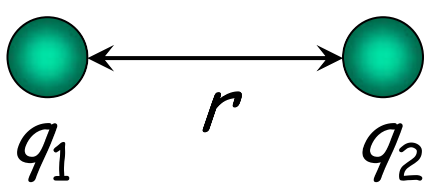
Shielding effect

- Effective nuclear charge, Z_{eff}, experienced by an electron is less than the actual nuclear charge, Z
- Electrons in the outermost shell are repelled (shielded) by electrons in the inner shells. This repulsion counteracts the attraction caused by the positive nuclear charge

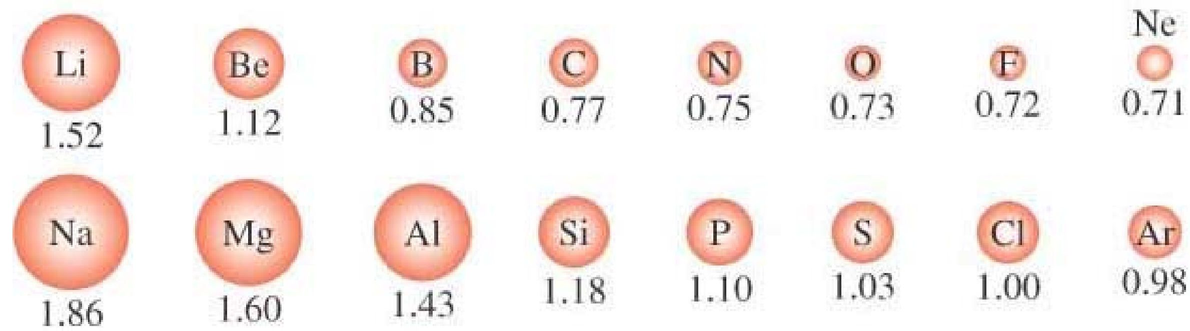
- Coulomb's Law:



$$F \propto -\frac{q_1 \cdot q_2}{r^2}$$

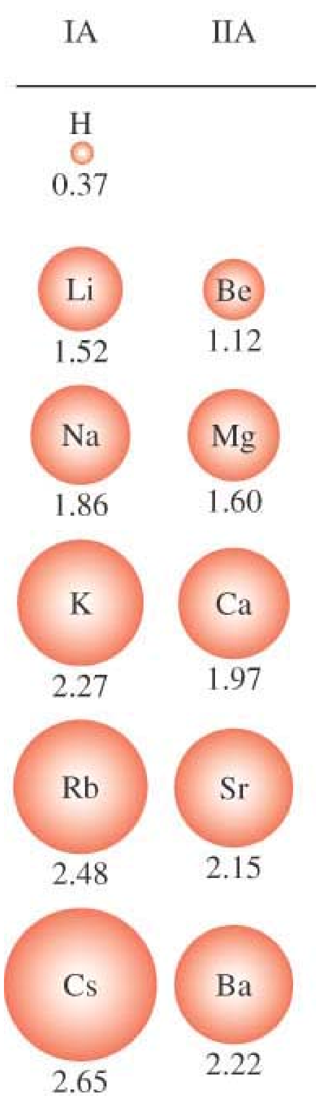
Atomic Radii: Periodicity

$$F \propto -\frac{q_1 \cdot q_2}{r^2}$$

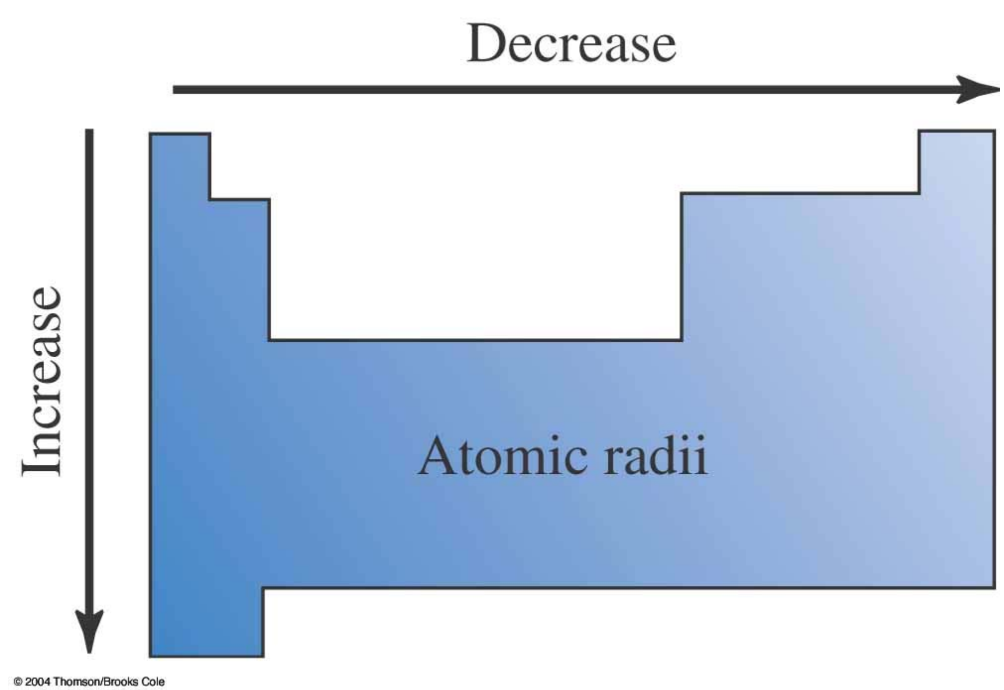


- As we move from left to right along the period, the effective nuclear charge "felt" by the outermost electron increases while the distance from the nucleus doesn't change that much (electrons are filling the same shell)
- Outermost electrons are attracted stronger by the nucleus, and the atomic radius decreases

Atomic Radii: Periodicity



- As we move down the group, the principal quantum number increases and the outermost electrons appear farther away from the nucleus – the atomic radius increases



Ionization Energy

- If sufficient energy is provided, the attraction between the outer electron and the nucleus can be overcome and the electron will be removed from the atom

- First ionization energy (IE_1)
  - The minimum amount of energy required to remove the most loosely bound electron from an isolated gaseous atom to form a 1+ ion

$$Na(g) + 496 \text{ kJ/mol} \longrightarrow Na^+(g) + e^-$$

Ionization Energy

- Second ionization energy (IE_2)
  - The minimum amount of energy required to remove the 2nd electron from a gaseous 1+ ion

IE_1: $Ca(g) + 590\ kJ/mol \longrightarrow Ca^+(g) + e^-$

IE_2: $Ca^+(g) + 1145\ kJ/mol \longrightarrow Ca^{2+}(g) + e^-$

  - The 2nd electron “feels” higher nuclear charge (stronger attractive force) since the electron-electron repulsion has been decreased: $IE_2 > IE_1$

Ionization Energy: Trends

- Coulomb's Law: $F \propto -\frac{q_1 \cdot q_2}{r^2}$

- IE_1 increases from left to right along a period since the effective nuclear charge (Z_{eff}) "felt" by the outermost electrons increases
- There are some exceptions to this general trend caused by additional stability of filled and half-filled subshells (orbitals with the same ℓ)
- IE_1 decreases as we go down a group since the outermost electrons are farther from the nucleus

Example

- Arrange these elements based on their first ionization energies
  - Sr, Be, Ca, Mg

Successive Ionization Energies

Group and element	IA Na $[Ne]3s^1$	IIA Mg $[Ne]3s^2$	IIIA Al $[Ne]3s^2 3p^1$
IE_1 (kJ/mol)	496 Na^+	738 Mg^+	578 Al^+
IE_2 (kJ/mol)	4,562 Na^{2+}	1,451 Mg^{2+}	1,817 Al^{2+}
IE_3 (kJ/mol)	6,912 Na^{3+}	7,733 Mg^{3+}	2,745 Al^{3+}
IE_4 (kJ/mol)	9,540 Na^{4+}	10,550 Mg^{4+}	11,580 Al^{4+}

Ionization Energy: Periodicity

- Important conclusions
  - Atoms of noble gases have completely filled outer shell, the smallest radii among the elements in the same period, and the highest ionization energies
  - Atoms of metals, especially those to the left in the periodic chart, ionize easily forming cations and attaining the electron configuration of noble gases
  - Atoms of nonmetals, especially those to the right in the periodic chart, are very unlikely to loose electrons easily – their ionization energies are high

Halogens & Noble Gases

H	$1s^1$	He	$1s^2$
F	$[He]2s^22p^5$	Ne	$[He]2s^22p^6$
Cl	$[Ne]3s^23p^5$	Ar	$[Ne]3s^23p^6$
Br	$[Ar]3d^{10}4s^24p^5$	Kr	$[Ar]3d^{10}4s^24p^6$
I	$[Kr]4d^{10}5s^25p^5$	Xe	$[Kr]4d^{10}5s^25p^6$
At	$[Xe]4f^{14}5d^{10}6s^26p^5$	Rn	$[Xe]4f^{14}5d^{10}6s^26p^6$

Electron Affinity

- For most nonmetals, it is much easier to achieve the stable electron configuration of a noble gas by gaining rather than loosing electrons
- Therefore, nonmetals tend to form anions
- Electron affinity is a measure of an atom's ability to form negative ions
- The amount of energy absorbed when an electron is added to an isolated gaseous atom to form an ion with a 1- charge

$$Cl(g) + e^- \longrightarrow Cl^-(g) + 349\ kJ/mol$$

Electron Affinity

- Sign conventions for electron affinity
  - If electron affinity > 0 energy is absorbed
  - If electron affinity < 0 energy is released

- Compare cation- and anion-forming processes:

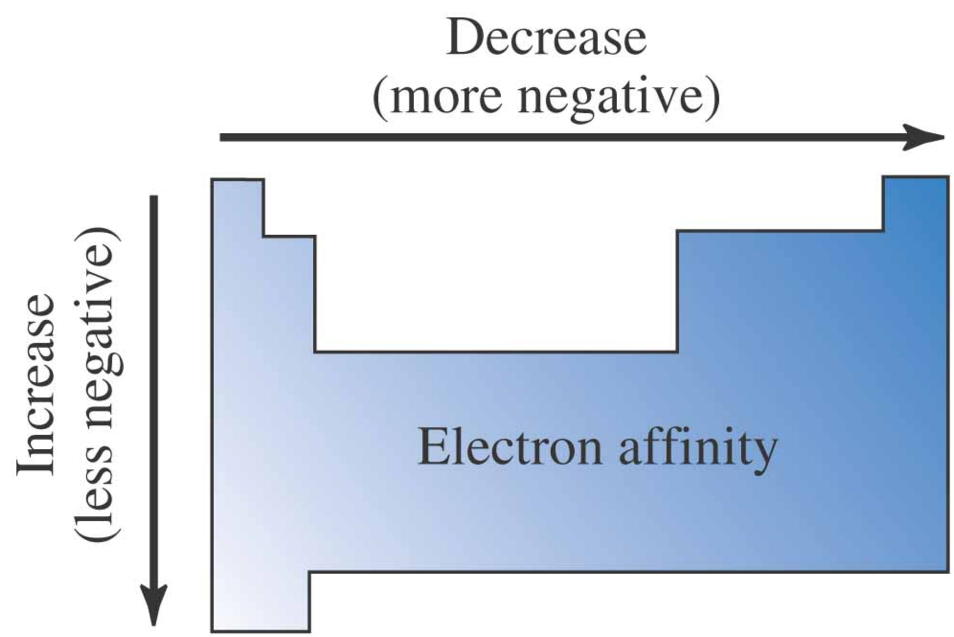
IE_1: $Na(g) + 496\ kJ/mol \longrightarrow Na^+(g) + e^-$

EA: $Cl(g) + e^- \longrightarrow Cl^-(g) + 349\ kJ/mol$

or $Cl(g) + e^- - 349\ kJ/mol \longrightarrow Cl^-(g)$

Electron Affinity: Trends

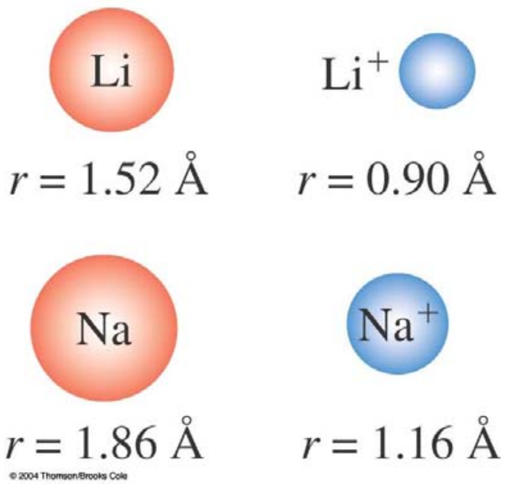
- EA becomes more negative on going from left to right along a period
- There are some exceptions to this general trend caused by additional stability of filled and half-filled subshells (orbitals with the same ℓ)
- EA becomes less negative as we go down a group because the attraction of the outermost electrons to the nucleus weakens

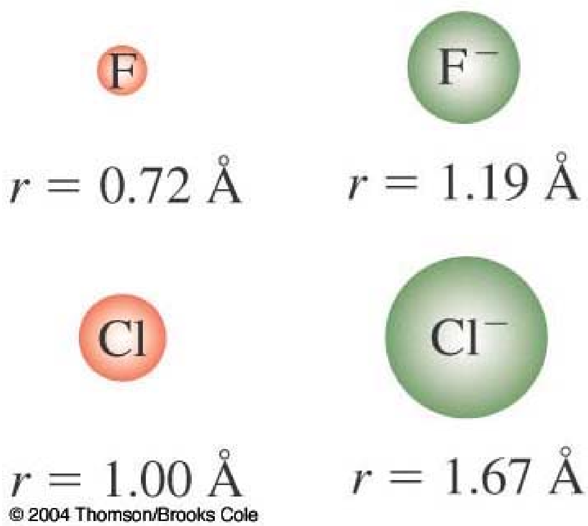


Electron Affinity: Periodicity

- Important conclusions
  - Noble gases have completely filled outer shell and therefore zero electron affinity
  - Nonmetals, especially halogens, gain electrons easily forming anions and attaining the electron configuration of noble gases
  - Metals are usually quite unlikely to gain electrons and form anions

Ionic Radii





- When atom looses an electron, its radius always decreases
  - Cations (positive ions) are always smaller than their respective neutral atoms
- When atom gains an electron, its radius always increases
  - Anions (negative ions) are always larger than their respective neutral atoms

Isoelectronic Species

- Species of different elements having the same electron configuration

N	$[He]2s^22p^3$	N^{3-}	$[He]2s^22p^6$
O	$[He]2s^22p^4$	O^{2-}	$[He]2s^22p^6$
F	$[He]2s^22p^5$	F^-	$[He]2s^22p^6$
Ne	$[He]2s^22p^6$	Ne	$[He]2s^22p^6$
Na	$[He]2s^22p^63s^1$	Na^+	$[He]2s^22p^6$
Mg	$[He]2s^22p^63s^2$	Mg^{2+}	$[He]2s^22p^6$
Al	$[He]2s^22p^63s^23p^1$	Al^{3+}	$[He]2s^22p^6$

Radii of Isoelectronic Ions

An isoelectronic series of ions

	N^{3-}	O^{2-}	F^{-}	Na^{+}	Mg^{2+}	Al^{3+}
Ionic radius (Å)	1.71	1.26	1.19	1.16	0.85	0.68
No. of electrons	10	10	10	10	10	10
Nuclear charge	+7	+8	+9	+11	+12	+13

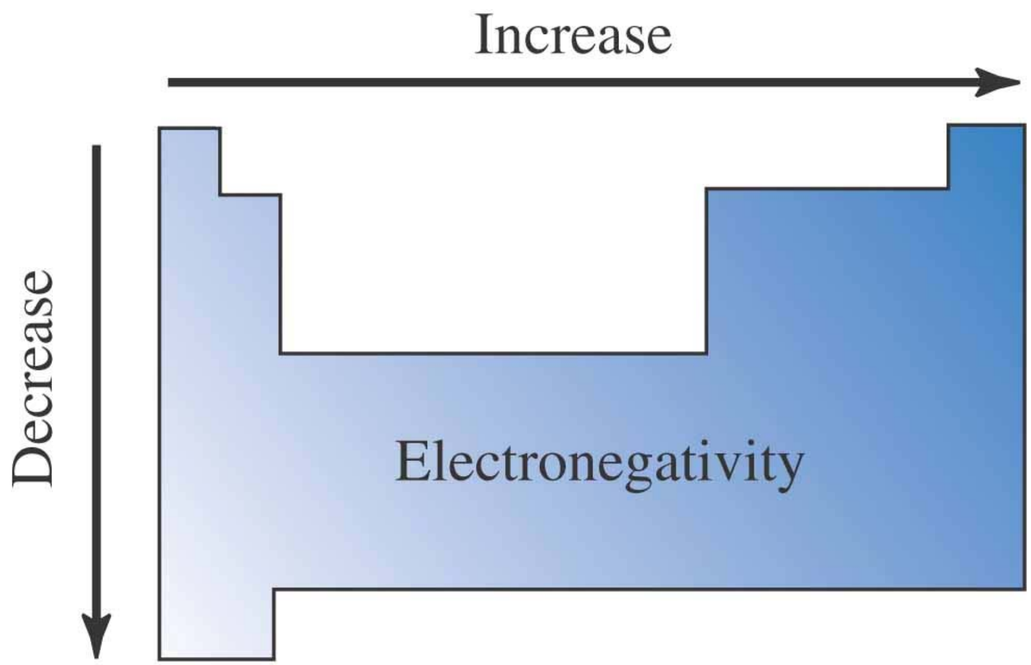
- In an isoelectronic series of ions
  - The number of electrons remains the same
  - The nuclear charge increases with increasing atomic number, and therefore the ionic radius decreases

Electronegativity

- Measures the tendency of an atom to attract electrons when <u>chemically combined with another element</u>
  - If element "likes" electrons – high electronegativity (electronegative element)
  - If element "dislikes" electrons – low electronegativity (electropositive element)
- Sounds like the electron affinity but <u>different</u>
  - Electron affinity measures the degree of attraction of an electron by a single atom forming an anion
  - Electronegativity measures the attraction of electrons to the atom <u>in chemical compounds</u>

Electronegativity

- The scale for electronegativity was suggested by Linus Pauling
- It is a semi-qualitative scale based on data collected from studying many compounds



Example

- Arrange these elements based on their electronegativity
  - Se, Ge, Br, As
  - Be, Mg, Ca, Ba

Oxidation Numbers

- When an element with high electronegativity (nonmetal) reacts with an element with low electronegativity (metal), they tend to form a chemical compound in which electrons are stronger attracted to the nonmetal atoms
- This brings us to the important concept of <u>oxidation numbers</u>, or oxidation states
  - The number of electrons gained or lost by an atom of the element when it forms a chemical compounds with other elements

Oxidation Numbers: Rules

1) The oxidation number of the atoms in any free, uncombined element, is zero
2) The sum of the oxidation numbers of all atoms in a compound is zero
3) The sum of the oxidation numbers of all atoms in an ion is equal to the charge of the ion

Oxidation Numbers: Rules

4) The oxidation number of <u>fluorine</u> in all its compounds is –1
5) The oxidation number of <u>other halogens</u> in their compounds is usually –1
6) The oxidation number of <u>hydrogen</u> is +1 when it is combined with more electronegative elements (most nonmetals) and –1 when it is combined with more electropositive elements (metals)
7) The oxidation number of oxygen in most compounds is –2
8) Oxidation numbers for other elements are determined by the number of electrons they need to gain or lose in order to attain the electron configuration of a noble gas

Oxidation Numbers: Examples

- H_2O
- CH_4
- NH_4Cl
- NaH
- CaH_2
- KCl
- $RbNO_3$
- $SrSO_4$
- $CaBr_2$
- CO
- CO_2
- Mg_3N_2
- P_4O_{10}
- $(NH_4)_2S$
- BeF_2
- SO_2

Reading Assignment

- Go through Lecture 10 notes
- Read Sections 4-4 through 4-6 of Chapter 4
- Read Chapter 6 completely
- Learn Key Terms from Chapter 6 (p. 260-261)

Important Dates

- Thursday (10/6) – review session on electron configurations, 6:00-8:00 p.m. in Room 105 Heldenfels
- Homework #3 due by 10/10 @ 9:00 p.m.
- Monday (10/10) and Tuesday (10/11) – lecture quiz #3 based on Chapters 5&6