

## Effective Nuclear Charge: ( $Z_{\text{eff}}$ )

The  $e^-$ 's residing in the shells between the nucleus and the valence shells are called intervening  $e^-$ 's. These  $e^-$ 's reduce the force of attraction between the nucleus and the outer most shell  $e^-$ 's. The reduction produced in the force of attraction due to the presence of intervening  $e^-$ 's is called shielding (or) screening effect.

With the decrease in the force of attraction caused by the shielding effect of intervening  $e^-$ 's, the actual nuclear charge (which is equal to the atomic no..  $Z$  of the element) is decreased by the quantity  $\sigma$  (sigma) which is called screening constant. The decreased nuclear charge which is obviously equal to ( $Z - \sigma$ ) is called effective nuclear charge and is denoted by  $Z_{\text{eff}}$ .

$$\text{Thus } Z_{\text{eff}} = Z - \sigma \text{ (or) } Z_{\text{eff}} = Z_{\text{actual}} - \sigma$$

$\sigma$  is a measure of the extent to which the intervening  $e^-$ 's screens the outer-most shell  $e^-$  from the nuclear pull.

Hence  $Z_{\text{eff}}$  is defined as "the actual nuclear charge ( $Z$ ) minus the screening constant ( $\sigma$ )".

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produced by the  $e^-$ 's residing between the nucleus and outer-most shell  $e^-$ .

Factors affecting the magnitude of  $\sigma$  &  $Z_{eff}$  and their variations in the periodic table:

1) Number of intervening  $e^-$ 's:

Greater is the number of  $e^-$ 's intervening between the nucleus and the outermost shell, more will be the magnitude of  $\sigma$  and hence the magnitude of  $Z_{eff}$  will decrease, to a greater extent. When we move down a group, the number of intervening  $e^-$ 's increases and hence the magnitude of  $\sigma$  also increases. The increase in the value of  $\sigma$  decreases the value of  $Z_{eff}$ . Thus on going down a group the magnitude of  $Z_{eff}$  goes on decreasing.

2) Size of the atom:

With the increase in the size of the atom,  $Z_{eff}$  decreases. Thus :

- Since atomic size increases in going down the group  $Z_{eff}$  decreases in the same direction.
- Since the size of atom decreases as we move along a period from left to right,  $Z_{eff}$  increases in the same direction.

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Calculation of  $\sigma$  and  $Z_{eff}$  by Slater's Rules:

The value of  $\sigma$  and hence that of  $Z_{eff}$  can be calculated by using Slater's rules. According to these rules, the value of  $\sigma$  for a given  $e^-$  is estimated as follows.

1. Write down the complete electronic configuration of the element and divide the  $e^-$ s into the following orbitals, from inside of the atom

(1s), (2s, 2p); (3s, 3p); (3d); (4s, 4p); (4d); (4f); ...

2. Now select the  $e^-$  for which the value of  $\sigma$  is to be calculated. For this calculation add up the contributions to  $\sigma$  for other  $e^-$ s according to the following rules.

Type of  $e^-$

Contributions to  $\sigma$

for each  $e^-$  of this type

a) All  $e^-$ s in groups outside

the chosen  $e^-$

0

b) All other  $e^-$ s on the same

0.30 for (1s  $e^-$ )

group of chosen  $e^-$

0.35 (for other  $e^-$ s)

c) All the  $e^-$ s immediately inside  
( $n-1$ )

0.85

d) All the  $e^-$ s further inside

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**Problem:**

- 1) calculate the effective nuclear charge experienced by  $\text{As}^{2-}$  in K atom.

**Solution:**

The E.C of K atom

$$Z = 19 \quad 1s^2 2s^2 2p^6, 3s^2 3p^6, 4s^1$$

This atom has 4 shells in all.

$$Z_{\text{eff}} = Z - \sigma$$

$$= 19 - (0.85 \times \text{No. of } e^- \text{s in 3rd shell}) +$$

$$1.00 \times \text{Total no. of } e^- \text{s in the inner shells})$$

$$= 19 - (0.85 \times 8 + 1.00 \times 12)$$

$$= 19 - 6.8 + 10$$

$$Z_{\text{eff.}} = 19 - 16.8 = 2.20$$

- 2) Calculate the  $Z_{\text{eff}}$  experienced by the last  $e^-$  in an atom whose E.C is  $1s^2 2s^2 2p^6, 3s^2 3p^5$ .

**Solution:**

The atomic number  $Z$  of the element having this E.C is 17. and it has 3 shells in all.

$$\therefore Z_{\text{eff}} = Z - \sigma$$

$$= 17 - [(0.85 \times \text{No. of } e^- \text{s in 3rd shell}) +$$

$$0.85 \times \text{No. of } e^- \text{s in the 2nd shell}) +$$

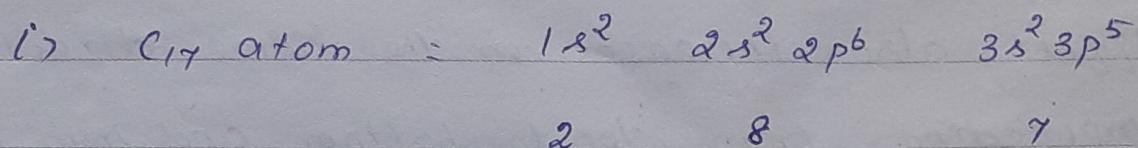
$$1.00 \times \text{Total no. of } e^- \text{s in the inner shells}]$$

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$$\begin{aligned}
 &= 17 - [(0.35 \times 6) + (0.85 \times 8) + (1 \times 2)] \\
 &= 17 - [2.1 + 6.8 + 2] \\
 &= 17 - 10.9 = 6.1
 \end{aligned}$$

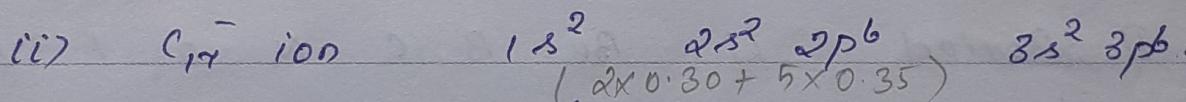
3) calculate  $\sigma_{\text{eff}}$  for the last  $e^-$  in i) Cl atom ( $Z=17$ ) and  $\text{Cl}^-$  ion.

**Solution:**



$\sigma$  for  $3p^1 e^-$  (last  $e^-$ ) of Cl atom

$$\begin{aligned}
 \sigma_{\text{eff}} &= 17 - \frac{(2 \times 0.30 + 4 \times 0.35)}{(0.35 \times 6 + 0.85 \times 8 + 1.00 \times 2)} \\
 &= 17 - \frac{(2.1 + 6.8 + 2)}{10.8} \\
 &= 17 - 10.9 = 6.1 \quad 6.2
 \end{aligned}$$



$$\begin{aligned}
 \sigma_{\text{eff}} &= 17 - \frac{(0.35 \times 7 + 0.85 \times 8 + 1.00 \times 2)}{0.35} \\
 &= 17 - \frac{11.25}{0.35} = 5.95 \quad 5.85
 \end{aligned}$$

**Variation of  $\sigma$  (screening effect) in the Periodic Table**

The magnitude of screening constant is a measure of the extent to which the  $e^-$ s intervening between the nucleus and the valence shell shield valence shell  $e^-$ s from the nucleus.

Thus, in going from left to right in a period atomic and ionic size (radii) decrease with increase of atomic number.

b) In a group:

In going down a group of  $s\&p$  block elements, the atomic & ionic size (radii) both increase with the increase in atomic number.

As the number of shells increases when we go down the group, the outer most e<sup>-</sup>s get farther and farther away from the nucleus and hence atomic & ionic size (radii) increase. Thus, it is due to progressive addition of a new shell that the atomic or ionic radii increase when we proceed from top to bottom in a group.

A cation is smaller in size than its parent atom.

We know that the cation is formed by the removal of one or more e<sup>-</sup>s from the atom. Thus, a cation has lesser no. of e<sup>-</sup>s than its parent atom. As the no. of e<sup>-</sup>s decrease, the magnitude of screening constant  $\sigma$  also decreases. This increases the effective nuclear charge  $Z_{eff}$ .

## Variation of $Z_{\text{eff}}$ in the Periodic Table:

### a) In Period:

The value of  $Z_{\text{eff}}$  increases when we proceed from left to right in a period of the P.T.

When we proceed from left to right across a period, the atomic no. or  $Z$  increases by 1 at each next element and the next element has one more valence  $e^-$  with its effective repulsion equal to 0.35 and therefore

$$\begin{aligned} Z_{\text{eff}} \uparrow \text{by } & 1 - 0.35 && (\text{1 the } \uparrow \text{ in at.no.} \\ & = 0.65. && \text{of next element} - \\ & & & 0.35 \text{ effective} \\ & & & \text{repulsion of the} \\ & & & \text{extra } e^-) \end{aligned}$$

from member to member.

Consequently the effective nuclear charge of each next atom is greater by 0.65 than the previous atom.

II Period Li Be B C N O F Ne

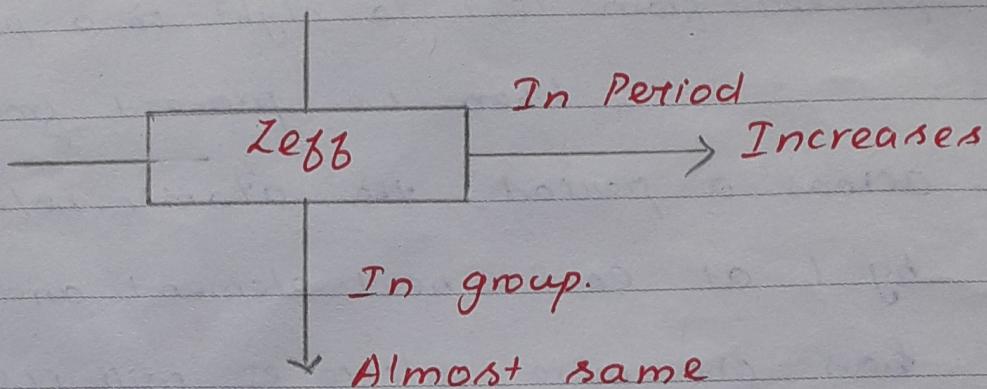
$Z_{\text{eff}}$	1.30	1.95	2.6	3.25	3.9	4.65	5.2	5.85
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### b) In group: (when $S \uparrow$ so $Z$ also $\uparrow$ )

When we descent a group, the values of  $Z_{\text{eff}}$  remain almost same as is evident from the values of Group IA elements

Group I	Li	Na	K	Rb	Cs	Fr
$Z_{eff}$	1.8	0.2	0.2	0.2	0.2	0.2

(The 1st element in the groups is a typical case)



### Electronic Configuration:

The distribution of e<sup>-</sup>s in various shells, sub-shells and orbitals of an atom is called its electronic configuration.

### Representation of Electronic Configuration:

The electronic configuration of an atom is written as in terms of  $nl^x$  notation where l indicates the sub-shell as given below.

Value of l : 0 1 2 3

Sub-shell : s p d f

where x - the no. of e<sup>-</sup>s present in the sub-shell given by l.

n - Indicates the shell no.

l - sub-shell.

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For ex.,  $3p^2$  in which  $n=3$ ;  $x=2$  &  $l=1$  (p-subshell)  
indicates that 2 e<sup>-</sup>s are present in the p sub-shell.

Max. number of e<sup>-</sup>s in a sub-shell is equal to  
 $2(2l+1)$ . where  $l=0, 1, 2$  (or) 3 for s, p, d or f.  
subshells.

Value of l :	0	1	2	3
Sub-shell :	s	p	d	f
Max. no. of e <sup>-</sup> s $2(2l+1)$ :	2	6	10	14

**Aufbau Principle:** The orbitals are filled up with the e<sup>-</sup>s in the increasing order of their energy.

Orbitals being filled →

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d ...

Atomic & Ionic sizes across the periods & groups:

a) In a period:

We know that the number of shells in all the elements of a given period remains the same, but the value of effective nuclear charge, increases from left to right. The increased effective nuclear charge pulls the electron cloud of the atom nearer to the nucleus and thus the size of the atoms and ions goes on decreasing from left to right.

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Thus, in going from left to right in a period atomic and ionic size (radii) decrease with increase of atomic number.

b) In a group:

In going down a group of  $s$  &  $p$  block elements, the atomic & ionic size (radii) both increase with the increase in atomic number.

As the number of shells increases when we go down the group, the outer most  $e^-$ s get farther and farther away from the nucleus and hence atomic & ionic size (radii) increase. Thus, it is due to progressive addition of a new shell that the atomic or ionic radii increase when we proceed from top to bottom in a group.

A cation is smaller in size than its parent atom.

We know that the cation is formed by the removal of one or more  $e^-$ s from the atom. Thus, a cation has lesser no. of  $e^-$ s than its parent atom. As the no. of  $e^-$ s decrease, the magnitude of screening constant  $\sigma$  also decreases. This increases the effective nuclear charge  $Z_{eff}$ .

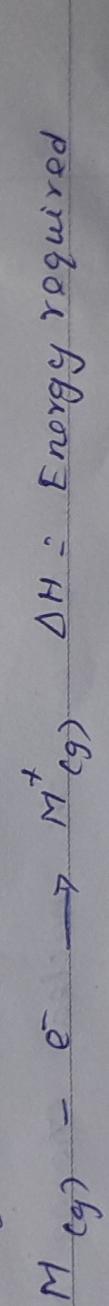
which pulls the  $e^-$  cloud of the cation inward nearer to the nucleus thus makes a smaller ion size than the parent atom.

Anion is bigger in size than its parent atom:

Anion is formed by adding one more  $e^-$ s to the neutral atom. Thus anion has more  $e^-$ s than the parent atom. This increases the magnitude of screening constant  $\sigma$ , which decreases the effective nuclear charge. This pulls the  $e^-$  cloud of the anion outward away from the nucleus thus makes the anion larger in size than its parent atom.

### Tonisation Energy : (IE)

It is defined as the amount of energy required to remove an  $e^-$  from the valence shell of the isolated gaseous atom of the element.



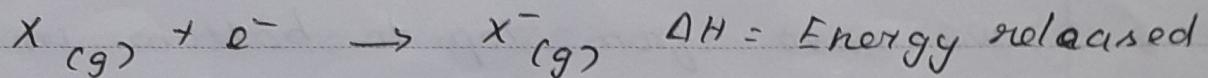
Since, IE is the energy required, it is represented with a positive sign, and it is an endothermic process variation in a period:

On proceeding from left to right

1)  $e^-$  increases. With the increasing shielding effect, the ionization energy decreases.

## Electron Affinity:

It is defined as the amount of energy released when an  $e^-$  is added to the valence shell of an isolated gaseous atom, to convert into its negative ion.



Exothermic process.

### a) Variation in a period:

On moving from alkali metals to halogens in a period, the size of the atoms decreases as the nuclear charge increases. Both these factors increase the force of attraction between the nucleus and the  $e^-$  being added and hence the atom has a greater tendency to attract the  $e^-$  towards itself.

Thus the EA values go on increasing when we move from alkali metals to halogens.

### b) Variation in a group:

On moving down a group, both the size of the atom & the nuclear charge increase. The increase in atomic size tends to decrease the EA values while the increase in nuclear charge tends

Increase the EA values. The net result is that the effect produced by the progressive increase of the atomic size outweighs the effect produced by the progressive increase in nuclear charge and consequently the EA goes on decreasing, as we move from top to bottom in a group.

### Electronegativity:

When two different atoms in a molecule are bonded together by a covalent bond, the e<sup>-</sup> pair forming the covalent bond is not shared equally by both the atoms. Rather, the electron pair lies nearer to one atom than the other.

The relative tendency of a bonded atom in a molecule to attract the shared e<sup>-</sup> pair towards itself is termed as its electronegativity.

### Variation in a period:

In going from left to right in a period of 8 s p-block elements, the EN values increase, because

i) there is a decrease in size of the atoms.

Smaller atoms have greater tendency to attract the electrons towards themselves. i.e smaller atoms have higher EN values.

ii) On moving from left to right in a period, there is an increase in I.E & E.A of the elements. The atoms of the elements which have higher value of I.E & E.A also have higher E.N.

Variation in a group:

In going down the group of s-block elements, the EN value decrease, because

i) there is an increase in the size of the atoms & hence EN value decrease.

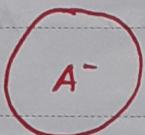
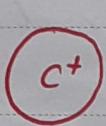
ii) As the value of I.E & EA decreases down the group EN value also decrease.

Polarizability - Fajan's Rules:

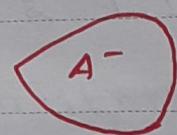
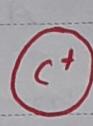
Polarization of Ions:

When a cation  $C^+$  of an ionic molecule  $C^+A^-$  approaches closely the anion  $A^-$ , the cation  $C^+$  withdraws the e<sup>-</sup>s of the anion towards

Itself and the symmetrical shape of the electron cloud of the anion gets distorted. Thus, the e<sup>-</sup> cloud of the anion no longer remains symmetrical but is elongated towards the cation. In other words anion A<sup>-</sup> is distorted by the cation C<sup>+</sup> and this phenomenon is called distortion or polarisation of Anion A<sup>-</sup> by the cation C<sup>+</sup>.



No polarisation.



Polarised anion.

The cation C<sup>+</sup> is also deformed by the anion A<sup>-</sup>, but due to smaller size of the cation, its e<sup>-</sup>s are strongly held and hence the cation is not polarised to an appreciable extent by a nearby anion i.e. the polarisation of cation by anion is negligible and hence we generally do not consider the polarisation of cation by anion.

The ability of a cation to polarise a nearby anion is called its polarising power or ability and the tendency of an anion to get distorted or polarised by a cation is called polarisability.

In  $\text{SnCl}_4$  molecule,  $\text{Sn}$  has +2 charge and in  $\text{SnCl}_2$  molecule,  $\text{Sn}$  has +4 charge. Because of higher positive charge on  $\text{Sn}^{4+}$ ,  $\text{Sn}^{4+}$  ion polarises  $\text{Cl}^-$  ion more strongly than  $\text{Sn}^{2+}$ . Hence polarising power of  $\text{Sn}^{4+} > \text{Sn}^{2+}$ .

**Ex. for ②** Let us consider the hydrides namely  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  &  $\text{HF}$ . Here, the magnitude of negative charge decreases from  $\text{CH}_4$  to  $\text{HF}$ .

i.e.  $\text{C}^{-4} > \text{N}^{-3} > \text{O}^{-2} > \text{F}^-$ . This order shows that  $\text{H}^+$  can not polarise  $\text{F}^-$  ion to any significant extent whereas it polarised  $\text{C}^{-4}$ ,  $\text{N}^{-3}$ ,  $\text{O}^{-2}$  ions to a great extent.

### 2. Size of the cation:

Smaller is the size of the cation higher is its polarising power to polarise a given nearby anion.

### 3. Size of the anion:

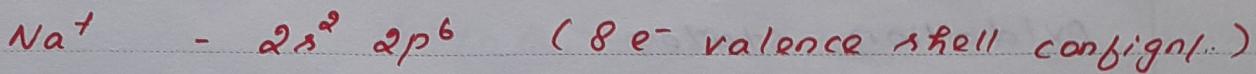
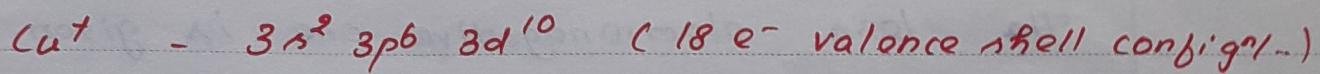
Larger is the size of the anion, more strongly or more easily it will be polarised by a given cation because the e<sup>-</sup>s of the outermost shell of an anion are less firmly bound to the

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nucleus and hence can be easily withdrawn by the cation easily.

#### 4. Electronic configuration of the cation:

Let us consider two different cations like  $\text{Cu}^+$  &  $\text{Na}^+$  which have nearly the same size and same charge.



A cation with 18  $e^-$  valence shell configuration has greater polarising power because of the fact that the d's of the 18  $e^-$  shell shield the nuclear charge of its cation less effectively than 8  $e^-$  shell.

#### Oxidation states (Oxidation Number):

Oxidation number also called oxidation state, the total number of e's that an atom either gains or loses in order to form a chemical bond with another atom.

#### Oxidation states - Calculations:

1. The oxidation state of an uncombined element is zero. O.N of an element may be a whole no. or it may be fractional.

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2. The sum of the oxidation states of all the atoms or ions in a neutral compound is zero.
3. The sum of the oxidation states of all atoms in an ion is equal to the charge on the ion.
4. The more electronegative element in a substance is given a negative oxidation state. The less electronegative one is given a positive oxidation state.
5. Some elements almost always have the same oxidation states in their compounds:

Group I (metals) always +1

Group II .. always +2

Oxygen usually -2 (except in peroxides)

Hydrogen usually +1 (except in hydrides)

Fluorine always -1.

Chlorine halogen state

Problem:

Calculate the oxidation number of

i) Cr in  $\text{Na}_2\text{Cr}_2\text{O}_7$  ii) Mn in  $\text{KMnO}_4$

iii) S in  $\text{H}_2\text{SO}_4$

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i) Cr in  $\text{Na}_2\text{Cr}_2\text{O}_7$ .

$$\text{Na}_2\text{Cr}_2\text{O}_7 = 0$$

$$(2x+1) + 2x + (7x-2) = 0.$$

$$2 + 2x - 14 = 0.$$

$$2x = 14 - 2 = 12.$$

$$x = \frac{12}{2} = +6.$$

ii) Mn in  $\text{KMnO}_4$ 

$$\text{KMnO}_4 = 0$$

$$+1 + x - 8 = 0.$$

$$x = 8 - 1 = +7$$

iii) S in  $\text{H}_2\text{SO}_4$ 

$$\text{H}_2\text{SO}_4.$$

$$+2 + x + (-8) = 0.$$

$$x = 8 - 2 = +6.$$

v) Calculate the oxidation number of i) Mn in  $\text{MnO}_4^-$ &  $\text{MnO}_4^{2-}$  ion ii) Cr in  $(\text{Cr}_2\text{O}_7)^{2-}$  &  $(\text{CrO}_4)^{2-}$  iii) S in  $\text{S}_2\text{O}_7^{2-}$ i) Mn in  $\text{MnO}_4^-$ Mn in  $\text{MnO}_4^{2-}$ 

$$\text{MnO}_4 = -1$$

$$\text{MnO}_4 = -2$$

$$x + (-8) = -1$$

$$x + (-8) = -2$$

$$x = 8 - 1 = +7.$$

$$x = 8 - 2 = +6.$$

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Find out the formal charge on each O atom in phosphate ion. ( $\text{PO}_4^{3-}$ )

$$\left. \begin{array}{l} \text{Formal charge on each O atom} \\ \text{in } \text{PO}_4^{3-} \text{ ion} \end{array} \right\} = \frac{\text{Total no. of charges on } \text{PO}_4^{3-} \text{ ion}}{\text{Total no. of oxygen atoms in } \text{PO}_4^{3-} \text{ ions.}}$$

$$= -\frac{3}{4} = -0.75$$

Calculate the oxidation state of N in  $\text{NH}_4\text{NO}_3$

Oxidation numbers of two N atoms in  $\text{NH}_4\text{NO}_3$  are different.  $\text{NH}_4\text{NO}_3$  is made of  $\text{NH}_4^+$  &  $\text{NO}_3^-$

In  $\text{NH}_4^+$  ion

$$x + (+4) = +1$$

$$x = +1 - 4 = -3. \quad \therefore \text{O.N of N} = -3$$

In  $\text{NO}_3^-$  ion

$$\text{O.N of N} = +5$$

$$x + (-6) = -1$$

$$x = -1 + 6 = +5$$

$$\text{Average O.N of N atom} = \frac{+5 + (-3)}{2} = +1.$$

What are ionic radii?  $Rb^+$  has ionic radius (152 pm) larger than  $Sr^{2+}$  (118 pm) give reasons.

Neutral atoms that have lost an  $e^-$  exhibit a positive charge and are called cations. Those cations are smaller than their respective atoms, this is because, when an  $e^-$  is lost,  $e^-e^-$  repulsion decreases, and the protons are better able to pull the remaining  $e^-s$  towards the nucleus. A second lost  $e^-$  further reduces the radius of the ion. For instance, the ionic radius of  $Fe^{2+}$  is 76 pm while that of  $Fe^{3+}$  is 65 pm. If creation of an ion involves completely emptying an outer shell, then —

$NaCl$  is ionic whereas  $AlCl_3$  is covalent.

During the formation of an ionic bond when two oppositely charged ions of unequal size closely approach each other, the ion is smaller size attracts outermost  $e^-s$  of the other ion and repels the net result is the distortion or polarization of the larger ion.

This distortion is generally done by the cation as its size is smaller than anion. The  $e^-$  cloud of the anion no longer remains symmetrical but it is elongated towards