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 (Na₂O, CaO, BaO, …)
– Nonmetals tend to form covalent oxides that act as acids in water → acidic oxides (CO₂, SO₃, …)
– Most metalloids and some metals form amphoteric oxides → can act as acids or bases in water (Al₂O₃, GeO₂, …)

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]5s² → Sr²⁺ → [Kr]
Ga → [Ar]4s²3d¹⁰⁴p¹ → Ga³⁺ → [Ar]3d¹⁰

Pseudo-noble gas configuration → [Noble](n-1)d¹⁰

Na₂O + H₂O → 2NaOH ← (strongly basic)
P₄O₁₀ + H₂O → H₃PO₄ ← (weakly acidic)
SO₃ + H₂O → H₂SO₄ ← (strongly acidic)
Al₂O₃ + 6H⁺ → 2Al³⁺ + 3H₂O ← (amphoteric)
Al₂O₃ + 2OH⁻ + 3H₂O → 2Al(OH)₄⁻ ←
– **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.

\[
Pb \rightarrow [Xe]6s^24f^{14}5d^{10}6p^2
\]
\[
Pb^{2+} \rightarrow [Xe]6s^24f^{14}5d^{10} \quad Pb^{4+} \rightarrow [Xe]4f^{14}5d^{10}
\]

**Pseudo-noble gas config.** → [Noble]*(n-2)*f^{14}(n-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+}.

\[
Co \rightarrow [Ar]4s^23d^7 \quad Co^{3+} \rightarrow [Ar]3d^6
\]

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

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

\[
N \rightarrow [He]2s^22p^3 \quad N^{3-} \rightarrow [He]2s^22p^6 \rightarrow [Ne]
\]

---

• **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.

\[
V \rightarrow [Ar]4s^23d^3 \quad V^{3+} \rightarrow [Ar]3d^2
\]

More paramagnetic (more unpaired e⁻)

• **Ionic sizes** (ionic radii)
  – Part of the distance between the centers of two neighboring ions in an ionic solid (*O²⁻* 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 than 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 Cl\(^-\), Ca\(^{2+}\) and Sc\(^{3+}\)

Isoelectronic, electron configuration of argon [Ar]

\[ \Rightarrow \text{Sc}^{3+} < \text{Ca}^{2+} < \text{Cl}^- \text{ (atomic number ↓)} \]

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

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

Mg\(^{2+}\) < Ca\(^{2+}\) (Mg is above Ca) \[ \Rightarrow \text{Mg}^{2+} < \text{Ca}^{2+} < \text{Ca} \]