Readings for today: Section 1.14 – Electronic Structure and the Periodic Table, Section 1.15, 1.16, 1.17, 1.18, and 1.20 - The Periodicity of Atomic Properties. (Same sections in 5th and 4th ed.)

Read for Lecture #9: Sections 2.1-2.3 – Ionic Bonds, Sections 2.14-2.16 - Covalent Bonds, Section 2.5-2.6 – Lewis Structures (Same sections in 5th and 4th ed.)

Topics:

I. The Periodic table / Periodic trends
   A. Ionization energy (IE) and Photoelectron spectroscopy
   B. Electron affinity (EA)

I. THE PERIODIC TABLE / PERIODIC TRENDS

1869 Dmitri Mendeleev (Russian, 1834-1907) introduced a periodic table based on reoccurring physical properties and chemical properties of the elements. Some examples of grouping by properties:

- Li, Na, and K were originally grouped together in a column because they are all soft, malleable, reactive metals.
- He, Ne, and Ar were grouped together because of their inertness.

Elements that are in the same column have related valence electron configurations:

- Li, Na, and K have _________ valence e⁻ in an s-state.
- He, Ne, and Ar have ______________ shells.

But column number does not determine all chemical/biological properties.

A. IONIZATION ENERGY (IE)

IE is the minimum energy required to remove an electron from an atom. IE refers to the first IE unless otherwise specified.

\[ \text{IE} = \text{binding energy} \] of the most weakly bound electron.

Ionization energy definitions:

\[ B(1s^22s^22p^1) \quad \text{---} \quad B^+ (1s^22s^2) + e^- \quad \Delta E = \text{IE} = -E_{2p} \]

IE = first IE: energy to remove an e⁻ from the HOAO (highest occupied atomic orbital).

\[ B^+ (1s^22s^2) \quad \text{---} \quad \text{---} + e^- \quad \Delta E = \text{IE}_2 = -E_{2s} \text{ for } B^+ \]

IE₂ = second ionization energy. IE₂ is always higher than the first IE.

\[ B^{+2} (1s^22s^1) \quad \text{---} \quad \text{---} + e^- \quad \Delta E = \text{IE}_3 = -E_{2s} \text{ for } B^{+2} \]

IE₃ = third ionization energy.
Figure to the right shows that successive ionization energies of a few different elements. Note the great increase in the energy required to remove an electron from an inner shell.

Consider the energy required to remove electrons from the 2s orbital from B⁺ versus B:

\[
\begin{align*}
B(1s^22s) & \rightarrow \ B^-(1s^22s^-) + e^- \quad \Delta E = \text{IE}_1 = \underline{\quad} \\
B(1s^22s^22p) & \rightarrow \ B^+(1s^22s^-2p^-) + e^- \quad \Delta E = \text{IE}_2 = \underline{\quad}
\end{align*}
\]

Are these two \(\Delta E\)'s equal? \underline{\quad}

A 2s-electron in the B⁺ ion has less shielding. The B⁺ ion therefore feels a \underline{\quad} \text{Z}_{\text{eff}} and requires \underline{\quad} energy to be pulled away from the nucleus.

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**Periodic trends in ionization energy:**

Across a row, IE \underline{\quad}. Z increases, but \(n\) (the shell) stays constant. The outermost e⁻ is bound more tightly to the nucleus and requires more \(E\) to be ejected.

Down a column, IE \underline{\quad}. Although Z increases as you go down a column, so does \(n\). Shells are well-separated in space, so electrons in larger \(n\) are farther away from the nucleus. A large distance from the nucleus dominates over the increased Z, making electrons less strongly bound and therefore decreasing IE.

Some “glitches” in the trend occur due to subshell structure: for example, \(\text{IE}_{2s} \underline{\quad} \text{IE}_n\)

\[
\begin{align*}
\text{IE}_{2s} & \quad \text{IE}_n \\
\text{IE}_{1s} & \quad \text{IE}_n
\end{align*}
\]
The BE gained by increased Z in B doesn’t compensate for extra energy required to reach p state, so IE of B lower than for Be.

**PHOTOELECTRON SPECTROSCOPY (PES) IS USED TO DETERMINE IE VALUES!** Similar concept to photoelectric effect!

Consider that a 1e is removed from each subshell:

$$\text{E}_i = \text{IE} + \text{K.E.}$$

If $E_i = 1254$ eV, then:

- **Ne 2p:** $\text{IE}_n = \text{______ eV}$ $\text{K.E.}_n = 1232$ eV
- **Ne 2s:** $\text{IE}_s = \text{______ eV}$ $\text{K.E.}_s = 1206$ eV
- **Ne 1s:** $\text{IE}_1 = \text{______ eV}$ $\text{K.E.}_1 = 384$ eV

Each line on the spectrum corresponds to a different initial orbital energy from which electrons were ejected.

Orbital E in multi-electron atoms depends on two quantum numbers, and .

**PES Example:** If a certain element being studied by X-ray photoelectron spectroscopy displays an emission spectrum with 5 distinct kinetic energies. Assuming each distinct K.E. is due to a different subshell, what are all of the possible elements that could produce this spectrum?

- First, determine the orbitals that the spectral lines are originating from , , , , and .
• The elements that have electrons in (only) these orbitals are


B. ELECTRON AFFINITY (EA or E.)
The ability of an atom (or ion) to gain electrons: \[ \text{Cl} + e^- \rightarrow \text{Cl}^- \] \[ \Delta E = -349 \text{ kJ/mol} \]

energy is released --- ion is ________ stable than atom

Electron affinity, EA, is defined as \[ \text{EA} = -\Delta E \]

So, EA for Cl is \[ \text{EA} = \underline{\phantom{100}} \text{ kJ/mol} \]

Unlike IE (which is always positive), EA can be positive or negative.

\[ \text{N} + e^- \rightarrow \text{N}^- \] \[ \Delta E = 7 \text{ kJ/mol} \]

So EA = -7 kJ/mole for N --- the -1 ion is ________ stable than atom

General trends in EA:

Noble gases (group VIII) have _____________ EA because addition of an electron would require the occupation of a new shell.

Halogens (group VII) have the largest EA's because the extra e^- fills a “hole” in the p-subshell to give a complete shell.