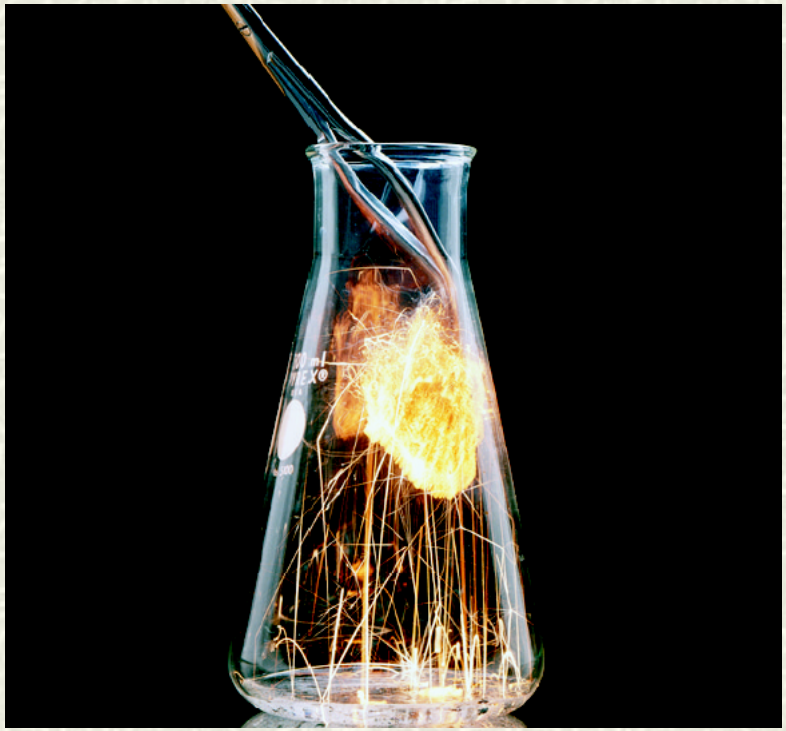
CHAPTER 6

- Chemical Periodicity



Chapter Goals

1. **More About the Periodic Table**

Periodic Properties of the Elements

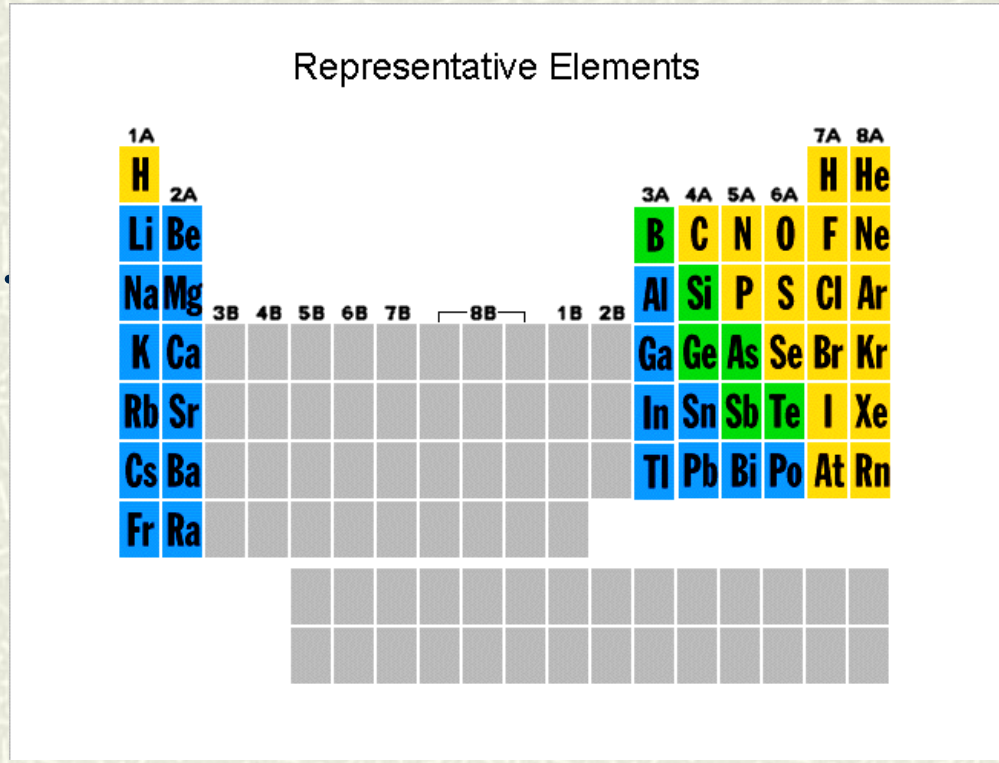
2. **Atomic Radii**
3. **Ionization Energy**
4. **Electron Affinity**
5. **Ionic Radii**
6. **Electronegativity**

More About the Periodic Table

- Establish a classification scheme of the elements based on their electron configurations.
- **Noble Gases**
  - All of them have completely filled electron shells.
- Since they have similar electronic structures (**full *s* and *p* orbitals**), their chemical reactions are similar.
  - He $1s^2$
  - Ne [He] $2s^2\ 2p^6$
  - Ar [Ne] $3s^2\ 3p^6$
  - Kr [Ar] $4s^2\ 4p^6$
  - Xe [Kr] $5s^2\ 5p^6$
  - Rn [Xe] $6s^2\ 6p^6$

More About the Periodic Table

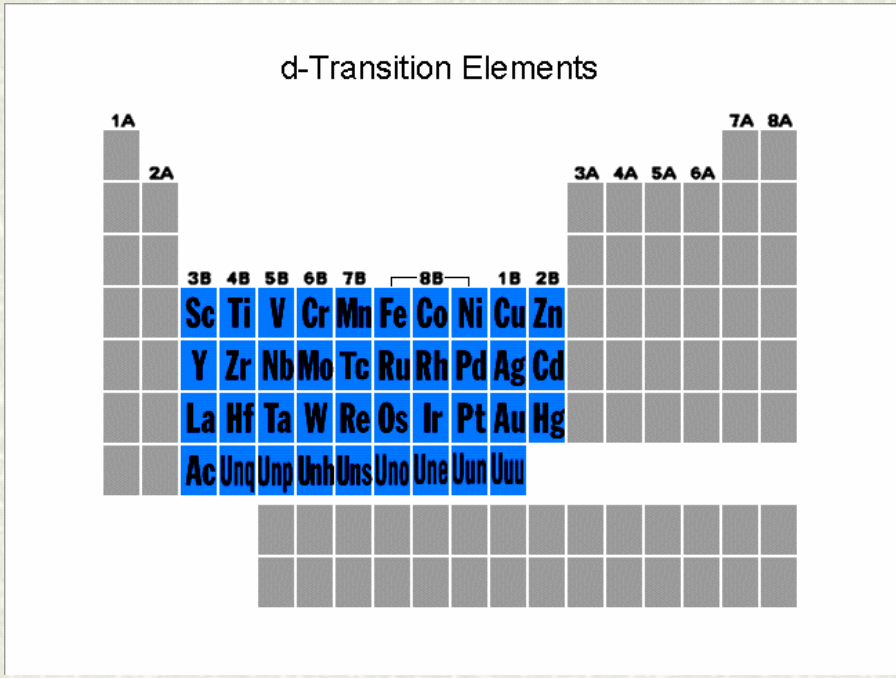
- **Representative Elements**
  - Are the elements in A groups on periodic chart.



- These elements will have their "last" electron in an outer *s* or *p* orbital.

More About the Periodic Table

- ***d*-Transition Elements**
  - Elements on periodic chart in B groups.

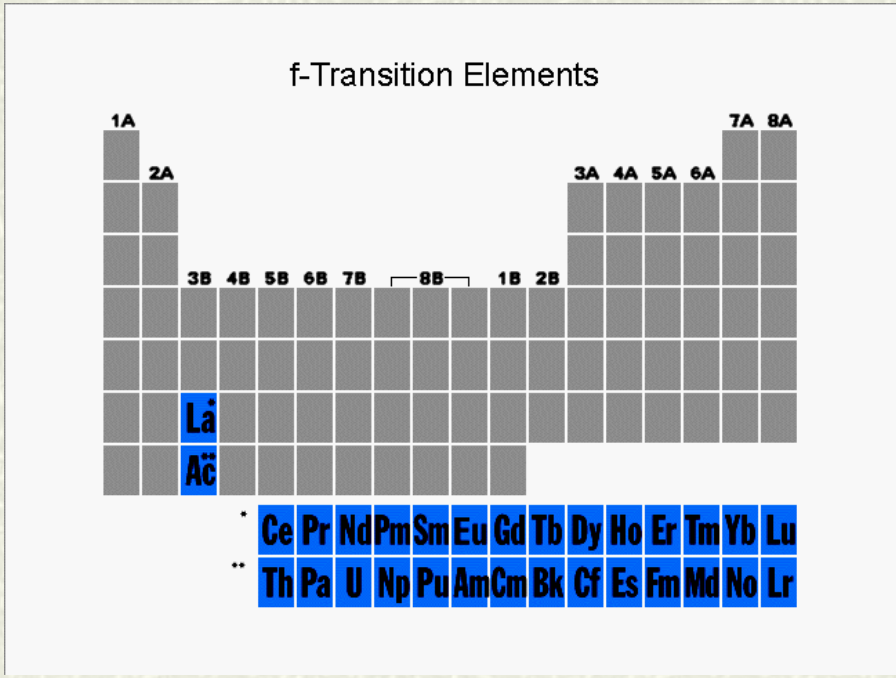


- Each metal has *d* electrons.
  - ns (n-1)*d* configurations

- These elements make the transition from metals to nonmetals.

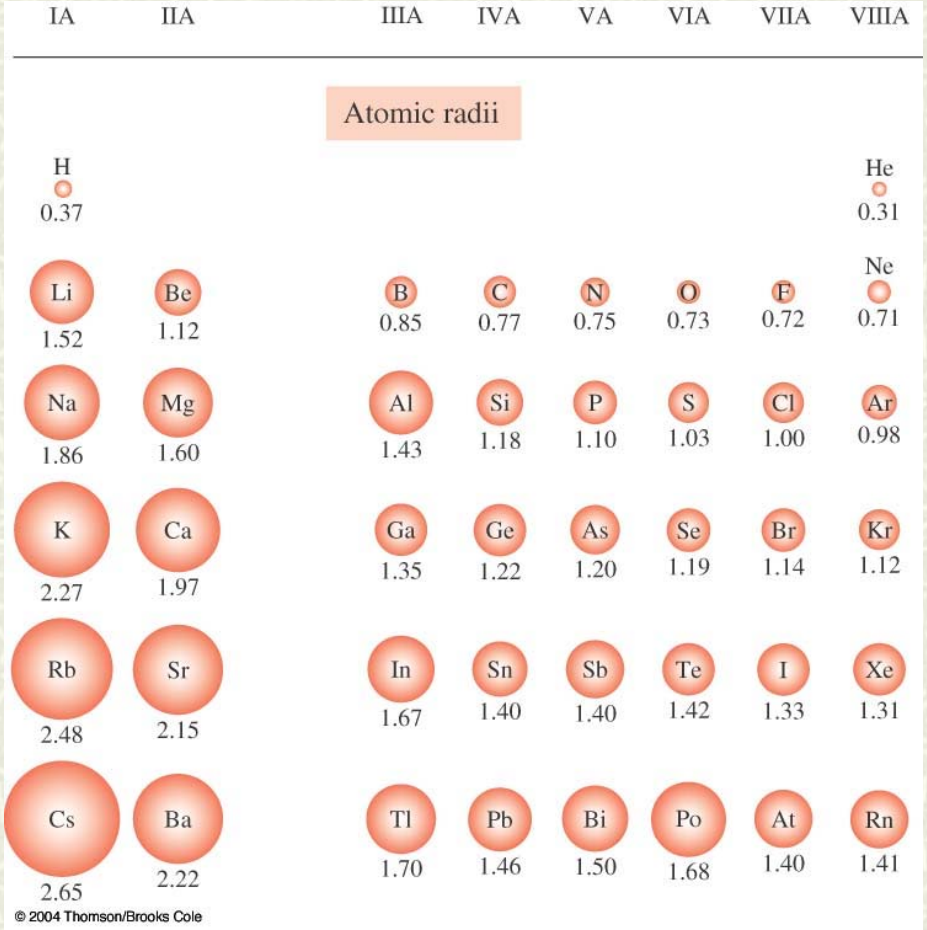
More About the Periodic Table

- ***f* - transition metals**
  - Sometimes called inner transition metals.
- Electrons are being added to *f* orbitals.
- Consequently, very slight variations of properties from one element to another.
- ***Outermost*** electrons have the greatest influence on the chemical properties of elements.



Periodic Properties of the Elements – Atomic Radii

- Atomic radii describes the relative sizes of atoms.
- Atomic radii increase within a column going from the top to the bottom of the periodic table.
- Atomic radii decrease within a row going from left to right on the periodic table.



Atomic Radii

- The reason the atomic radii decrease across a period is due to ***shielding*** or ***screening*** effect.
  - Effective nuclear charge, Z_{eff}, experienced by an electron is less than the actual nuclear charge, Z.
  - The inner electrons block the nuclear charge's effect on the outer electrons.
- Moving across a period, each element has an increased nuclear charge and the electrons are going into the same shell (2s and 2p or 3s and 3p, etc.).
  - Consequently, the outer electrons feel a stronger effective nuclear charge.
  - For Li, $Z_{eff} \sim +1$
  - For Be, $Z_{eff} \sim +2$

Atomic Radii

- **Example: Arrange these elements based on their atomic radii.**
  - **Se, S, O, Te**
- **Example: Arrange these elements based on their atomic radii.**
  - **P, Cl, S, Si**
- **Example: Arrange these elements based on their atomic radii.**
  - **Ga, F, S, As**

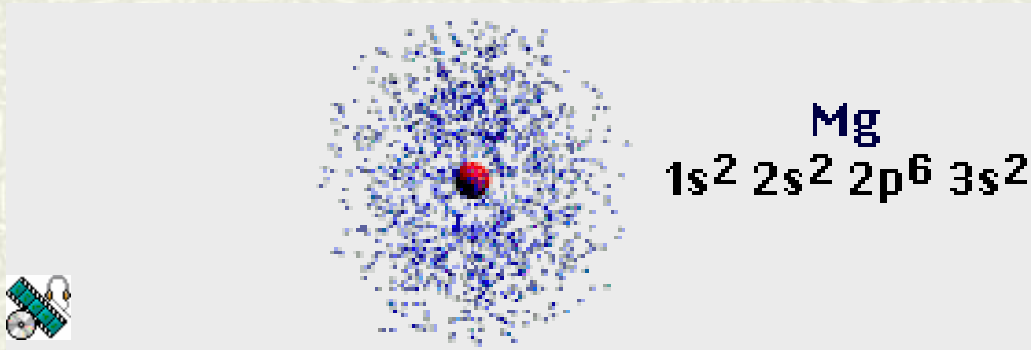
Redox Reactions

- **Why do metals losa electrons in their reactions?**
- **Why does Mg form Mg^{2+} ions and not Mg^{3+}?**
- **Why do nonmetals take on electrons?**

Ionization Energy

Ionization Energy

- **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.



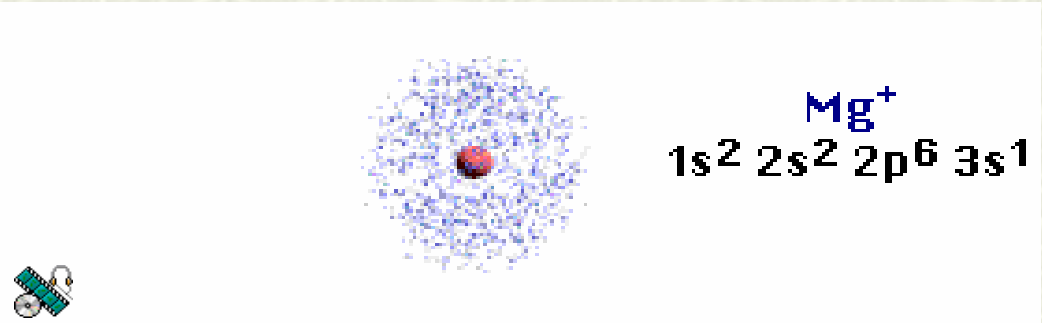
- **Symbolically:**

$Atom_{(g)} + energy \rightarrow ion^{+}_{(g)} + e^{-}$

$Mg_{(g)} + 738kJ/mol \rightarrow Mg^{+} + e^{-}$

Ionization Energy

- **Second ionization energy (IE_2)**
  - The amount of energy required to remove the second electron from a gaseous 1+ ion.



- **Symbolically:**
  - **$ion^+ + energy \rightarrow ion^{2+} + e^-$**

    $Mg^+ + 1451\ kJ/mol \rightarrow Mg^{2+} + e^-$

    Mg^+ has 12 protons and only 11 electrons. Therefore, IE for $Mg^+ > Mg$

❖ **Atoms can have 3rd (IE3), 4th (IE4), etc. ionization energies.**

Ionization Energy

Periodic trends for Ionization Energy:

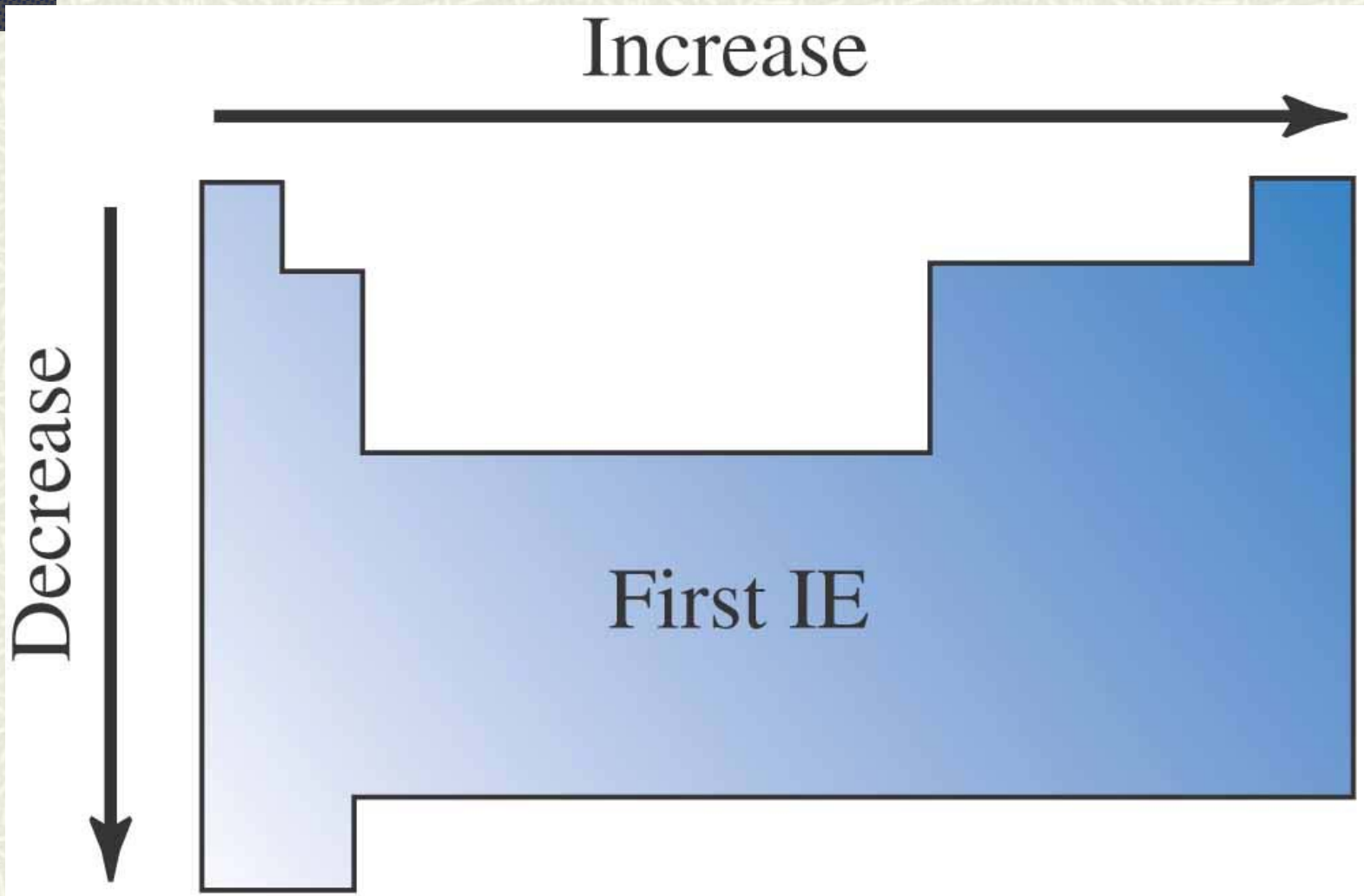
- $IE_2 > IE_1$ It always takes more energy to remove a second electron from an ion than from a neutral atom.
- IE_1 generally increases moving from IA elements to VIIIA elements.

  Important exceptions at Be & Mg, N & P, etc. due to filled and half-filled subshells.

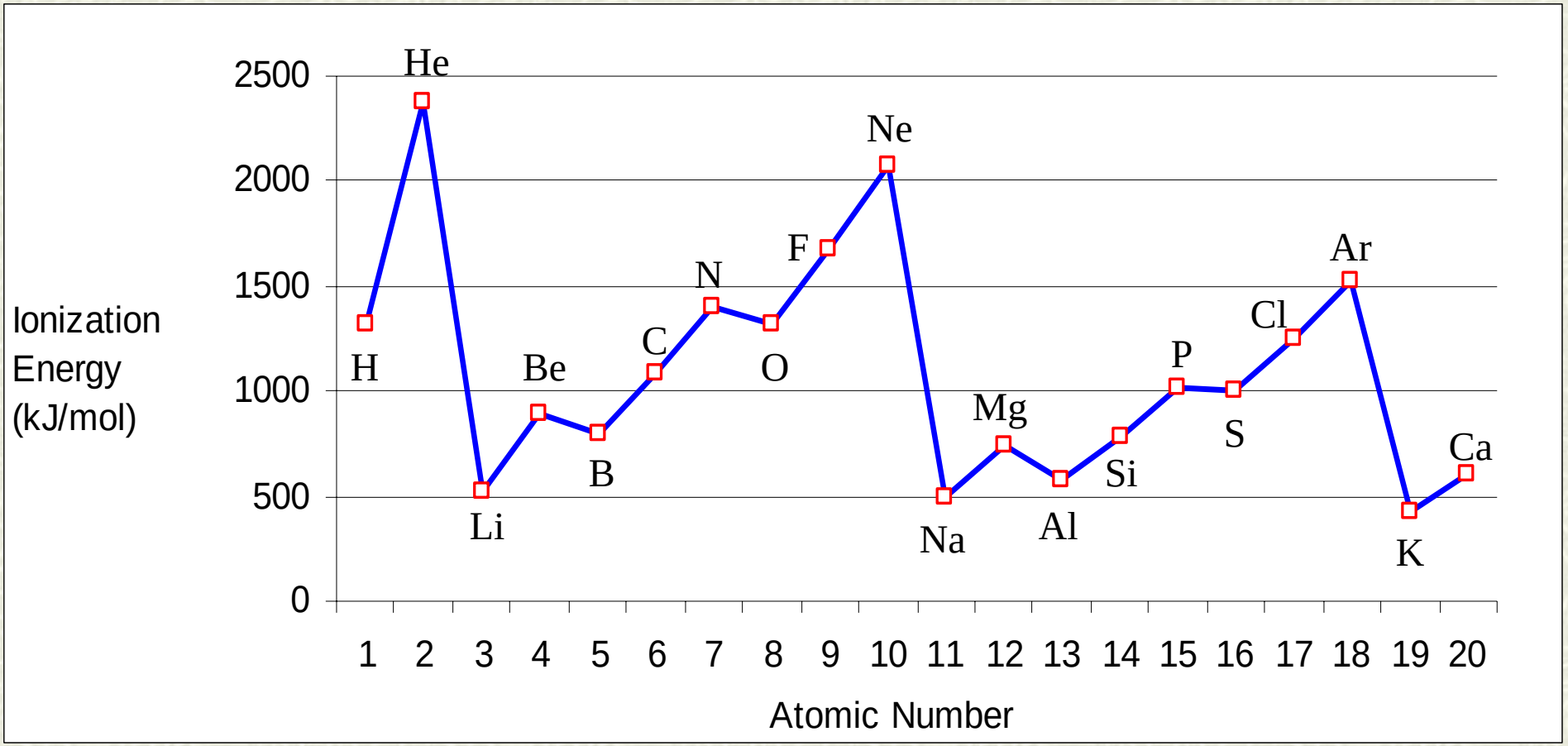
  - IE_1 generally decreases moving down a family.

    IE_1 for Li > IE_1 for Na, etc.

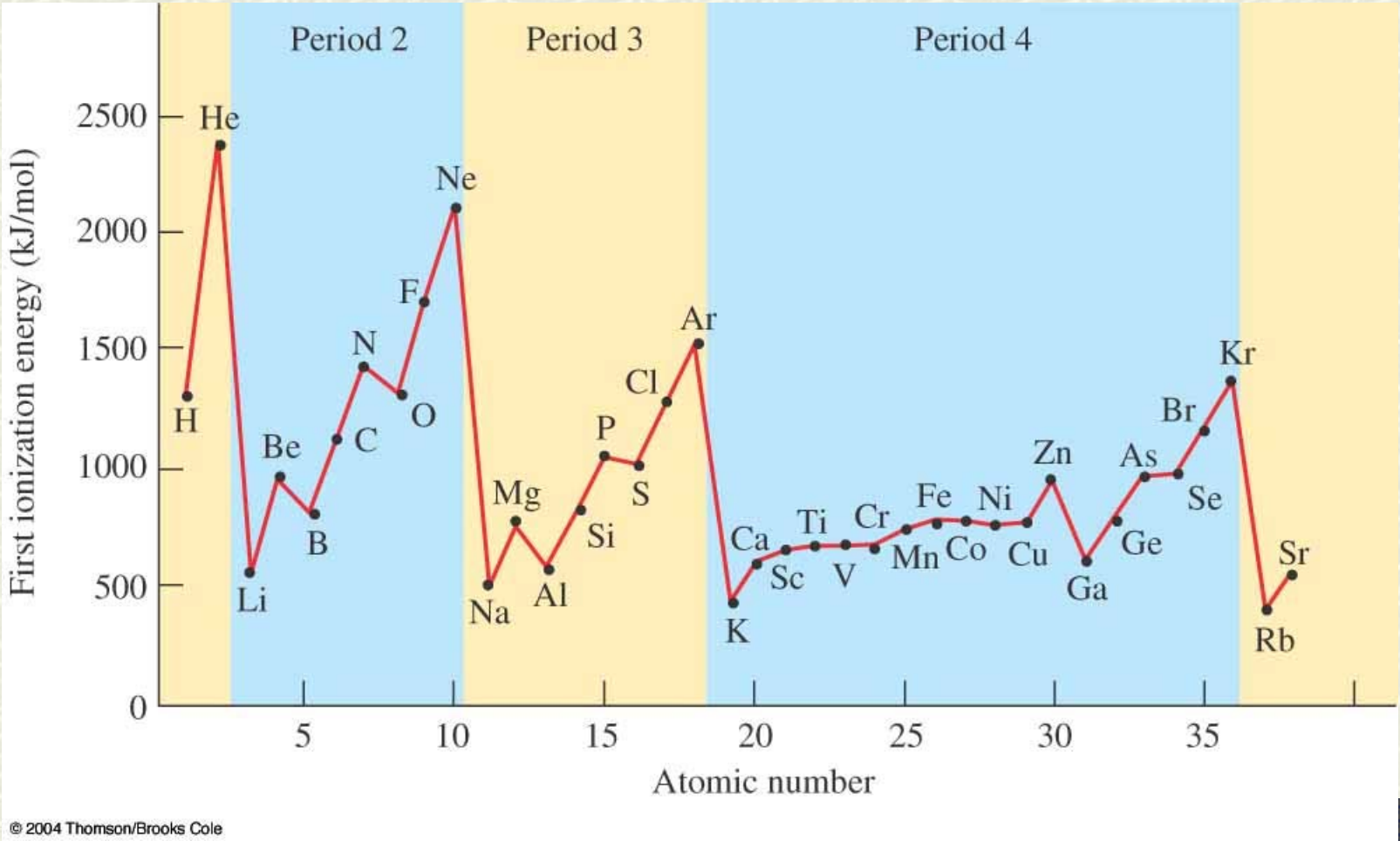
Ionization Energy



First Ionization Energies of Some Elements



First Ionization Energies of Some Elements



Ionization Energy

- **Example: Arrange these elements based on their first ionization energies (IE).**
  - **Sr, Be, Ca, Mg**

- **Example: Arrange these elements based on their first IE.**
  - **Al, Cl, Na, P**

- **Example: Arrange these elements based on their first IE.**
  - **B, O, Be, N**

Ionization Energy

- First, second, third, etc. ionization energies exhibit periodicity as well.
- Look at the following table of ionization energies versus third row elements.
  - Notice that the energy increases enormously when an electron is removed from a completed electron shell.

Ionization Energy

Group and element	IA Na	IIA Mg	IIIA Al	IVA Si
IE_1 (kJ/mol)	496	738	578	786
IE_2 (kJ/mol)	4562	1451	1817	1577
IE_3 (kJ/mol)	6912	7733	2745	3232
IE_4 (kJ/mol)	9540	10,550	11,580	4356

Ionization Energy

- The reason Na forms Na^{+} and not Na^{2+} is that the energy difference between IE_1 and IE_2 is so large.
  - Requires more than 9 times more energy to remove the second electron than the first one.

- The same trend is persistent throughout the series.
  - Thus Mg forms Mg^{2+} and not Mg^{3+}.
  - Al forms Al^{3+}.

Electron Affinity

- **Electron affinity** is the amount of energy ***absorbed*** when an electron is added to an isolated gaseous atom to form an ion with a **1- charge**.

- Electron affinity is a measure of an atom's ability to form negative ions.

- Symbolically:

$$\mathbf{atom(g) + e^- + EA \rightarrow ion^-(g)}$$

Electron Affinity

Sign conventions for electron affinity.

If electron affinity > 0 energy is absorbed.

If electron affinity < 0 energy is released.

Two examples of electron affinity values:

$$Mg_{(g)} + e^- + 231\ kJ/mol \rightarrow Mg^-_{(g)}$$

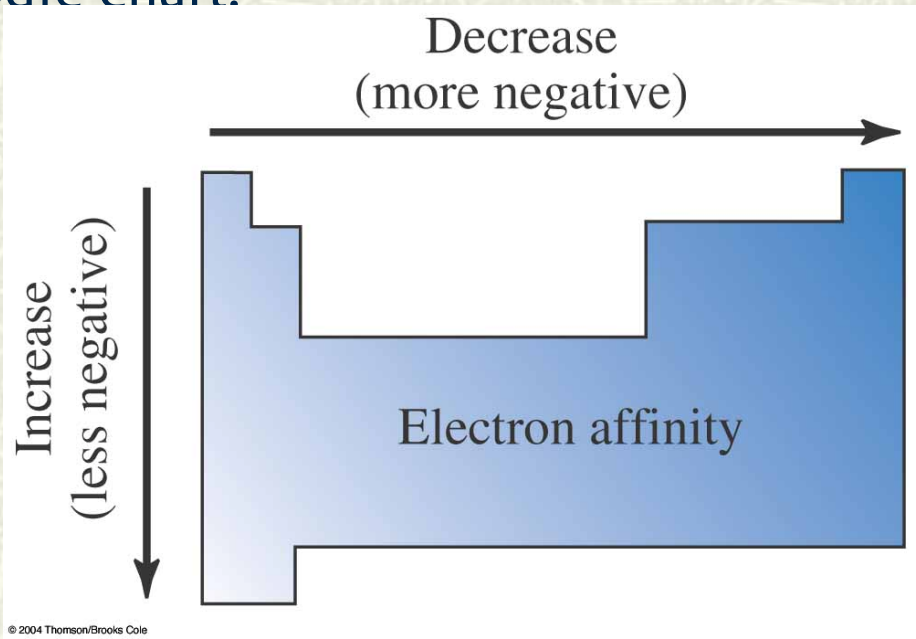
EA = +231 kJ/mol

$$Br_{(g)} + e^- \rightarrow Br^-_{(g)} + 323\ kJ/mol$$

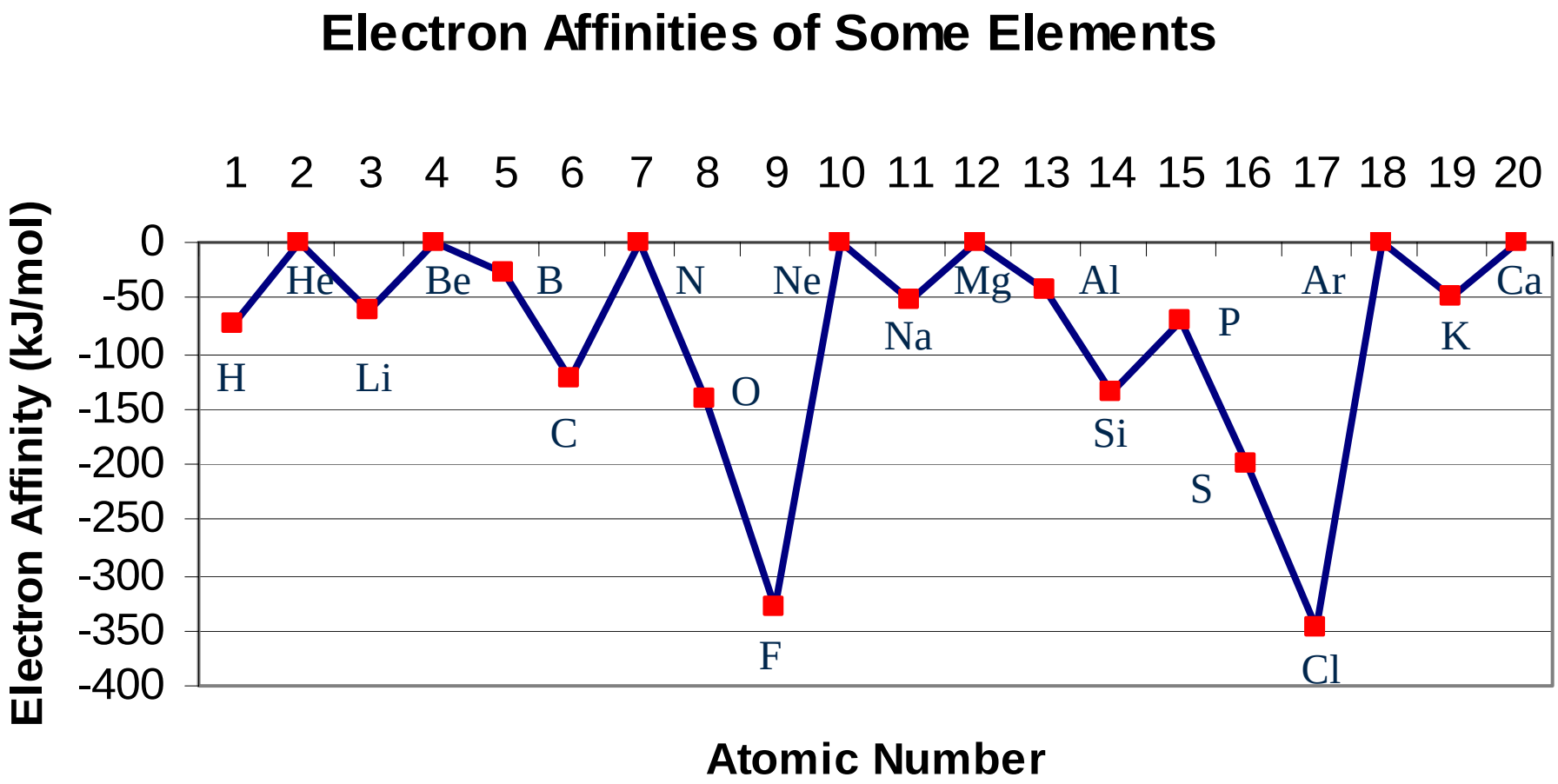
EA = -323 kJ/mol

Electron Affinity

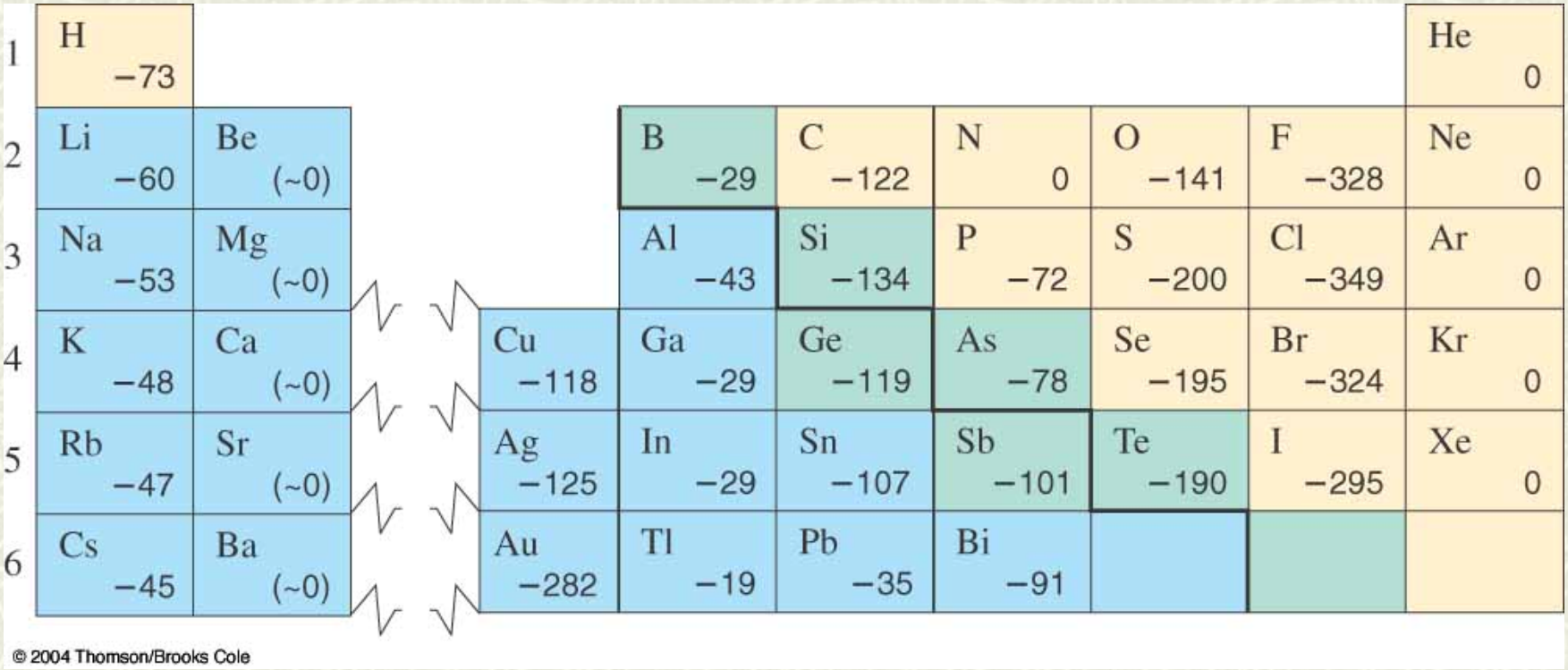
- General periodic trend for electron affinity is
  - the values become **more negative** from **left to right** across a period on the periodic chart.
  - the values become **more negative** from **bottom to top** up a row on the periodic chart.



Electron Affinity



Electron Affinity



Electron Affinity

- **Example: Arrange these elements based on their electron affinities.**
  - **Al, Mg, Si, Na**

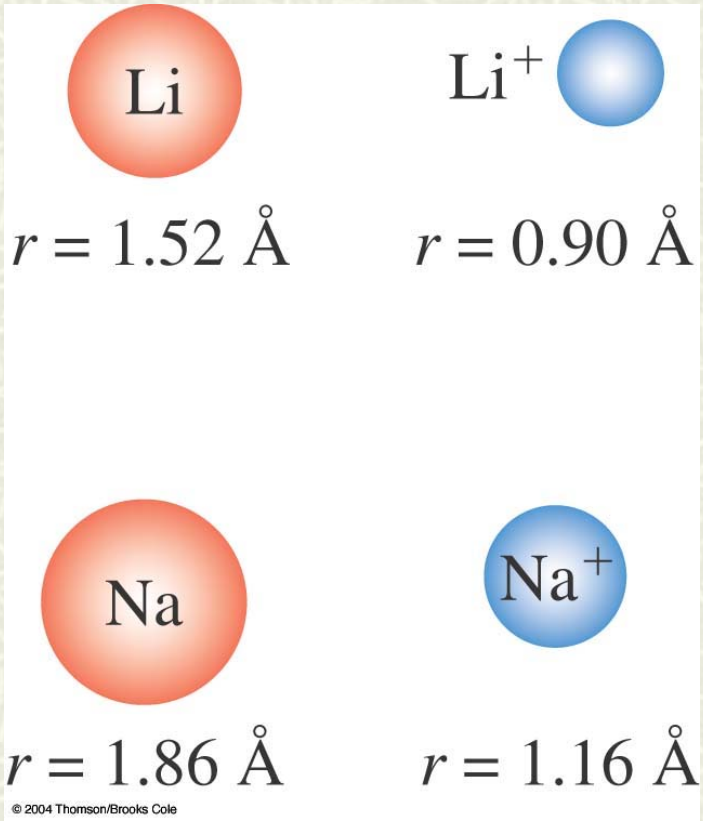
- **Example: Arrange the following elements in order of increasing values of electron affinity, i.e., from most negative to least negative.**

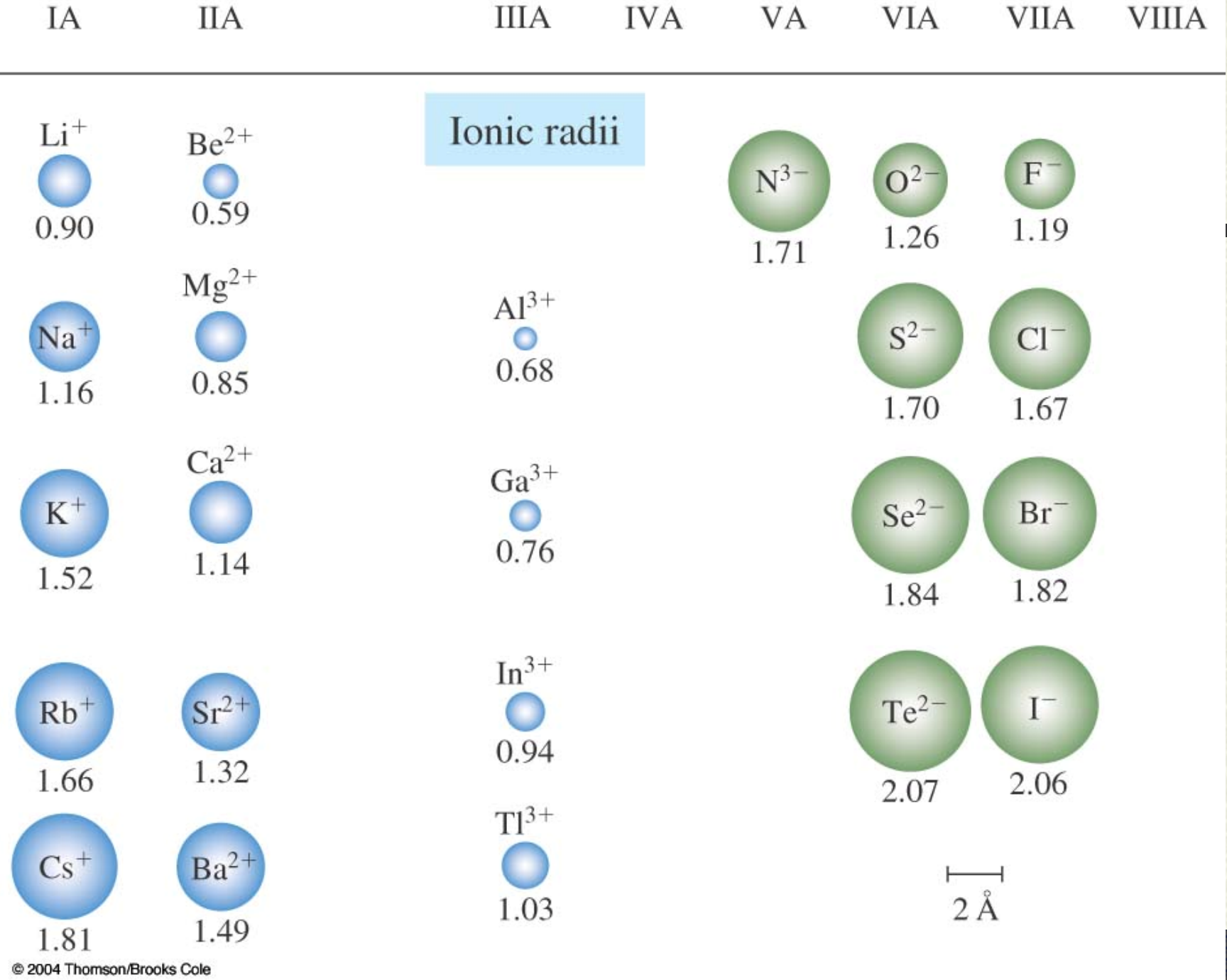
Cl, Se, S, Cs, Rb, Te

(a) Cl < S < Se < Rb < Te < Cs
(b) Cl > Te > Se > S > Rb > Cs
(c) Cl > Se > S > Te > Rb > Cs
(d) Cl < S < Se < Te < Cs < Rb
(e) Cl < S < Se < Te < Rb < Cs

Ionic Radii

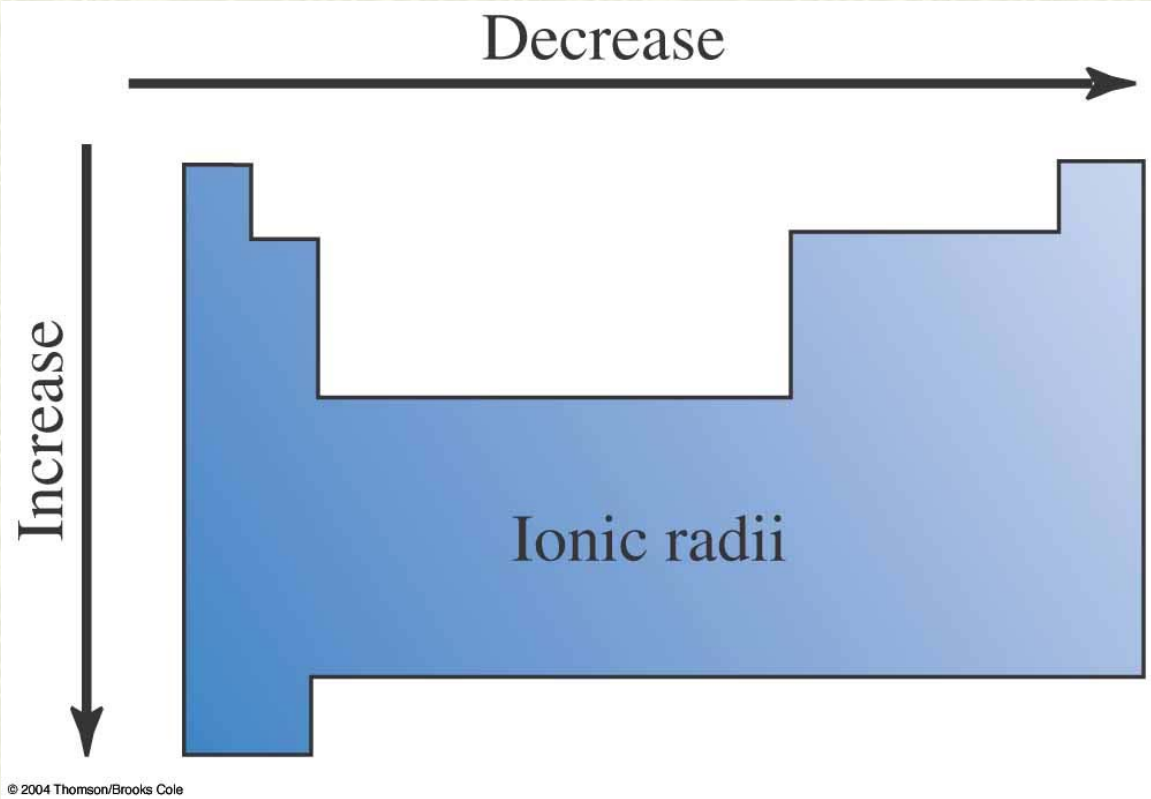
- Cations are always ***smaller*** than their respective neutral atoms.





Ionic Radii

- Anions are always ***larger*** than their neutral atoms.



Ionic Radii

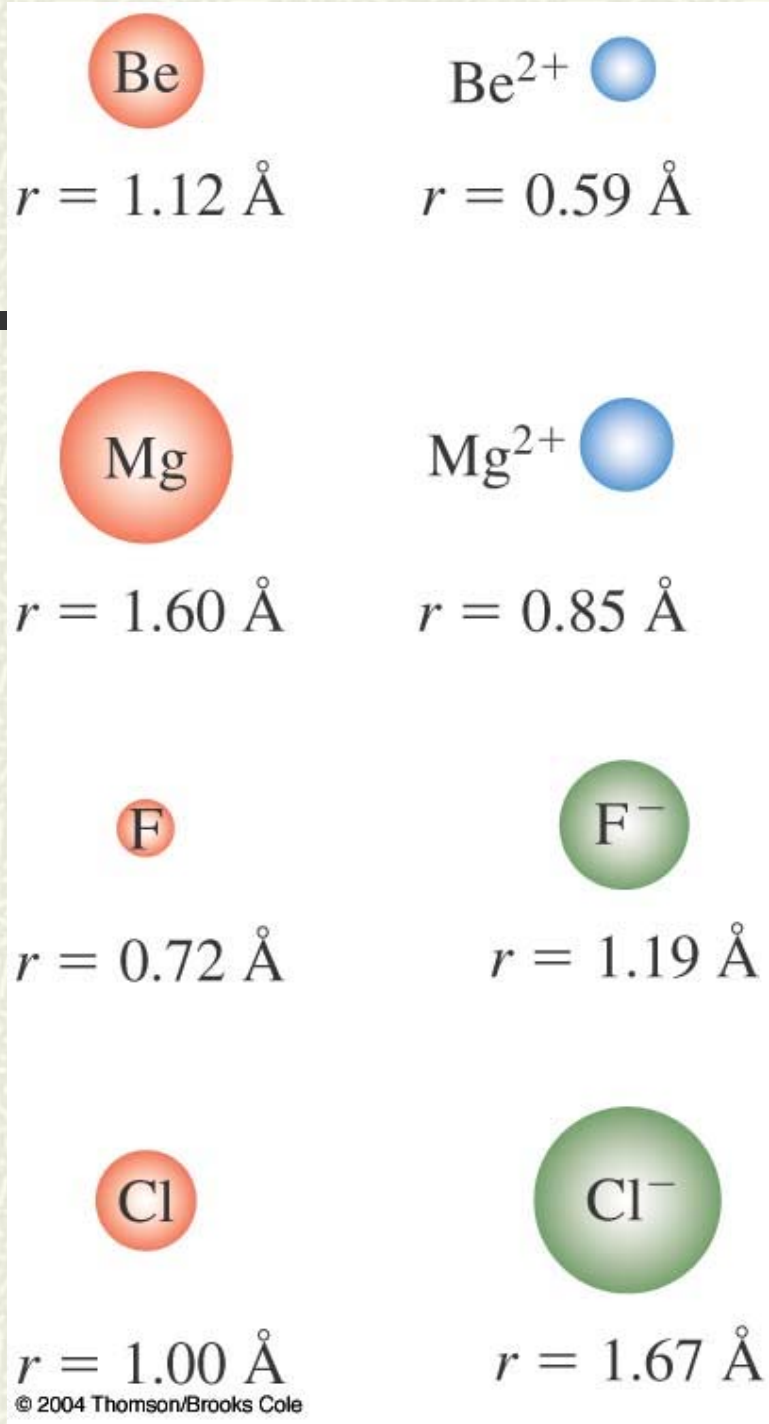
- Cations radii decrease from left to right across a period.
  - Increasing nuclear charge attracts the electrons and decreases the radius.

Ion	Rb^{+}	Sr^{2+}	In^{3+}
Ionic Radii(Å)	1.66	1.32	0.94

Ionic Radii

- Anions radii decrease from left to right across a period.
  - Increasing electron numbers in highly charged ions cause the electrons to repel and increase the ionic radius.

Ion	N^{3-}	O^{2-}	F^{1-}
Ionic Radii(Å)	1.71	1.26	1.19


Be
Be^{2+}
$r = 1.12$ Å
$r = 0.59$ Å
Mg
Mg^{2+}
$r = 1.60$ Å
$r = 0.85$ Å
F
F^-
$r = 0.72$ Å
$r = 1.19$ Å
Cl
Cl^-
$r = 1.00$ Å
$r = 1.67$ Å
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Ionic Radii

- Example: Arrange these elements based on their ionic radii.
  - Ga^{3+}, K^{+}, Ca^{2+}
- Example: Arrange these elements based on their ionic radii.
  - Cl^{-}, Se^{2-}, Br^{-}, S^{2-}

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

Problem

1- Which of the following statements is CORRECT with regard to atomic or ionic size?

(1) $S^{2-} < Cl^{-}$ (2) $Br < Br^{-}$ (3) $Li^{-} < Li$ (4) $P < N$

2- Select the largest species from the following group:

(A) Mg (B) Cl (C) S (D) Al

3- Select the smallest species from the following group:

(A) Fe^{3+} (B) Fe^{2+} (C) Fe^{+} (D) Fe

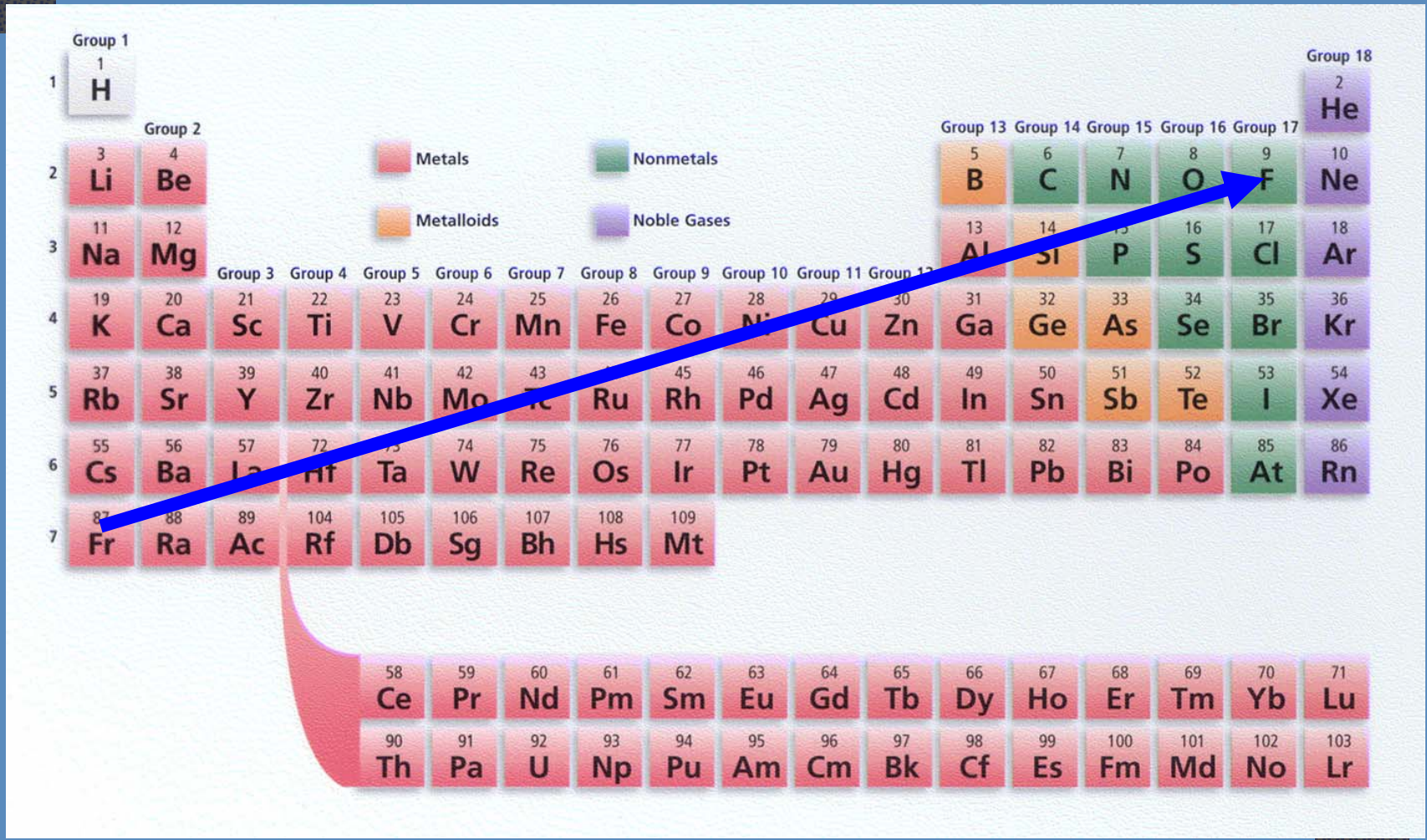
4- Select the element with the lowest ionization energy (the easiest to ionize):

(A) Ga (B) In (C) B (D) Al

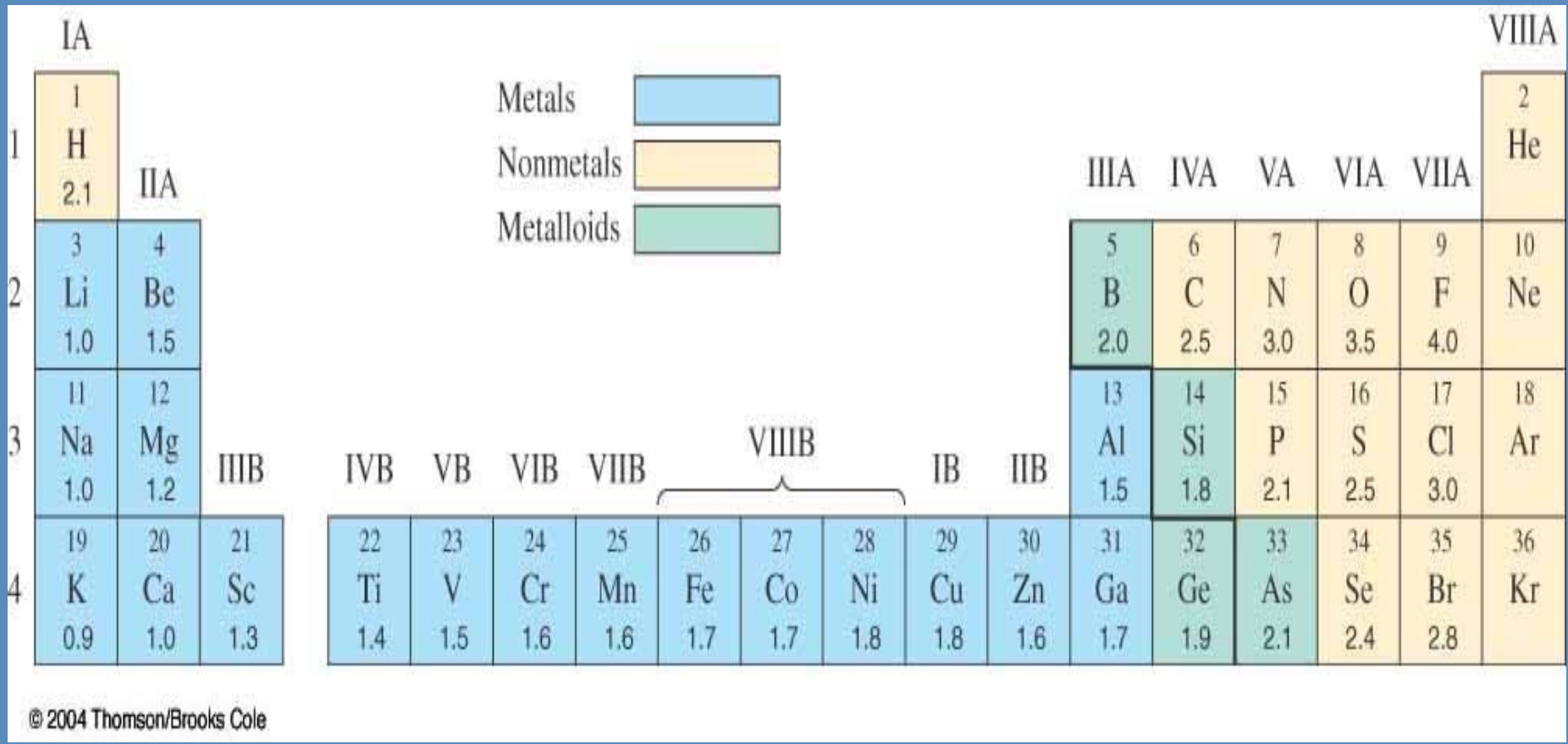
Electronegativity

- **Electronegativity** is a measure of the **relative tendency** of an atom to attract electrons to itself when ***chemically combined with another element***.
  - Electronegativity is measured on the **Pauling scale**.
  - ***Fluorine is the most electronegative element***.
  - ***Cesium and francium are the least electronegative elements*.**
- For the representative elements, electronegativities usually increase from left to right across periods and decrease from top to bottom within groups.

Electronegativity



Electronegativity



Electronegativity

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

Homework Assignment

One-line Web Learning (OWL):

Chapter 6 Exercises and Tutors – Optional

End of Chapter 6