U.G. SEMESTER-IV

MJC-5 (T) : Inorganic Chemistry (s,p,d,f block elements)

Unit-1 : Periodic table and periodicity of elements
Topic : Slater's Rules (part-1)

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Slaters Rule:

Slater's Rules are a set of empirical rules used in chemistry to estimate the effective nuclear charge (Z_{eff}) for an electron in a multi-electron atom. Understanding Z_{eff} is crucial for comprehending atomic properties like ionization energy, electron affinity, and atomic radius. These rules are particularly helpful for undergraduate students as they provide a systematic way to approximate electron shielding, a concept that can be challenging to grasp intuitively.

Introduction to Effective Nuclear Charge (Z_{eff})

In a hydrogen atom, the electron experiences the full nuclear charge. However, in multi-electron atoms, electrons are simultaneously attracted to the nucleus and repelled by other electrons. This electron-electron repulsion effectively "shields" the outer electrons from the full nuclear charge, leading to a reduced effective nuclear charge. This shielding effect determines how strongly the outer electrons are bound to the nucleus.

The concept of effective nuclear charge can be expressed by the following equation:

$$Z_{eff} = Z - S$$

Where:

- Z_{eff} is the effective nuclear charge.

- Z is the atomic number (the actual nuclear charge).

- S is the shielding constant (also known as the screening constant).

Slater's Rules provide a method to calculate S based on the electron configuration of the atom.

The Origin and Basis of Slater's Rules

John C. Slater developed these rules in 1930. While quantum mechanical calculations provide more accurate values for Z_{eff}, Slater's Rules offer a straightforward, approximate method that is surprisingly effective for many purposes. The rules are based on the idea that electrons in different shells and subshells contribute differently to the shielding experienced by a particular electron.

The rules group electrons into "shells" or "groups" based on their principal quantum number (n) and, to some extent, their azimuthal quantum number (l). The shielding constant is then calculated by summing contributions from all electrons closer to the nucleus or in the same electron group as the electron of interest.

Slater's Rules: Step-by-Step Calculation of S

To apply Slater's Rules, follow these steps:

1. Write the electron configuration of the atom in the following order of groups: $(1s)(2s, 2p)(3s, 3p)(3d)(4s, 4p)(4d)(4f)(5s, 5p)$...Electrons in the same parentheses are considered to be in the same group.

2. Identify the electron for which you want to calculate Z_{eff}. This is often an outermost valence electron, but it can be any electron in the atom.

3. Determine the contributions to the shielding constant (S) from other electrons based on the following rules:

   o Electrons in groups to the right of the target electron's group: These electrons contribute 0 to S. (i.e., electrons further out from the nucleus do not shield the target electron).

   o Electrons in the same group as the target electron ([ns, np] group): Each other electron in the same (ns, np)group contributes 0.35 to S.

      ▪ *Exception:* If the target electron is in the $(1s)$group, the other $(1s)$electron contributes 0.30 to S.

   o Electrons in the $(n-1)$group (the shell immediately inside the target electron's shell):

      ▪ If the target electron is an (ns, np)electron, each electron in the $(n-1)s, (n-1)p, (n-1)d$group contributes 0.85 to S.

      ▪ If the target electron is an (nd)or (nf)electron, each electron in any $(n-1)$group (i.e., all electrons with principal quantum number $n-1$) contributes 1.00 to S.

   o Electrons in groups $(n-2)$and further in (all inner shells):

      ▪ Each electron in these inner shells contributes 1.00 to S.

Detailed Rules for Calculating the Shielding Constant (S)

Let's break down the rules for calculating Smore systematically:

Rule 1: Electron Grouping

First, arrange the electron configuration into "groups" as follows:

$$(1s)(2s, 2p)(3s, 3p)(3d)(4s, 4p)(4d)(4f)(5s, 5p)...$$
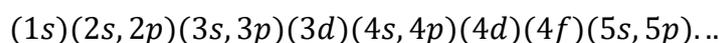
Rule 2: Contribution of Electrons to S

Now, select the electron for which you want to calculate Z_{eff}. Let's call this the "target electron."

- Electrons to the right of the target electron's group: Any electron in a group listed to the right of the target electron's group contributes 0 to the shielding constant (S).

  - *Example:* If your target electron is a $3p$ electron, $4s$ or $4p$ electrons will not contribute to its shielding.

- Electrons in the same group as the target electron:

  - If the target electron is in an (ns, np) group: Each *other* electron in that same (ns, np) group contributes 0.35 to S.

    - *Example:* For a $2p$ electron, if there are two $2s$ electrons and three other $2p$ electrons in the $(2s, 2p)$ group, the contribution from these other electrons would be $(2 \times 0.35) + (3 \times 0.35)$

  - *Special Case for 1s electrons:* If the target electron is a $1s$ electron, the *other* $1s$ electron (if present) contributes 0.30 to S.

- Electrons in the $(n-1)$ group (the next innermost principal shell):

  - If the target electron is an (ns, np) electron: Each electron in the $(n-1)$ shell (i.e., all $(n-1)s$, $(n-1)p$, and $(n-1)d$ electrons, if present) contributes 0.85 to S.

    - *Example:* For a $3s$ electron, the $2s$, $2p$, and $2d$ (if any) electrons would each contribute 0.85.

  - If the target electron is an (nd) or (nf) electron: Each electron in *any* shell with principal quantum number $(n-1)$ (i.e., all electrons in $(n-1)s, (n-1)p, (n-1)d, (n-1)f$ groups) contributes 1.00 to S.

    - *Example:* For a $3d$ electron, all $2s$, $2p$, and $2d$ electrons would each contribute 1.00.

- Electrons in groups $(n-2)$ and further in (all inner shells): Each electron in shells with principal quantum numbers $(n-2)$, $(n-3)$ and so on, contributes 1.00 to S.

  - *Example:* For a $3s$ electron, the $1s$ electrons would each contribute 1.00.

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