5.111 Principles of Chemical Science
Fall 2008

5.111 Lecture Summary #9

Readings for today: Section 1.14 (1.13 in *3rd ed*) – Electronic Structure and the Periodic Table, Section 1.15, 1.16, 1.17, 1.18, and 1.20 (1.14, 1.15, 1.16, 1.17, and 1.19 in 3rd ed) - The Periodicity of Atomic Properties.
Read for Lecture #10: Sections 2.14-2.16 (2.15-2.17 in *3rd ed*) - The Strengths and Lengths of Covalent Bonds, Section 2.5 (*2.6 in 3rd ed*) – Lewis Structures, Sections 2.6 (2.7 in *3rd ed*) – Lewis Structures for Polyatomic Species.

Exam 1: Complete exam information will be provided in Lecture 10.

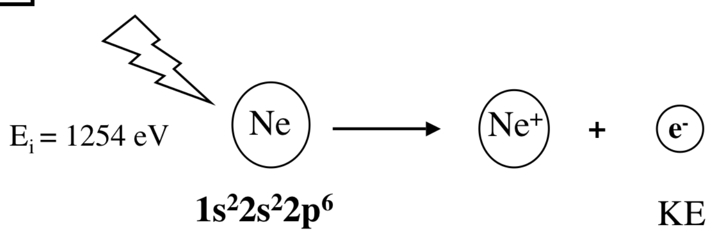
Topics: **I.** Photoelectron spectroscopy
II. The periodic table / periodic trends
- **A.** Ionization energy (IE)
- **B.** Electron affinity (EA)
- **C.** Electronegativity
- **D.** Atomic radius

III. Isoelectronic atoms and ions

I. PHOTOELECTRON SPECTROSCOPY (PES)

PES can determine orbital energies directly. (Similar concept to photoelectric effect!)

$E_i = IE + KE$ IE = _____ - _____   (Recall for the photoelectric effect: $E_i = \phi + KE$)



IE_{2p} = ________eV   KE = 1232 eV

IE_{2s} = ________eV   KE = 1206 eV

IE_{1s} = ________eV   KE = 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 depend 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. 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 ____.

II. 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. He left space for missing elements (1/3 naturally occurring elements were unknown!) 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.

PERIODIC TRENDS

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.

IE = ________ (binding energy) of the most weakly bound electron.

Ionization energy definitions:

$B(1s^2 2s^2 2p^1) \longrightarrow B^+(1s^2 2s^2) + e^-$ $\quad \Delta E = E_{prod} - E_{react} = \mathbf{IE} = -E_{2p}$

IE ≡ first IE: energy to remove an e^- from the HOAO (highest occupied atomic orbital).

$B^{+}(1s^2 2s^2)$ $\longrightarrow$ ____________ $+ e^-$ $\Delta E = \mathbf{IE_2} = -E_{2s}$ for B^+

$IE_2 \equiv$ second ionization energy. IE_2 is always higher than the first IE.

$B^{+2}(1s^2 2s^1)$ $\longrightarrow$ ____________ $+ e^-$ $\Delta E = \mathbf{IE_3} = -E_{2s}$ for B^{+2}

$IE_3 \equiv$ third ionization energy

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

$B^{+}(1s^2 2s^2)$ $\longrightarrow$ $B^{+2}(1s^2 2s^1) + e^-$ $\Delta E = IE_2 =$ ____________

$B(1s^2 2s^2 2p^1)$ $\longrightarrow$ $B^{+}(1s^2 2s^1 2p^1) + e^-$ $\Delta E = IE_{2s} =$ ____________

Are these two ΔE's equal? ________

A 2s-electron in the B^+ ion has less shielding.

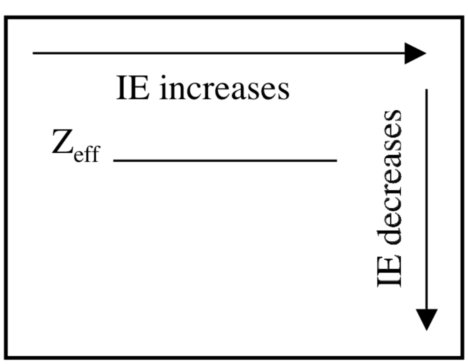
- It therefore feels a ______________ Z_{eff} and
- requires ____________ energy to be pulled away from the nucleus.

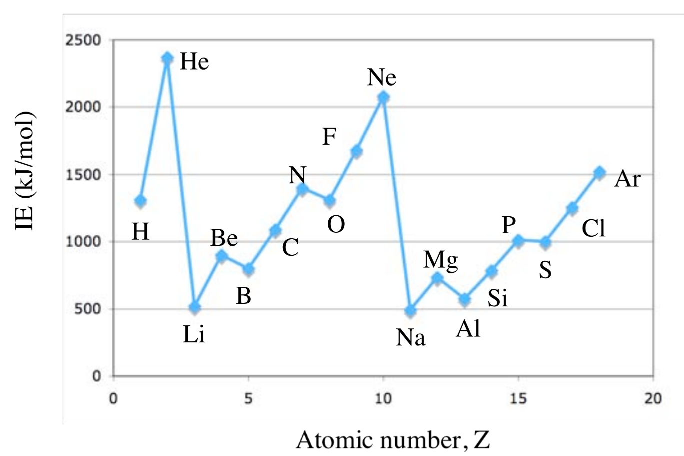
Periodic trends in ionization energy:

Across a row, IE ______________. 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 ______________. 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 awa from the nucleus. A large distance from the nucleus dominates over the increased Z, making electrons less strongly bound and therefore decreasing IE.

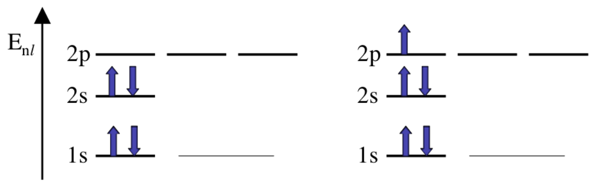
General trends

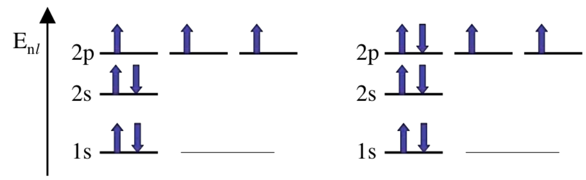




Some "glitches" in the trend occur due to subshell structure:

for example, $IE_B < IE_{Be}$ $IE_O < IE_N$





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.

The BE gained by increased Z in O doesn't compensate for repulsion between $2e^-$s in same state.

B. ELECTRON AFFINITY (EA or E_{ea})

The ability of an atom (or ion) to gain electrons: ______ **+ e^- ⇒** ______

$$Cl + e^- \longrightarrow Cl^- \qquad \Delta E = -349 \text{ kJ/mol}$$

energy is released --- ion is __________stable than atom

Electron affinity, EA, is defined as $\boxed{EA = -\Delta E}$

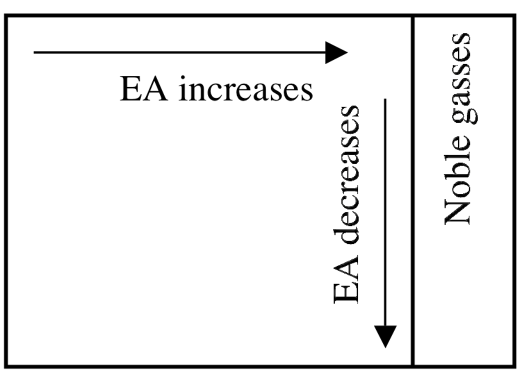
So, EA for Cl is EA = __________ kJ/mol

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

$$N + e^- \longrightarrow N^- \qquad \Delta E = 7 \text{ kJ/mol}$$

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 occupying 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.

C. ELECTRONEGATIVITY (χ)

Electronegativity is the net ability of an atom to attract an electron from another atom. Linus Pauling first proposed this idea in 1932. His electronegativity scales are in general use today.

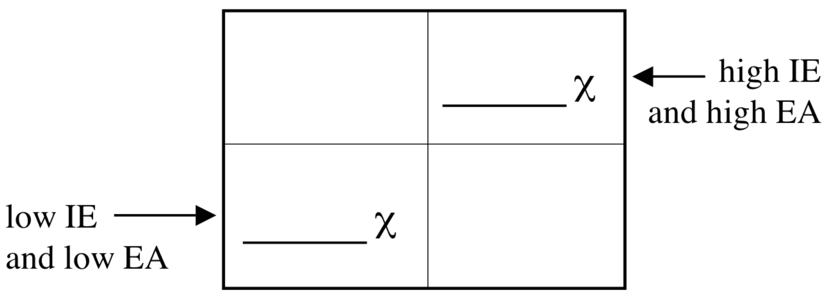
Mulliken's electronegativity scale developed 2 years later is conceptually easier.

electronegativity (χ) $\propto$ ______ (______ + ______)

An atom with high electronegativity is an electron ________________ .

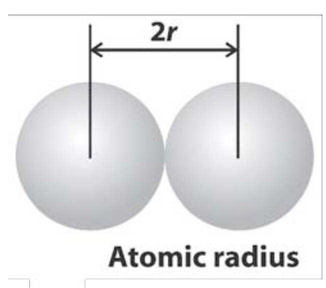
An atom with low electronegativity is an electron _________________ .

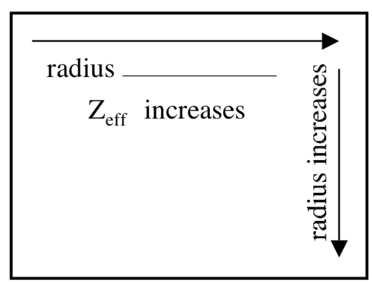
General trends for electronegativity:



D. ATOMIC RADIUS

The atomic size is defined as the value of r below which 90% of electron density is contained. This is the atomic radius.





The role of atomic radius in ion channel selectivity :

Ion channels

* regulate the influx of ions into cells.
* enable rapid electric signaling in neurons.

Regulation and selectivity are essential.

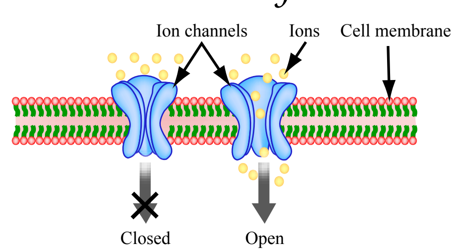


Figure by MIT OpenCourseWare.

Sodium ion channels are selective for Na^+ in the presence of other ions, including K^+. Sodium channels include a tiny pore (~0.4 nm wide) that is *just* wide enough to accommodate a sodium ion and associated water molecule. Too small for potassium!

III. ISOELECTRONIC - having same electron configuration

For example, all **$1s^2$ $2s^2$ $2p^6$** ions are isoelectronic with Ne.

_____, _____, _____, Ne, _____, _____, _____, _____

larger radius than neutral parent

smaller radius than neutral parent