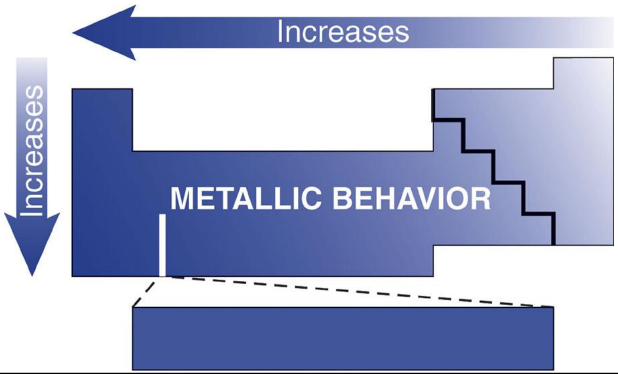
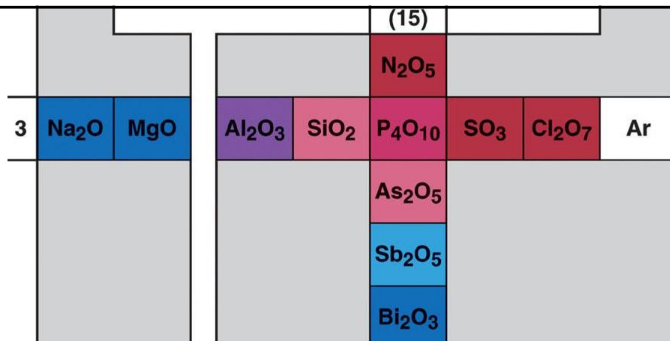
8.4 Atomic Structure and Chemical Behavior

Trends in Metallic Behavior

- Related to the trends in the size, ***I*** and ***A***



- Relative tendency to lose or gain electrons
  - The tendency to form cations increases to the left and toward the bottom (***I*** decreases)
  - The tendency to form anions increases to the right and toward the top (***A*** increases)
- Elemental oxides
  - **Metals** tend to form ionic oxides that act as bases in water → **basic oxides** (Na_2O, CaO, BaO, …)
  - **Nonmetals** tend to form covalent oxides that act as acids in water → **acidic oxides** (CO_2, SO_3, …)
  - Most **metalloids** and **some metals** form **amphoteric oxides** → can act as acids or bases in water (Al_2O_3, GeO_2, …)



$Na_2O + H_2O \rightarrow 2NaOH$ ← (strongly basic)

$P_4O_{10} + H_2O \rightarrow H_3PO_4$ ← (weakly acidic)

$SO_3 + H_2O \rightarrow H_2SO_4$ ← (strongly acidic)

$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$ ← (amphoteric)

$Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2Al(OH)_4^-$ ↵

Properties of Monatomic Ions

- Electron configurations of **cations**
  - For ***s*- and *p*-elements**, electrons are lost first from the ***np*** subshell followed by the ***ns*** subshell
  - All valence electrons are lost until a **noble gas** (or a **pseudo-noble gas**) **configuration** is achieved (high stability)

Example: Write the electron configurations of the stable cations of **Sr** and **Ga**.

Sr → [Kr]5*s*² $\quad$ **Sr^{2+} → [Kr]**

Ga → [Ar]4*s*²3*d*¹⁰4*p*¹ $\quad$ **Ga^{3+} → [Ar]3*d*¹⁰**

Pseudo-noble gas configuration → [Noble](*n*-1)*d*¹⁰

- **Inert pair** effect – the ***np***-electrons have higher energy than the ***ns***-electrons and are lost first, so the two ***ns***-electrons may or may not be lost (for the heavier metals in the ***p***-block → In, Tl, Sn, Pb, and Bi)

Example: Write the electron configurations of the two common cations of **Pb**.

Pb → [Xe]$6s^2 4f^{14} 5d^{10} 6p^2$

Pb^{2+} → [Xe]$6s^2 4f^{14} 5d^{10}$ **Pb^{4+} → [Xe]$4f^{14} 5d^{10}$**

Inert pair

Pseudo-noble gas config. → [Noble]$(n\text{-}2)f^{14}(n\text{-}1)d^{10}$

- For ***d*-elements**, electrons are lost first from the ***ns*** subshell followed by the ***(n-1)d*** subshell
- In general, not all valence electrons are lost and more than one cations are possible

Example: Write the electron configuration of **Co^{3+}**.

Co → [Ar]$4s^2 3d^7$ **Co^{3+} → [Ar]$3d^6$**

- Electron configurations of **anions**
  - Electrons are added until a noble-gas configuration is reached

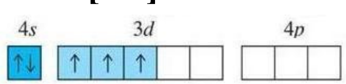
Example: Write the electron configuration of the **nitride** ion.

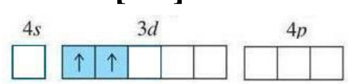
N → [He]$2s^2 2p^3$ **N^{3-} → [He]$2s^2 2p^6$ → [Ne]**

- **Magnetic properties** of atoms and ions
  - Species with unpaired electrons are **paramagnetic** (attracted by magnetic fields)
  - Species having all electrons paired are **diamagnetic** (not attracted by magnetic fields)

Example: Write the electron configurations of **V** and **V^{3+}** and determine which species is more paramagnetic.

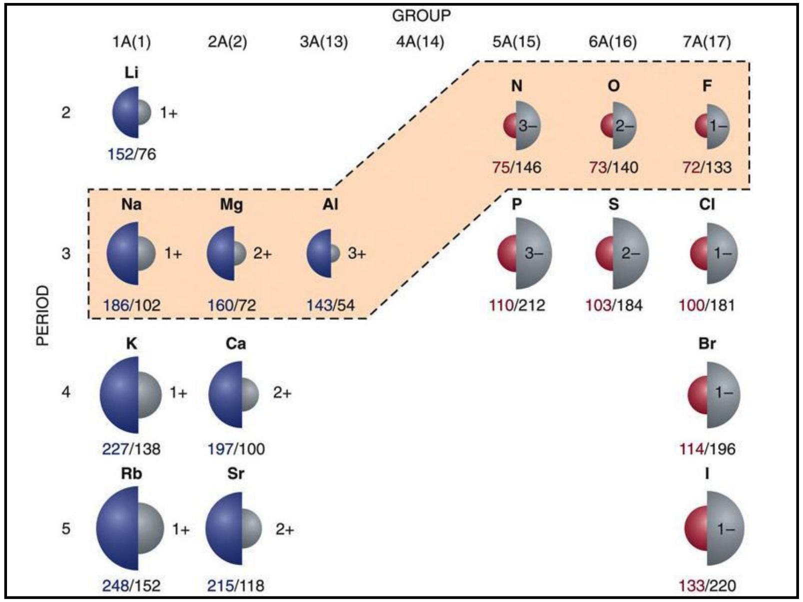
V → [Ar]$4s^2 3d^3$ **V^{3+} → [Ar]$3d^2$**





More paramagnetic (more unpaired e$^-$)

- **Ionic sizes** (ionic radii)
  - Part of the distance between the centers of two neighboring ions in an ionic solid (**O^{2-}** is used as a standard with radius 140 pm)
- **Cations** are smaller than their parent atoms
  - Cation size decreases as charge increases for the different cations of an element
- **Anions** are larger then their parent atoms
- Ionic sizes of cations as well as anions follow the same trends in the periodic table as the sizes of atoms (increase down and to the left)
  - In a given period, the anions are larger than the cations



- **Isoelectronic species** – atoms and ions with the same number of electrons (have the same electron configuration)
  - Size decreases with increasing the atomic number of the element (nuclear charge increases)

Example: Compare the sizes of $\mathbf{Cl^-}$, $\mathbf{Ca^{2+}}$ and $\mathbf{Sc^{3+}}$

Isoelectronic, electron configuration of argon **[Ar]**

$\Rightarrow$ $Sc^{3+} < Ca^{2+} < Cl^-$ **(atomic number ↓)**

Example: Compare the sizes of **Ca**, $\mathbf{Ca^{2+}}$ and $\mathbf{Mg^{2+}}$

$\mathbf{Ca^{2+} < Ca}$ **(cation is smaller)**

$\mathbf{Mg^{2+} < Ca^{2+}}$ **(Mg is above Ca)** $\Rightarrow$ $Mg^{2+} < Ca^{2+} < Ca$