

## Variation of Ionization Energy with Atomic Number

For a many electron atom  $E_{PE} = -\langle Ze^2/r \rangle$

Here the **brackets** represent an average -- we must take an average because the electron does not remain at one fixed value of r .

Earlier, we noted that  $E_{orb} = -Ze^2/2 \langle 1/r \rangle$

These averages are dominated by contributions at **SMALL** r. When r is **SMALL**, (1/r) is **LARGE**; thus, the larger the fraction of its time an electron spends at **SMALL** r, the **MORE NEGATIVE**  $-Ze^2/2 \langle 1/r \rangle$  will be, and the **ELECTRON** will be "BOUND" **MORE TIGHTLY** to the nucleus (i.e  $E_{orb}$  will be more **NEGATIVE**)

### Four factors determine the value of $E_{orb}$

1. **Increasing Nuclear Charge Ze**
  2. **Screening Effects**
  3. **Electron Repulsion Effects**
  4. **Value of  $\langle 1/r \rangle$**
- **The predominant screening of VALENCE ELECTRONS is by INNER SHELL (OR CORE) ELECTRONS i.e. Valence electrons are predominantly screened by ELECTRONS OF LOWER PRINCIPAL QUANTUM NUMBER**
  - **s, p, d, f .... electrons of a given principal quantum number PENETRATE to the nucleus to different extents**  
**ns > np > nd > nf -- thus ns electrons are screened (by inner electrons) LESS than np electrons which are screened LESS than nd electrons etc.**
  - **Electrons of the SAME PRINCIPAL QUANTUM NUMBER screen each other -- this is a SMALLER EFFECT and we will treat it as a secondary effect in our discussions**

#### Observation

$I_1(\text{He}) > I_1(\text{H})$

#### Rationale

Increasing Z modified by electron repulsion

$I_1(\text{Li}) < I_1(\text{He})$

Z **increases** from 2 to 3, but **SCREENING** of 2s electrons by 1s electrons largely offsets this with the result that  $Z_{eff}$  is much closer to 1. In addition, since the 2s electron spends **MOST** of its time

**FURTHER** from the nucleus than does the 1s electron,  
 $\langle 1/r \rangle_{2s} < \langle 1/r \rangle_{1s}$  Both factors serve to make  $I_1(\text{Li})$  **SMALL**

$$I_1(\text{Be}) > I_1(\text{Li})$$

Z increases from 3 to 4; imperfect screening of 2s electrons by the 1s electrons results in  $2 < Z_{\text{eff}} < 4$ . A consideration of electron repulsion effects would **LOWER**  $I_1(\text{Be})$ . Clearly the increase in  $Z_{\text{eff}}$  which accompanies the increase in Z is the dominant factor.

$$I_1(\text{B}) < I_1(\text{Be})$$

**Note: the most loosely bound electron is removed from a 2p orbital.** Since  $Z_{\text{eff}}(2p) < Z_{\text{eff}}(2s)$  -- a 2p electron is screened more effectively by the inner 1s electrons,  $E_{2p} > E_{2s}$ . Thus even though Z increases from 4 to 5, the fact that a 2p electron **PENETRATES LESS STRONGLY (than does a 2s electron) to the NUCLEUS, results in a SMALLER  $I_1$  for B.** Thus screening effects dominate

$$I_1(\text{C}) > I_1(\text{B})$$

The electron configuration of C is  $1s^2 2s^2 2p^2$   
The electron configuration of B is  $1s^2 2s^2 2p^1$ .  
Thus, in both cases the most loosely bound electron is removed from a **SINGLY OCCUPIED 2p orbital -- electron repulsion effects are unimportant.** The explanation lies in the fact that  $Z_{\text{eff}}(2p_{\text{C}}) > Z_{\text{eff}}(2p_{\text{B}})$  because  $Z_{\text{C}} > Z_{\text{B}}$  and electrons are screened to approximately the same extent -- recall screening is **DOMINATED** by the **INNER** electrons

$$I_1(\text{N}) > I_1(\text{C})$$

Similar to the last case

$$I_1(\text{O}) < I_1(\text{N})$$

The electron configuration of O is  $1s^2 2s^2 2p^4$ .  
The electron configuration of N is  $1s^2 2s^2 2p^3$ .  
Since  $Z_{\text{O}} > Z_{\text{N}}$ , and since the 2p electron in O should be shielded by the inner electrons to approximately the same extent as the 2p electron in N, such considerations suggest that  $I_1(\text{O}) > I_1(\text{N})$ . However, the 2p electron in O is removed from a **DOUBLY OCCUPIED ORBITAL, while the 2p electron in N is removed from a SINGLY**

**OCCUPIED ORBITAL.** Electron repulsion effects would suggest  $I_1(\text{O}) < I_1(\text{N})$ . Since the experimental observation is  $I_1(\text{O}) < I_1(\text{N})$ , this indicates that electron repulsion effects are sufficient to offset the effects of increasing  $Z_{\text{eff}}$ .

Clearly there is no way in Chemistry 10 that we could **PREDICT** this result -- rather we will attempt to **rationalize** the trends in Ionization Energies.

The variations in  $I_1$  values as we go across the **FIRST TRANSITION METAL SERIES** are much smaller than those found for elements in the first three rows of the periodic table. Why is this?

### Rationale

The most loosely bound electron is **ALWAYS REMOVED FROM THE 4s ORBITAL**. At first sight, this may seem puzzling. However, recall that the 3d and 4s levels are extremely close in energy, and it turns out that the energy required to produce the ionization:



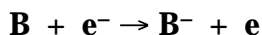
is **LESS** than that required to produce the ionization:



As  $Z$  increases in steps of 1 as we go from Sc to Zn, additional electrons are being placed in 3d orbitals (examine the electron configurations of Sc through Zn). Each additional 3d electron screens, to a very large extent, the 4s electrons from the increased value of  $Z$ . **The overall result is that  $Z_{\text{eff}}(4s)$  changes relatively little as we go from Sc to Zn and the  $I_1$  values show little change across the elements of the first transition metal series.**

### Electron Affinities

**Definition:** EA is the ENERGY LIBERATED when an electron is ATTACHED to a GASEOUS NEUTRAL ATOM, B, to form the GASEOUS ANION  $B^-$



(clearly, it could also be defined as the energy **REQUIRED** to ionize the most loosely bound electron in the GASEOUS ANION to produce a neutral gaseous atom).

The variations of Electron Affinity with  $Z$  can be rationalized in a similar manner to Ionization Energies. The Electron Affinities of the **HALOGENS** are **HIGH**.

The electron configurations for ALL the halogens can be written in the form:



**Observation:** The gross trend in  $e$  values is that they increase as we go across a row of the periodic table.

**Rationale:** As  $Z$  increases in a given row the  $np$  electrons "feel" **an INCREASING VALUE OF  $Z_{\text{eff}}$** . Since they are screened most strongly by electrons of **LOWER PRINCIPAL QUANTUM NUMBER**, an increase in  $Z$  results in a significant increase in  $Z_{\text{eff}}$ . In this case such effects outweigh the effects of electron repulsion. Such ideas also explain the **stability of rare gas configurations**.

In a rare gas, the  $np$  electron is difficult to ionize -- this is because the  $np$  electron in a rare gas "feels" **THE LARGEST  $Z_{\text{eff}}$  of any element in the SAME ROW of the periodic table**.

The electron affinities of the rare gases are **LOW** -- this is because the added electron will go into an orbital of the **NEXT HIGHEST PRINCIPAL QUANTUM NUMBER** -- in a given row of the periodic table, this is **THE MOST WEAKLY BOUND ELECTRON**

The electron affinity **DECREASES** as we go down a **COLUMN** of the periodic table -- here the electron is being placed in an orbital of **HIGHER PRINCIPAL QUANTUM NUMBER**. An electron in a higher principal quantum number orbital is much more likely to be found further from the nucleus and thus **IS LESS TIGHTLY BOUND** ( $\langle 1/r \rangle$  **DECREASES** as  $n$  **INCREASES**)

### Electronegativity (the Mulliken definition)

The electronegativity measures the **RELATIVE** tendency of two atoms that are bonded together to **ATTRACT THE SHARED ELECTRONS IN THE BOND** (this may be somewhat clearer after we have discussed bonding). It is essentially an empirical concept. The electronegativity of atom  $B$ ,  $c_B$ , is defined as follows:

$$c_B = \{I_B + E_{AB}\} / 2$$

The proportionality constant is chosen so that the electronegativity of  $F$ ,  $c_F$ , is 4.00.

Atoms on the left hand side of the periodic table have **SMALL  $c$  VALUES** -- they have **LOW  $I$  AND LOW  $EA$  VALUES**. Such atoms give up an electron **EASILY** and have relatively **LITTLE** tendency to attract an additional one.

Such elements have **METALLIC CHARACTER**, and their chemistry in aqueous solution is that of **POSITIVELY CHARGED IONS**

Example 1. Alkali metal chemistry in solution is the chemistry of  $\text{Na}^+$ ,  $\text{K}^+$ , ...

Why isn't  $\text{Na}^{2+}$  observed frequently? -- the second ionization energy of Na is **MUCH TOO LARGE**.

Example 2. Alkaline earth chemistry in aqueous solution is the chemistry of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , ... Here  $I_1$  is **SMALL** and  $I_2$  is **MODERATE IN SIZE**.

Atoms on the right hand side of the periodic table have **LARGE  $\chi$  VALUES** -- they have **HIGH I and HIGH EA VALUES**. Such atoms give up an electron **WITH GREAT DIFFICULTY** and have a **STRONG TENDENCY to attract an additional one**.

Such elements are **NON-METALLIC** and their chemistry in aqueous solution is that of **NEGATIVELY CHARGED IONS**.

Example: Halogen chemistry in aqueous solution is the chemistry of  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  etc. Why don't we observe  $\text{F}^{2-}$  in aqueous solution?