Greenwood & Earnshaw

2nd Edition

Chapter 2

Chemical Periodicity

And the

Periodic Table

Value of the Periodic Chart

- **Early Chemists: Similarities between elements produced general order, facilitated the recognition of electronic structure and properties; pinpointed “missing elements”.**

- **Modern Chemists: Examination of subtle differences in properties & behavior provide insight into new relationships and modes of chemical and electronic interaction. Prediction of chemical behavior of new elements where short half-lives can make trial & error very costly.**

Molar Volume of Elements in the solid state. Lowest in the middle of each period, highest for alkali metals, decreasing in both directions. A result of the interplay between atomic size & elemental bonding type. *Inverse of the densities.*

Alkali metals are large diameter atoms coupled with weak one electron metallic bonding.

Noble gases are small atoms but are atomic.

Halogens are small, bimolecular.

Middle of periods are median sized atoms with extensive 3D covalent or metallic networks.

Questions to Research

- **Why do Eu and Yb represent striking anomalies in molar volumes and element solid-state densities? What electronic and bonding factors create these two clear exceptions to the trends represented by the other lanthanides?**

- **Given that “d” orbitals participate in metallic bonding, suggest a molecular orbital rationale for the density maxima represented by Ni, Ru, and Os. Can Np be considered in this group? Why or why not.**

Ionization Energies: Increase left to right in any period with fluctuations at half-filled and half-filled plus one electron configurations.

Electron affinities: Maxima occur at *filled minus one* shells with sub-maxima at *filled minus one* subshell electron configurations. The rare gases are near zero, *negative values* occur at ns^2 electron configurations. Fluctuations occur at half-filled/half-filled-minus-one subshell electron configurations.

Electronegativity

- **(IE + EA)/2 and scaled to F = 4.0 give values similar to Pauling's Scale and include the *rare gases*.**
- **Values increase left-to-right in any *short period*.**
- **Progressively more important peaks occur at the midpoints between empty and half-filled and between half-filled and filled subshells of the "d-block" elements. Note Au, gold, is more electronegative than At, astatine.**

Chemical Properties

- **Chemical Valence & Oxidation numbers are related to Group number (or positive Group number minus 10 values).**
- **Oxidation State value variations for main group non-metals is commonly eight. For main group metals negative oxidation states are limited by their low electron affinities.**
- **Oxidation State value variations for mid-transition metals can be as great as ten. Mn –3 to +7; Ru –2 to +8.**

Questions to Research

- **Why do fluorides and oxides stabilize the highest oxidation states in both d and p-block metals? The answer goes beyond electronegativity.**
- **What role do ligands play in the stabilization of the very low oxidation stations found in metal anions? Are other factors important?**
- **What factors affect the electronegativity of a given element when it undergoes chemical combination?**