2.6.1 Slater Rules for determining effective nuclear charge

Slater gave a set of empirical rules for calculating the effective nuclear charge (Z_{eff}) experienced by electrons in different orbitals. As stated above, the Z_{eff} acting on a given electron is calculated by subtracting the screening constant (S) from the atomic number Z (nuclear charge).

That is: $Z_{eff} = Z - S$

The 'Slater rules' for calculating screening on shielding constant (S) are as follows:

(1) The electronic configuration of the element is first written in the following order and groupings: (1*s*); (2*s*, 2*p*); (3*s*, 3*p*); (3*d*); (4*s*, 4*p*); (4*d*); (4*f*); (5*s*, 5*p*); (5*d*); (5*f*) and so on.

(2) For an electron considered in a group of *s*, *p* electrons the shielding constant (S) is the sum of the following contributions:

(*a*) No contribution for electrons in groups beyond the one considered.

(*b*) An amount of 0.35 for each electron in the group considered (except in 1*s* group where 0.30 is used instead of 0.35).

(*c*) An amount of 0.85 for each electron in the next inner shell ($n - 1$).

(*d*) An amount of 1.00 for each of all other inner shell electrons.

(3) For an electron considered in *d* or *f* group, rules 2*a* and 2*b* apply as such; however rules 2*c* and 2*d* are replaced with the rule that all other electrons lying to the left of *d* or *f* group contribute 1.00 each.

Example 11. **Calculate Z_{eff} faced by a 3*s* or 3*p* electron in phosphorus atom ($Z = 15$, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$)**

Solution. **Group configuration** = $(1s^2)\ (2s^2, 2p^6)\ (3s^2, 3p^3)$. Four other electrons in the group $(3s^2, 3p^3)$ contribute 4×0.35 and next inner shell contributes 8×0.85 and then the next 2×1.

For a 3*s* or 3*p* electron, $S = (2 \times 1.00) + (8 \times 0.85) + (4 \times 0.35)$

$$S = 2.00 + 6.80 + 1.40 = 10.20$$

$$Z_{eff} = 15 - 10.20 = 4.80$$

Example 12. **Calculate Z_{eff} experienced by a 2*p* electron in oxygen atom Z (8, $1s^2$, $2s^2\ 2p^4$)**

Solution. Group configuration = $(1s^2)$; $(2s^2\ 2p^4)$

There are 5 other electrons in group $(2s^2, 2p^4)$ under consideration which contribute 5×0.35 towards S. Next inner shell contributes 2×0.85. Thus for a 2*p* electron

$$S = (2 \times 0.85) + 5 \times (0.35) = 3.45$$

$$Z_{eff} = (8 - 3.45) = 4.55$$

Example 13. **Calculate Z_{eff} experienced by (*i*) 5*s* electron (*ii*) 4*d* electron in Ag atom (Z = 47, $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$, $4p^6$, $4d^{10}$, $5s^1$).**

Solution. Group configuration = $(1s^2)$, $(2s^2, 2p^6)$; $(3s^2, 3p^6)$; $(3d^{10})\ (4s^2, 4p^6)$, $(4d^{10})\ (5s^1)$

(*i*) **For 5*s* electron,** $S = (28 \times 1.00) + (18 \times 0.85) + (0 \times 0.35)$

$= 43.30$

$$Z_{eff} = 47 - 43.30 = 3.70$$

(*ii*) **For 4*d* electron,** $S = (36 \times 1.00) + (9 \times 0.35) + 0$

$= 39.15$

$$Z_{eff} = 47 - 39.15 = 7.85$$