U.G.SEMESTER-IV

MJC-5 (T)

Inorganic Chemistry: s-, p-, d- and f- block elements

Unit-I : Periodic Table and Periodicity of Elements

Topic- Effective Nuclear Charge (PART - 1)

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Think of **Effective Nuclear Charge** (Zeff) as the "net" pull an electron actually feels from the nucleus. It's the tug-of-war between the attractive power of the protons and the annoying interference of other electrons.

Here are the essential notes to help you master the concept.

1. The Core Concept

In a multi-electron atom, electrons aren't just attracted to the nucleus; they are also repelled by each other.

- **Nuclear Charge (Z):** The total number of protons in the nucleus.
- **Shielding (Screening) Effect:** Inner-shell electrons act as a "shield," blocking the full positive charge of the nucleus from reaching the outer (valence) electrons.
- **Effective Nuclear Charge (Zeff):** The actual net positive charge experienced by an electron.

The Mechanics of Shielding (The "Wall")

Shielding isn't a perfect barrier; it's a probability game. Electrons are constantly moving, but their average positions determine how much "shade" they provide.

- **Core Electrons vs. Valence Electrons:** Core electrons (the ones in full inner shells) are the primary shielders. They spend most of their time between the nucleus and the outer electrons, effectively neutralizing a portion of the nuclear charge.
- **The "Same-Shell" Effect:** Electrons in the same outer shell do shield each other, but very poorly (roughly 35% effectiveness). This is why Zeff increases so significantly as you move across a period—you are adding protons (full power) but only adding "weak" same-shell shields.

The Fundamental Equation

The relationship is expressed by the formula:

$Zeff = Z - S$

Where:

- Z is the atomic number (number of protons).
- S (or σ) is the shielding constant (the amount of charge blocked by other electrons).

2. Penetration: Why Orbitals Matter

Not all electrons at the same energy level experience the same Zeff. This is due to **penetration**—the ability of an electron to get close to the nucleus.

- **Orbital Shape:** An s-orbital is spherical and "penetrates" closer to the nucleus than a p,d, or f orbital.
- **The Result:** Because s-electrons spend more time near the nucleus, they experience a **higher Zeff** and are harder to remove than p-electrons of the same shell.

Energy Ordering: This is exactly why the 2s subshell fills before the 2p subshell. The 2s electrons "feel" the nucleus better, lowering their energy state.

3. Periodic Trends

Understanding how Zeff changes across the table explains why atoms behave the way they do.

Trend Direction	Change in Zeff	Why?
Across a Period (Left to Right)	**Increases**	Protons are added to the nucleus, but electrons are added to the *same* energy level. Shielding doesn't increase much, so the "pull" grows stronger.
Down a Group (Top to Bottom)	**Stays relatively constant** (or increases slightly)	While the nucleus gets stronger, new electron shells are added. The increased shielding mostly cancels out the extra protons.

4. Calculating Zeff (Slater's Rules)

To get a more precise value for S, chemists use **Slater's Rules**. While you don't always need the math for general chemistry, it's the "gold standard" for calculations:

1. **Group the electrons** by their orbital shells (e.g., [1s][2s,2p][3s,3p][3d][4s,4p]).
2. **Assign Shielding Values:**
   - Electrons in the same group shield by **0.35**.
   - Electrons in the $(n-1)$ shell shield by **0.85**.

    - Electrons in the $(n-2)$ shell or lower shield by **1.00** (total blockage).

Let’s look at a concrete example to see how the "perceived" charge drops. We will calculate the Zeff for a valence electron in **Nitrogen (Z = 7)**.

Electron Configuration: $(1s^2)(2s^2,2p^3)$

1. **Identify the target:** We are looking at one electron in the 2p shell.
2. **Calculate Shielding (S):**
    - The other **4** electrons in the same shell (n=2) each contribute **0.35**. $(4\times0.35=1.40)$
    - The **2** electrons in the inner shell (n=1) each contribute **0.85**. $(2\times0.85=1.70)$
    - **Total S** $= 1.40+1.70=3.10$
3. **Calculate Zeff:**
    - $Z_{eff}=7-3.10=3.90$

The Takeaway: Even though Nitrogen has 7 protons, its outer electrons only "feel" the pull of about 3.9 of them.

5. Periodic Consequences (The "Why")

Understanding Zeff allows you to predict chemical behavior without a textbook:

- **Transition Metal Irregularities:** In transition metals, d-electrons are added to an inner shell $(n-1)$. They are quite effective at shielding the outer s-electrons, which is why the atomic radii of transition metals don't shrink as drastically as main-group elements.
- **Cation vs. Anion Size:**
    - When an atom becomes a **Cation** (loses an electron), shielding decreases, Zeff increases, and the remaining electrons are pulled in tighter (**smaller ion**).
    - When it becomes an **Anion** (gains an electron), shielding increases, Zeff decreases slightly per electron, and the cloud expands (**larger ion**).

Summary Table: Zeff vs. Atomic Properties

Property	Relationship to Zeff	Reason
Atomic Radius	Inverse	Higher Zeff pulls the electron cloud closer to the center.
First Ionization Energy	Direct	Higher Zeff makes it "stickier" and harder to pull an electron away.
Electronegativity	Direct	A stronger "net pull" makes the atom better at hogging shared electrons.

Pro Tip: If you're ever stuck on a periodic table question, ask yourself: *"Is the nucleus getting stronger, or is the shielding getting thicker?"* Usually, Zeff is the answer.