Chemistry 1000 Lecture 9: Periodic trends

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A qualitatively correct result of the Bohr theory

- Some results of the Bohr theory are qualitatively correct, even for multi-electron atoms, but need to be reinterpreted.

- Recall, from Bohr theory, $r_n \propto n^2/Z$.

- We call a set of orbitals with the same n a shell.

- Orbitals in a shell are similar in size, proportional to n^2/Z_{eff} where Z_{eff} is an effective nuclear charge.

- The electron distribution of a closed shell (one in which all the orbital are filled) is spherical.
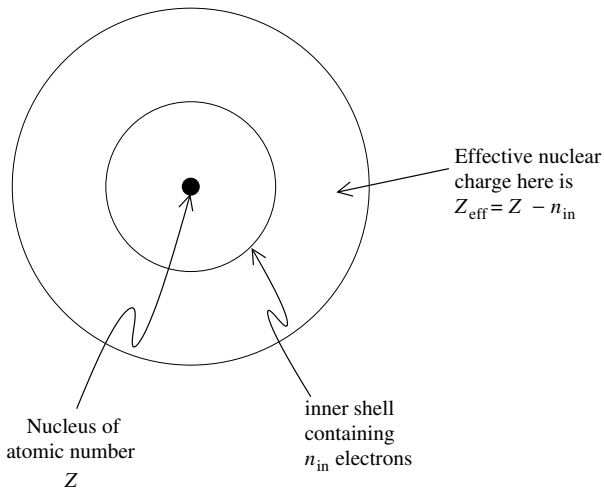
Effective nuclear charge

Theorem: The force on a test charge due to a spherical charge distribution is

- zero if the charge is inside the distribution, and
- equal to the force due to a single charge equal to the total charge of the distribution placed at the centre of the sphere if the test charge is outside the sphere.

What this means to us: An electron in a valence orbital feels a force toward the nucleus that is reduced by the repulsive force of the closed inner shells.
On the other hand, the valence orbitals have little effect on the inner shells.

Effective nuclear charge

Effective nuclear charge here is $Z_{\text{eff}} = Z - n_{\text{in}}$

inner shell containing n_{in} electrons

Nucleus of atomic number Z

Effective nuclear charge
Example

The effective nuclear charges experienced by the valence electrons in the second row of the periodic table are *roughly* as follows:

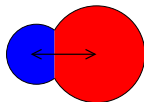| Element	Li	Be	B	C	N	O	F	Ne
Z	3	4	5	6	7	8	9	10
Z_{eff}	1	2	3	4	5	6	7	8

Atomic size

Orbitals don't have a sharp cut-off.

They are "spongy".

So how can we define an atomic size?

Covalent radius: From compounds with single covalent bonds, whether
network solids (e.g. diamond) or molecular compounds
(e.g. F_2)

For elements, the radius is half the distance between the
nuclei.

For compounds, the distance between the nuclei is the sum
of the radii.

Atomic size

Metallic radius: Same idea as the covalent radius, but in a metal.
What's the difference, then?
In a covalent compounds, some of the valence electrons are shared between two atoms.
In a metallic compound, the valence electrons are shared throughout the metal.

van der Waals radius: Mostly for noble gases, based on shortest distance between atoms in a solid crystal in which the atoms are not bonded to each other.

Important note: These radii are not strictly comparable to each other, so we should always *try* to compare measurements of the same kind.

Atomic size

- Atomic size increases as we move down a group because we are adding shells and $r \propto n^2/Z_{\text{eff}}$.

- In a period, for the main-group elements, Z_{eff} increases as we move from left to right, so atomic size decreases.

- In the transition metals, electrons are being added to an inner shell at the same rate as Z increases, so Z_{eff} for the outer-shell electrons is roughly constant. Atomic size is therefore roughly constant across the transition-metal part of a period (with some exceptions).
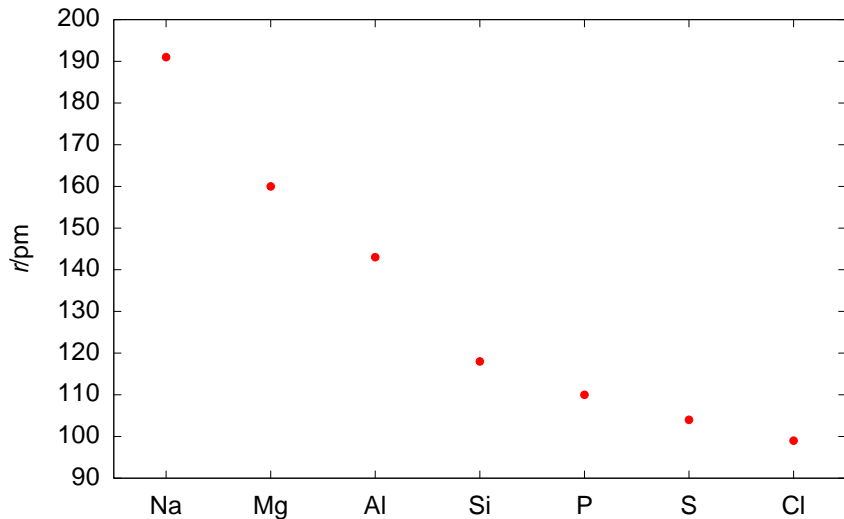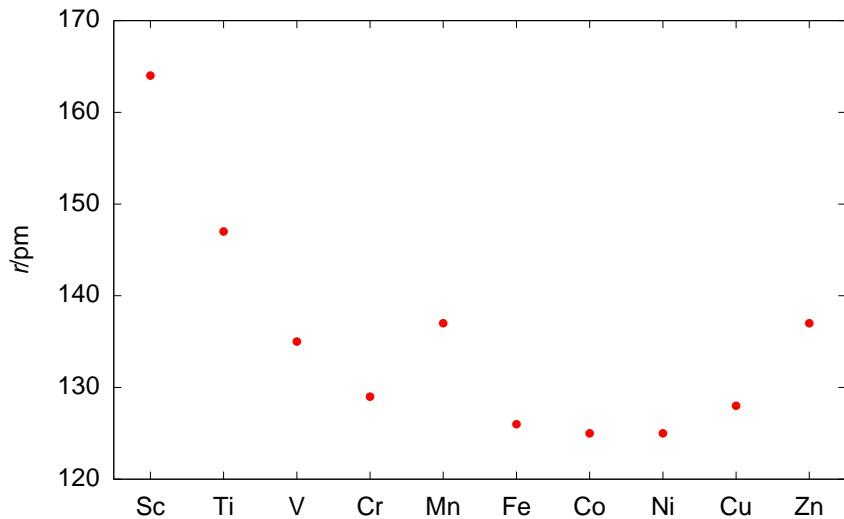
Atomic size

Trend down a group
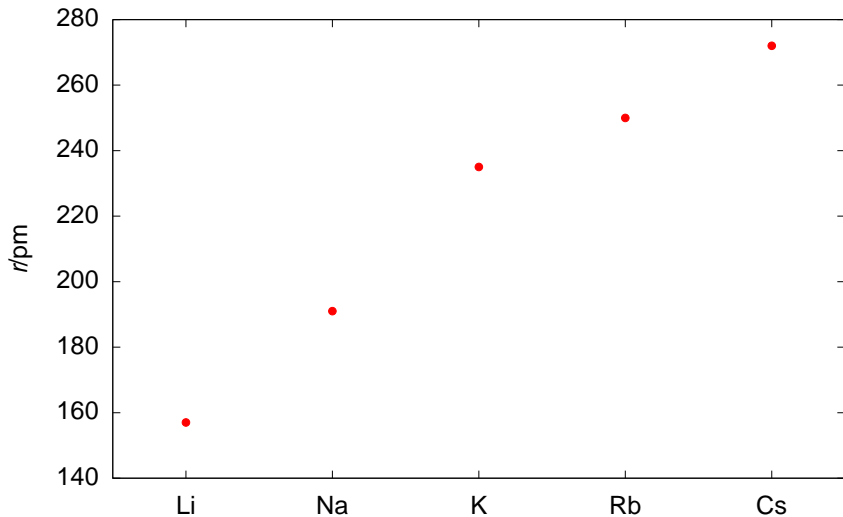
Atomic size

Trend across a period

Atomic size

Trend in a transition series

Ionic radius

- Measured analogously to covalent radius, but using crystals of an ionic compound.

- Bootstrapping problem: You need one radius in order to be able to assign the rest.
  Convention: $r(O^{2-}) = 1.40\,\text{Å}$

- Generally, similar trends observed as for atomic radii.

- Removing electrons (esp. if a shell is emptied) results in cations being smaller than the neutral atoms from which they are formed.

- The smallest ion in an isoelectronic series has the highest Z.

Ionic radius

Example: Put the following ions in order of increasing size: O^{2-}, F^-, Na^+, Mg^{2+}
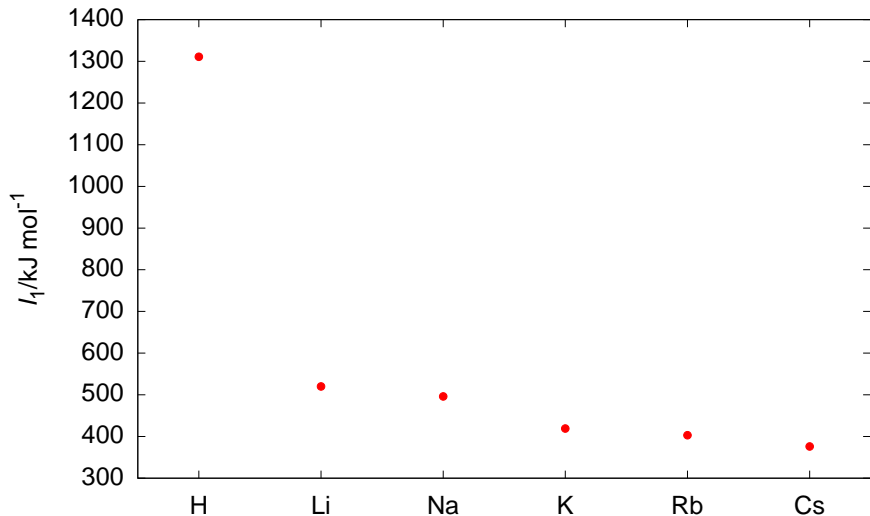
Ionization energy

- Ionization energy = 1st ionization energy = I_1

- Ionization energy decreases as we go down a group because the outer electrons are farther from the nucleus and thus more loosely held.

- As an overall trend, ionization energy increases as we move from left to right across a period because the effective nuclear charge increases and the size of the atom decreases, both of which increase the electrostatic force between the valence electrons and the nucleus.

- We must also consider electronic configuration.
  - Going from an ns^2 to an $ns^2 np^1$ configuration, the ionization energy decreases in the first few periods because the p orbital is higher in energy than the s.
  - Going from an $ns^2 np^3$ to an $ns^2 np^4$ configuration, the ionization energy decreases because pairing electrons in an orbital increases electron-electron repulsion, thus making it easier to remove one.

- Similar trends are observed in I_2, adjusted for the electronic configurations of the singly ionized atoms.
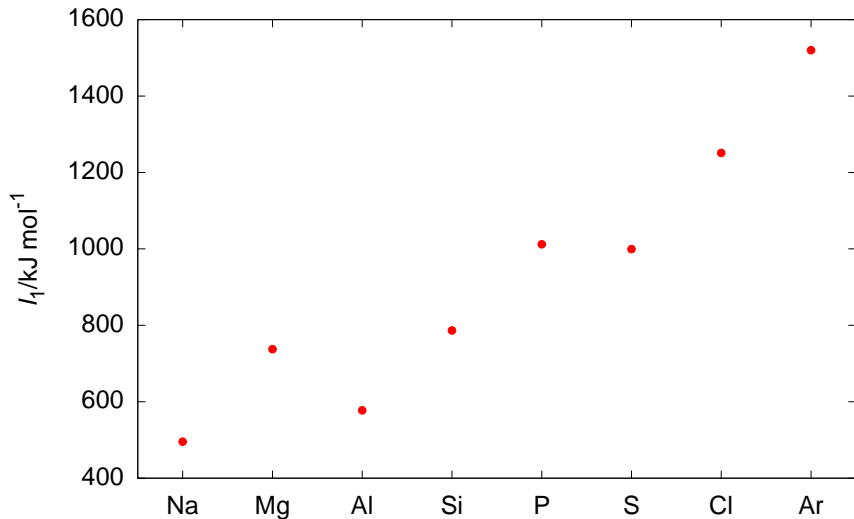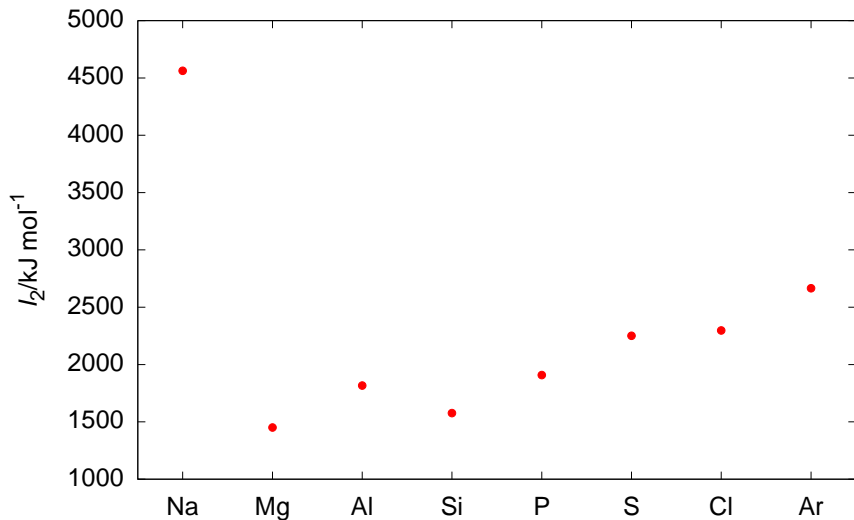
Ionization energy

Trend down a group

Ionization energy

Trend across a period for the 1st IE

Ionization energy

Trend across a period for the 2nd IE
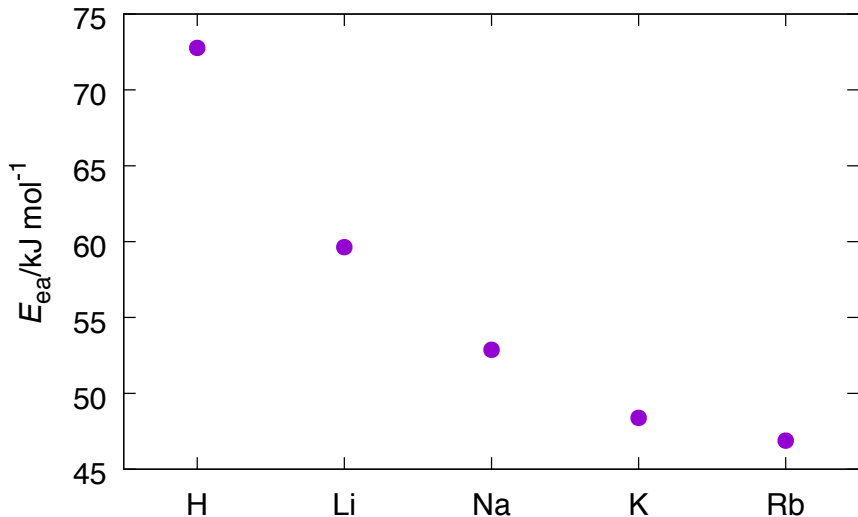
Electron affinity

- E_{ea} is the negative of the enthalpy change for the process $A + e^- \rightarrow A^-$ in the gas phase.

- ΔH for adding an electron to an atom is usually negative, so E_{ea} is positive.
  A larger value of E_{ea} means a stronger attraction for electrons.

- Some elements have essentially no ability to accept an additional electron.
  Examples: Be, Mg, N, noble gases. Why?

Electron affinity (continued)

- E_{ea} tends to become larger as we go from left to right in a period because of increasing effective nuclear charge and decreasing atomic radius.

- Exceptions to the previous observation can generally be rationalized in terms of the electron configurations of the atom and anion.

- E_{ea} *tends* to become smaller as we move down a group because of increasing atomic radius, but there are *many* exceptions.
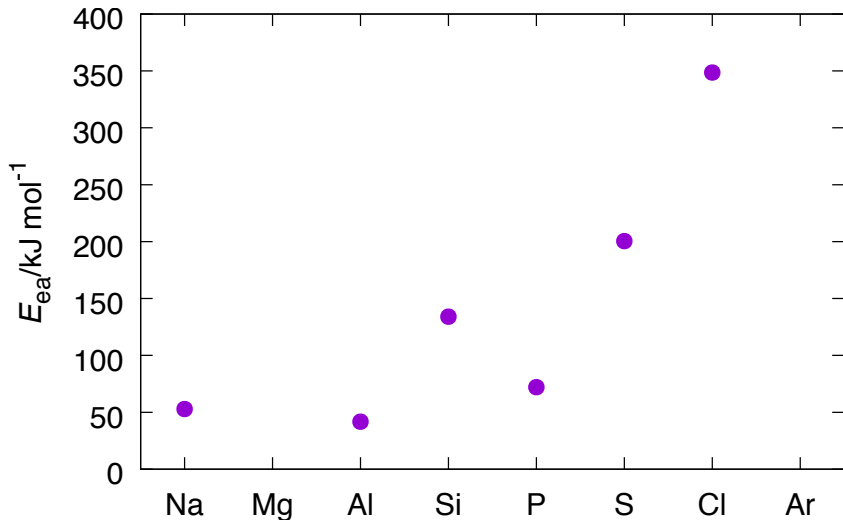
Electron affinity

Trend down a group

Electron affinity

Trend across a period
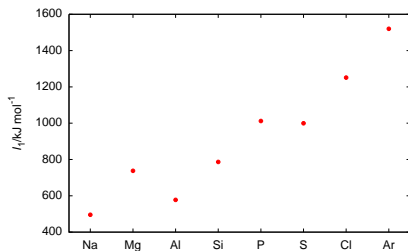
Is a full octet especially "stable"?

- Many people (including many chemists who should know better) will say that an octet electron configuration is especially stable.
  The first problem with this is that it's not clear what they mean by "stable".
- One might think this means that an octet is especially difficult to ionize.

Is a full octet especially "stable"?
(continued)

Counterexamples:

- If this were so, then the 1st ionization energy of a noble gas should be especially large. These are relatively large, but fully on-trend, so not "especially" large. The non-metallic p-block elements all tend to have large ionization energies.

Is a full octet especially "stable"?
(continued)

Counterexamples:

- Similarly, an electron from a species with a complete outer octet should be hard to remove. However, the electron affinity of fluorine, for example, which is the same as the ionization energy of the fluoride ion, is only $328\,\mathrm{kJ\,mol^{-1}}$, which isn't especially large.

So there's nothing special, per se, about an octet. Removing an electron (e.g.) always requires an electron acceptor. The question then becomes whether a sufficiently good electron acceptor can be found. Stability is not a matter that can be discussed without a physico-chemical context.
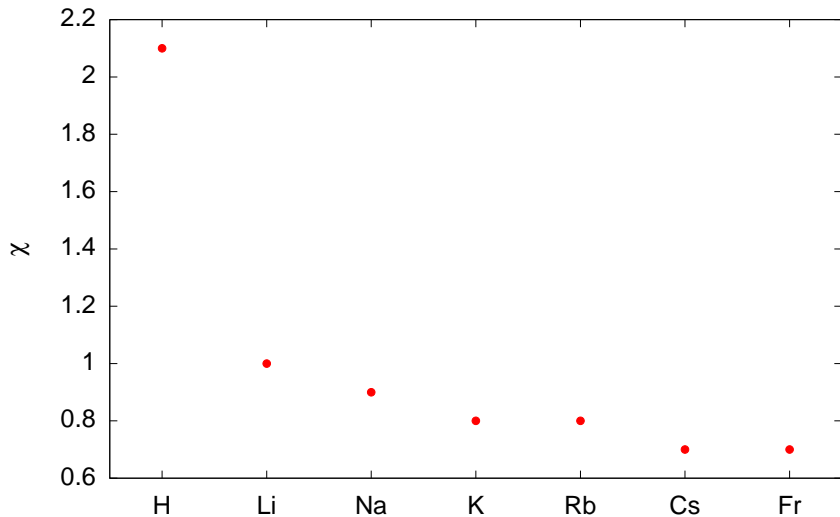
Electronegativity

- Usual symbol: χ

- An empirical measure of the tendency of an atom to attract electrons
  There are in fact several electronegativity scales.

- The Mulliken electronegativity scale is linearly related to $I + E_{ea}$.

  The more commonly used Pauling scale is based on bond dissociation energies, but correlates very well with the Mulliken scale.

- Electronegativity decreases as we go down a group.

- Electronegativity increases as we go from left to right across a period.

Electronegativity

Trend down a group for χ

Electronegativity

Trend across a period for χ