = 9 - 4.5 = 4.5$$

According to Pauling's method,

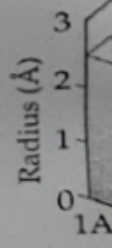
$$\therefore \frac{r_{Na^+}}{r_{F^-}} = \frac{Z_{F^-}^*}{Z_{Na^+}^*} = \frac{4.5}{6.5} \dots \dots \dots (ii)$$

Solving equation (i) and (ii),  $r_{Na^+} = 94.5 \text{ pm}$ .

$$r_{F^-} = 136.5 \text{ pm}$$

In a group

In a period



## Periodic Variation:

**In a group** a). For the R-elements, the atomic size increases with increase in the atomic number due to addition of new quantum shell and decreased ENC. This increase is maximum between the two lighter members and minimum between the two heavier members.

b). For the T-elements, such increase is much less compared to the R-elements. Between 3d & 4d series, 18 e- are added of which 10 are poorly shielding d e-. Hence, the effect of addition of a new quantum shell is not so effect and the radius increases down the group at much lower rate than the R-elements.

c). Between the 4d & 5d elements, 32 e- are added of which 10 are poorly shielding d e- and 14 are extremely poorly shielding f e-. As a result, the size of the atom lying below a group becomes almost same. Thus the pair of elements

(Zr & Hf), (Nb & Ta) and (Mo & W) has almost identical radii value.

**In a period** a). The atomic radii decreases steadily from left to right in a period as the e- are placed in the same shell in which mutual shielding is small than steady increase in ENC.

b). Small variation in the decreasing radii of the T.E. are due to the e- occupying the (n-1) d sub-shell in which mutual shielding is small.

c). Addition of e- in the (n-2) sub-shell for the inner-T.E. can not neutralize the increased nuclear charge due to poor shielding power of f e-. As a result, a regular decrease in the atomic radii from Ce(58) to Lu(71) is observed. This decrease in atomic radii, called the **lanthanide contraction**. This effect is so much that, on addition of new quantum shell for the post-lanthanide elements is almost completely neutralized and radii of the pair of elements in the same group viz. (Zr & Hf); (Nb & Ta); (Mo & W) are almost same.

