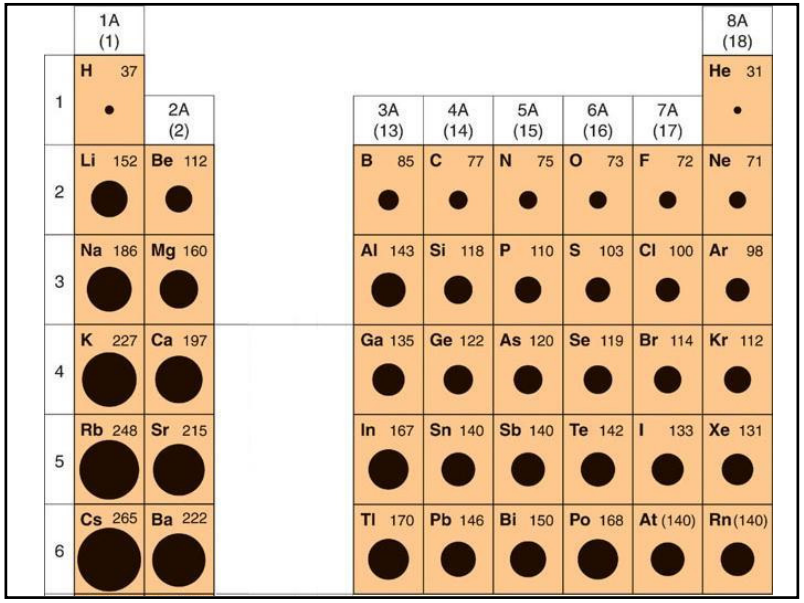
8.3 Periodic Trends in Atomic Properties

– Periodicity is based on the electron configuration which depends on the # of electrons which in turn depends on the number of protons (atomic #)

Trends in Atomic Size

- **Atomic radius** – half of the distance between the centers of two adjacent identical atoms
  - **Metallic radius** – for metals in the solid phase
  - **Covalent radius** – for nonmetals in molecules
- Atomic radii **increase down a group** and **decrease** from left to right **across a period** (for main group elements)



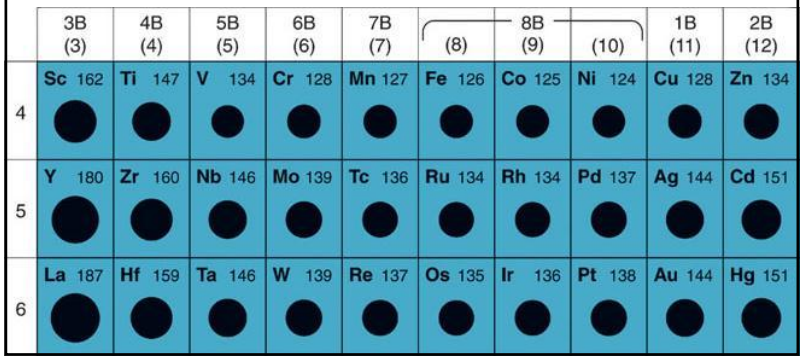
- **Down a group** – the valence shell **principal quantum number (*n*) increases** ⇒ orbitals and electron clouds become larger
- **Across a period** – the nuclear charge increases while the new electrons enter the same principal shell (do not shield each other effectively) ⇒ the **effective nuclear charge (Z_{eff}) increases** and draws the electrons closer to the nucleus

Example: Compare the sizes of **Ge**, **Sn** and **Se**.

Sn is below Ge ⇒ Sn>Ge

Ge is to the left of Se ⇒ Ge>Se

- For the **transition elements**, the size trend **across a period** is not as pronounced because electrons are added to inner shells which provides better shielding of the outer electrons, so Z_{eff} does not increase as much



Trends in Ionization Energy

- **Ionization energy (*I*)** – energy required to remove an electron from a gas-phase atom
  - **First** ionization energy (I_1) – to remove the 1st **e**$^-$

$$\mathbf{X(g) \rightarrow X^+(g) + e^-}$$

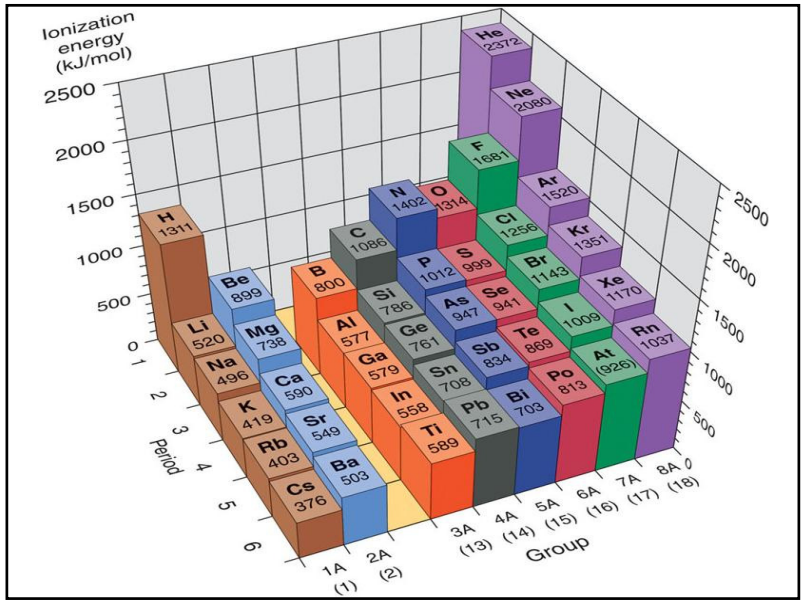
  - **Second** ionization energy (I_2) – to remove a 2nd **e**$^-$

$$\mathbf{X^+(g) \rightarrow X^{2+}(g) + e^-}$$

- Ionization energies are positive (endothermic) and become larger with every subsequent ionization

$$\mathbf{0 < I_1 < I_2 < I_3 < I_4 \ldots}$$

  - It's harder to remove an **e**$^-$ from a positive ion



- First ionization energies **decrease down a group** and **increase** from left to right **across a period** (with some exceptions)
  - **Down a group** electrons are removed from shells that are farther from the nucleus (less tightly bound)
  - **Across a period Z_{eff}** increases (valence electrons are more tightly bound to the nucleus)
- Low ionization energy accounts for the metallic character of elements in the lower left corner of the table (***s***, ***d***, ***f*** and some of the ***p*** block) – easy removal of **e**$^-$ provides better conductivity and tendency to form cations

- Irregularities in the ionization energy trends
  - Decrease in I_1 between groups 2(2A) and 13(3A) elements

group 2A → ns^2 **group 3A →** ns^2np^1

    - The ***n*p** electron is easier to remove than the ***n*s** electron – ***p***-subshells have higher energy and are less tightly bound
  - Decrease in I_1 between groups 15 and 16 elements

group 15(5A) → $ns^2np_x^1np_y^1np_z^1$

group 16(6A) → $ns^2np_x^2np_y^1np_z^1$

    - It's easier to remove the paired electron on the p_x-orbital – paired electrons repel each other stronger than unpaired electrons

- Considerable **jump** in the successive ionization energies occurs after removal of all valence electrons – core electrons are much more difficult to remove than valence electrons
  - explains the charges of stable metal cations

Na → [Ne]$3s^1$

I_1 = 496 kJ/mol, I_2=4562 kJ/mol

Stable cation → Na^+

Mg → [Ne]$3s^2$

I_1 = 738 kJ/mol, I_2 = 1450 kJ/mol, I_3 = 7734 kJ/mol

Stable cation → Mg^{2+}

Trends in Electron Affinity

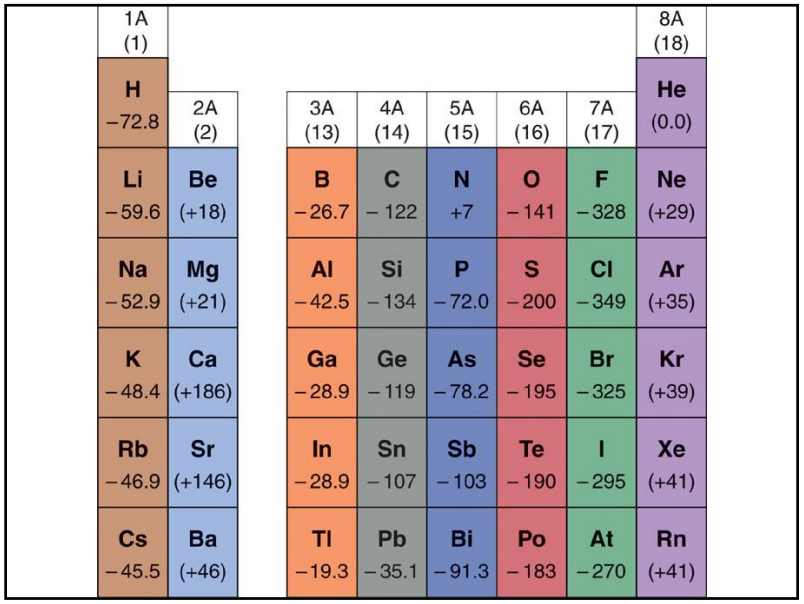
- **Electron affinity (*A*)** – energy associated with the addition of an electron to a gas-phase atom
  - **First** electron affinity (A_1) – to add the 1st e^-

$$X(g) + e^- \rightarrow X^-(g)$$

  - **Second** electron affinity (A_2) – to add a 2nd e^-

$$X^-(g) + e^- \rightarrow X^{2-}(g)$$

- Electron affinities can be either exothermic (-) or endothermic (+)
  - A_1 is typically (-) (exceptions: group 2A, 8A, …)
  - A_2, A_3 … are always positive
  - By convention, "larger" *A* is more exothermic (-)



- First electron affinities tend to be **larger (more exothermic) in the upper right corner** of the table similarly to the first ionization energies
- Successive electron affinities are smaller and smaller – more endothermic ($A_1 > A_2 > A_3$ ...)
  - It's harder to add an e^- to a negative ion
- Considerable **drop** in the successive electron affinities occurs after achieving a noble gas configuration – the new electrons are added to a higher principal shell
  - Explains the charges of the stable anions of groups 15, 16 and 17 (N^{3-}, O^{2-}, F^- …)

- Irregularities in the electron affinity trends
  - Decrease in A_1 between groups 1 and 2 elements

    group 1 → ns^1 **group 2 → ns^2**
    - For group 2 the new electron is added to the higher energy ***n*p** subshell
  - Decrease in A_1 between groups 14 and 15 element

    group 14 → $ns^2np_x^1np_y^1$

    group 15 → $ns^2np_x^1np_y^1np_z^1$
    - For group 15 the new electron is added to an already occupied ***n*p** orbital – pairing of electrons is energetically unfavorable (stronger repulsion)