

## 2.2. THE SLATER'S RULES

The screening constant is evaluated by the following empirical rules known as the Slater's rules:

- The various orbitals are grouped as follows and written in the order given below, starting from the side of the nucleus :  
 $(1s) (2s\ 2p) (3s\ 3p) (3d) (4s\ 4p) (4d) (4f) (5s\ 5p)$ , etc.
- For an electron in a group of  $s$ ,  $p$  electrons, the value of the screening constant  $S$  is the sum of the following contributions :
  - No contribution from any electron present in groups of orbitals lying on the right side of the group in which the electron (for which  $S$  is to be determined) is present.
  - A contribution of 0.35 from every other electron present in the group of orbitals (say,  $ns$ ) under consideration. A contribution of 0.30 from the other electron in  $1s$  orbital if the electron for which  $S$  is to be calculated belongs to  $1s$  orbital.
  - A contribution of 0.85 per electron from all electrons with quantum number  $n - 1$ , i.e. electrons present in  $(n - 1)$ th shell.
  - A contribution of 1.0 per electron from all electrons present in the  $(n - 2)$ th and the next inner shell.
- For an electron in a group of  $d$  or  $f$  electrons, the rules 2(i) and 2(ii) apply as such. However, the rules 2(iii) and 2(iv) are replaced by the rule that the contribution per electron from all electrons in the inner shells is 1.0.

We shall now apply these rules to calculate the effective nuclear charges for various electronic systems.

**Example 1.** What is the effective nuclear charge felt by  $1s$  electron of helium atom ?

**Solution :** The electronic configuration of helium atom is  $1s^2$

There is one more  $1s$  electron, apart from the electron for which  $Z_{\text{eff}}$  is to be calculated.

$\therefore$  The screening constant,  $S = 1 \times 0.30 = 0.30$

Hence,  $Z_{\text{eff}}$  felt by  $1s$  electron of helium atom =  $2 - 0.30 = 1.70$

**Example 2.** What is the effective nuclear charge felt by a  $2p$  electron of a nitrogen atom ? What will be the effective nuclear charge felt by its  $1s$  electron ?

**Solution :**  $Z_{\text{eff}}$  for  $2p$  electron :

Electronic configuration of N atom is  $1s^2\ 2s^2\ 2p^3$ .

$\therefore$  There are four other electrons in  $(2s\ 2p)$  group.

Screening constant  $S$  for  $2p$  electron =  $4 \times 0.35 + 2 \times 0.85 = 1.40 + 1.70 = 3.10$

$Z_{\text{eff}}$  felt by  $2p$  electron =  $Z_{\text{actual}} - S = 7 - 3.10 = 3.90$

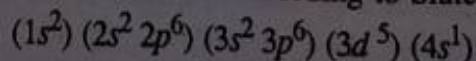
$Z_{\text{eff}}$  for  $1s$  electron :

$Z_{\text{eff}}$  felt by  $1s$  electron =  $Z_{\text{actual}} - S = 7 - 1 \times 0.30 = 6.70$

(There will be no contribution from  $(2s\ 2p)$  electrons in this case as per Slater's rule 2(i))

**Example 3.** Calculate the effective nuclear charge felt by a  $3d$  electron of chromium atom ( $Z = 24$ ).

**Solution :** The grouping of electrons in Cr atom according to Slater's rules is



There will be no contribution from 4s electron.  
 There are four other 3d electrons.

$$Z_{\text{eff}} \text{ felt by the } 3d \text{ electron of Cr atom} = 24 - (0.35 \times 4 + 1.0 \times 18) = 4.60$$

**The Effective Nuclear Charge at the Periphery of an Atom or an Ion.** The effective nuclear charge felt at the periphery of an atom or an ion is calculated by considering the screening of the nuclear charge by *all the electrons* present in the electronic configuration of the atom or the ion. The calculation of the effective nuclear charge at the periphery of an atom or an ion is illustrated below.

**Example 4.** Calculate the effective nuclear charge at the periphery of nitrogen atom ?

**Solution :** Imagine an 'extra electron' in the last filled orbital of nitrogen atom.  
 The screening constant  $S$  for this extra electron =  $5 \times 0.35 + 2 \times 0.85 = 3.45$   
 $Z_{\text{eff}}$  at the periphery of N atom =  $7 - 3.45 = 3.55$

**Example 5.** Calculate the effective nuclear charge at the periphery of chromium atom ?

**Solution :** Imagine an extra electron in the last filled orbital, i.e., the 4s orbital of the Cr atom.  
 The screening constant  $S$  for this extra electron =  $1 \times 0.35 + (8 + 5) \times 0.85 + 10 \times 1.0 = 21.40$   
 $Z_{\text{eff}}$  at the periphery of Cr atom =  $24 - 21.40 = 2.60$

**Example 6.** Calculate  $Z_{\text{eff}}$  for 3d electron, 4s electron and at the periphery of a Cu atom.

**Solution :** Electronic configuration of Cu atom is  $(1s^2)(2s^2 2p^6)(3s^2 3p^6)(3d^{10})(4s^1)$   
 $Z_{\text{eff}}$  felt by 3d electron =  $29 - (9 \times 0.35 + 18 \times 1.0) = 29 - (3.15 + 18) = 7.85$   
 (there is no contribution from 4s electron)  
 $Z_{\text{eff}}$  felt by 4s electron =  $29 - (0.35 \times 0 + 0.85 \times 18 + 1.0 \times 10)$   
 $= 29 - 25.30 = 3.70$   
 $Z_{\text{eff}}$  at the periphery of the atom =  $29 - (0.35 \times 1 + 0.85 \times 18 + 1.0 \times 10)$   
 $= 29 - (0.35 + 15.30 + 10.00) = 3.35$

**Practice Problems**

1. What is the effective nuclear charge felt by 3p electron of a chlorine atom ( $Z = 17$ ) ? [Ans : 6.1]
2. Calculate the effective nuclear charge felt by a 3d electron of cobalt atom ( $Z = 27$ ). [Ans. 6.9]

**2.3. APPLICATIONS OF SLATER'S RULES**

The Slater's rules are also applied to explain the following facts.

1. A 4s orbital is filled earlier than a 3d orbital. Consider a potassium atom ( $Z = 19$ ). In this case, 18 of 19 electrons occupy orbitals as in argon ( $1s^2 2s^2 2p^6 3s^2 3p^6$ ). The 19th electron may enter a 4s or a 3d orbital.

Let us calculate the  $Z_{\text{eff}}$  for the 19th electron when it enters the 4s orbital.  
 $Z_{\text{eff}} = 19 - (0 \times 0.35 + 8 \times 0.85 + 10 \times 1.0) = 19 - (16.80) = 2.20$

$$Z_{\text{eff}} \text{ felt by the 19th electron when it enters the } 3d \text{ orbital} \\ = 19 - (0 \times 0.35 + 18 \times 1.0) = 19 - 18 = 1.00$$

Thus, a 4s electron would be subjected to a greater electrostatic attraction (due to a higher effective nuclear charge of 2.20) than a 3d electron. Consequently, potassium atom with outer electronic configuration  $3s^2 3p^6 4s^1$  would be associated with lower energy than with outer electronic configuration  $3s^2 3p^6 3d^1$ . As a result, the configuration  $3s^2 3p^6 4s^1$  would be more stable than the configuration  $3s^2 3p^6 3d^1$ . Thus, a 4s orbital is filled earlier than a 3d orbital.

**2. The transition metal atoms lose ns electrons first during ionization.** Consider Mn atom with atomic number 25. It has a configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$  (arranged as per Slater's rules).

Let us calculate  $Z_{\text{eff}}$  felt by the 3d as well as the 4s electron.

$$Z_{\text{eff}} \text{ felt by the } 3d \text{ electron} = 25 - (0.35 \times 4 + 1.0 \times 18) = 5.60$$

$$Z_{\text{eff}} \text{ felt by the } 4s \text{ electron} = 25 - (1 \times 0.35 + 13 \times 0.85 + 10 \times 1.0) = 3.60$$

Evidently, the attraction between the 4s electron and the nucleus is less than the attraction between the 3d electron and the nucleus of Mn atom. Hence, the removal of the 4s electron from an isolated gaseous atom of Mn would be easier than the removal of the 3d electron from it.

**3. Trends in successive ionization energies.** The first ionization energy is always lower than the second ionization energy and second ionization energy is always lower than the third ionization energy and so on. This is because the effective nuclear charge goes on increasing with each removal of electron from an atom. (The student may verify this fact by taking a suitable example and calculating the effective nuclear charge for the unipositive, dipositive and tripositive ions).

**4. An anion is always bigger and a cation is always smaller in size than the parent atom.** Consider a chlorine atom with electronic configuration  $1s^2 2s^2 2p^6 3s^2 3p^5$ .

$$Z_{\text{eff}} \text{ felt by the last electron of chlorine atom} = 17 - (6 \times 0.35 + 8 \times 0.85 + 2 \times 1.0) = 6.10$$

$$Z_{\text{eff}} \text{ felt by the last electron of chloride ion} = 17 - (7 \times 0.35 + 8 \times 0.85 + 2 \times 1.0) = 5.75$$

As can be seen,  $Z_{\text{eff}}$  in the case of  $\text{Cl}^-$  ion is less than in the case of Cl atom. Therefore, the electrostatic attraction between the electrons and the nucleus is more in chlorine atom than in chloride ion. As a result, the nucleus would have lesser hold on electrons in the chloride ion than in chlorine atom. Consequently, the size of chloride ion will be larger than the size of chlorine atom.

Now consider a sodium atom with electronic configuration  $1s^2 2s^2 2p^6 3s^1$ .

$$Z_{\text{eff}} \text{ felt by the last electron of Na atom} = 11 - (0 \times 0.35 + 8 \times 0.85 + 2 \times 1.0) = 2.20$$

$$Z_{\text{eff}} \text{ felt by the last electron of Na}^+ \text{ ion} = 11 - (7 \times 0.35 + 2 \times 0.85) = 6.85$$

As can be seen,  $Z_{\text{eff}}$  in the case of Na atom is less than in the case of the  $\text{Na}^+$  ion. Therefore, the hold of the nucleus on the electrons is less in the case of Na atom than in the case of  $\text{Na}^+$  ion. Consequently, Na atom is bigger in size than the  $\text{Na}^+$  ion.

**5. The atomic size within a period goes on decreasing with increase in atomic number.** Consider the elements of the First transition series from Sc to Zn. The  $Z_{\text{eff}}$  goes on increasing with increase in atomic number. Therefore, the hold of the nucleus on the electrons also goes on increasing as we move from Sc to Zn. Hence, the atomic size goes on decreasing with increase in atomic number as we move along the series.

The Slater's rules are also applied for calculating electronegativities of atoms by Allred-Rochow method.