Chapter 7
Periodic Properties of the Elements
7.1 Development of Periodic Table

- Elements in the same group generally have similar chemical properties.
- Physical Properties are not identical, however.
Development of Periodic Table

Dmitri **Mendeleev** and Lothar **Meyer** independently came to the same conclusion about how elements should be grouped.
Mendeleev, for instance, predicted the discovery of germanium (which he called eka-silicon) as an element with an atomic weight between that of zinc and arsenic, but with chemical properties similar to those of silicon.
Periodic Trends

• In this chapter, we will rationalize observed trends in
  - Sizes of atoms and ions.
  - Ionization energy.
  - Electron affinity.
7.2 Effective Nuclear Charge

- In a many-electron atom, electrons are both **attracted** to the nucleus and **repelled** by other electrons.

- The nuclear charge that an electron experiences depends on both factors.
Effective Nuclear Charge

The effective nuclear charge, \( Z_{\text{eff}} \), is found this way:

\[
Z_{\text{eff}} = Z - S
\]

where \( Z \) is the atomic number and \( S \) is a screening constant, usually close to the number of inner electrons.
7.3 Sizes of Atoms

The bonding atomic radius is defined as one-half of the distance between covalently bonded nuclei.
Sizes of Atoms

Bonding atomic radius tends to...

...**decrease** from left to right across a row due to increasing $Z_{\text{eff}}$.

...**increase** from top to bottom of a column due to increasing value of $n$.
Sizes of Atoms Example

• Page 266: Use Figure 7.6 to determine the length of the C-S, C-H and S-H bond.
  - C-S Bond = radius of C + radius of S
  - C-H bond = radius of C + radius of H
  - S-H bond = radius of S + radius of H
Sizes of Atoms

- C-S bond = 1.79 Angstroms
- C-H bond = 1.14 Angstroms
- S-H bond = 1.39 Angstroms
Sizes of Atoms

• Referring to a periodic table, arrange (as much as possible) the following atoms in order of increasing size:
  ➢ Na, Be, Mg
Sizes of Atoms

• Answer: Be < Mg < Na
Sizes of Ions

<table>
<thead>
<tr>
<th>Group 1A</th>
<th>Group 2A</th>
<th>Group 3A</th>
<th>Group 6A</th>
<th>Group 7A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>Li</td>
<td>Be²⁺</td>
<td>Be</td>
<td>B</td>
</tr>
<tr>
<td>0.68</td>
<td>1.34</td>
<td>0.31</td>
<td>0.90</td>
<td>0.23</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Na</td>
<td>Mg²⁺</td>
<td>Mg</td>
<td>Al³⁺</td>
</tr>
<tr>
<td>0.97</td>
<td>1.54</td>
<td>0.66</td>
<td>1.30</td>
<td>0.51</td>
</tr>
<tr>
<td>K⁺</td>
<td>K</td>
<td>Ca²⁺</td>
<td>Ca</td>
<td>Ga³⁺</td>
</tr>
<tr>
<td>1.33</td>
<td>1.96</td>
<td>0.99</td>
<td>1.74</td>
<td>0.62</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>Rb</td>
<td>Sr²⁺</td>
<td>Sr</td>
<td>In³⁺</td>
</tr>
<tr>
<td>1.47</td>
<td>2.11</td>
<td>1.13</td>
<td>1.92</td>
<td>0.81</td>
</tr>
</tbody>
</table>

- Ionic size depends upon:
  - Nuclear charge.
  - Number of electrons.
  - Orbitals in which electrons reside.

- Neutral atoms in gray, cations in red, anions in blue.
Sizes of Ions

- **Cations** are smaller than their parent atoms.
  - The outermost electron is removed and repulsions are reduced.
Sizes of Ions

- **Anions** are larger than their parent atoms.

  - Electrons are added and repulsions are increased.
Sizes of Ions

- Ions **increase** in size as you go down a column.
  - Due to increasing **value of** \( n \).
Practice

• Arrange these atoms and ions in order of decreasing size: Mg$^{+2}$, Ca$^{+2}$, and Ca.
Answer

• Cations are smaller than their parent atoms, and so the Ca$^{+2}$ is smaller than Ca atom. Because Ca is below Mg in group 2A, Ca$^{+2}$ is larger than Mg$^{+2}$.
• Ca > Ca$^{+2}$ > Mg$^{+2}$
Practice

• Which of the following atoms and ions is largest?
  ➢ Sulfide ion, Sulfur atom, or oxide ion?
Answer

- Sulfide Ion
- Increase size as you down a column, and anions are larger than their parent atoms.
Sizes of Ions

- In an isoelectronic series, ions have the same number of electrons.
- Ionic size decreases with an increasing nuclear charge.
Practice

• Arrange the ions $K^+$, $Cl^-$, $Ca^{+2}$, and $S^{-2}$ in order of decreasing size.
Answer

• Isoelectronic series of ions – they all have 18 electrons.
• In such a series, size decreases as the nuclear charge (atomic number) of the ion increases. The atomic numbers of the ions are
  
  S = 16, Cl = 17, K = 19, Ca = 20.
  
  Thus, the ions decrease in size in the order
  
  Sulfide Ion > Chloride Ion > Potassium Ion > Calcium Ion
7.4 Ionization Energy

• Amount of energy required to remove an electron from the ground state of a gaseous atom or ion.
  
  ➢ **First** ionization energy is that energy required to remove first electron.
  
  ➢ **Second** ionization energy is that energy required to remove second electron, etc.
Ionization Energy

• It requires **more** energy to remove each successive electron.

• When all valence electrons have been removed, the ionization energy takes a quantum leap.

<table>
<thead>
<tr>
<th>Element</th>
<th>$I_1$</th>
<th>$I_2$</th>
<th>$I_3$</th>
<th>$I_4$</th>
<th>$I_5$</th>
<th>$I_6$</th>
<th>$I_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>495</td>
<td>4562</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(inner-shell electrons)</td>
</tr>
<tr>
<td>Mg</td>
<td>738</td>
<td>1451</td>
<td>7733</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>578</td>
<td>1817</td>
<td>2745</td>
<td>11,577</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>786</td>
<td>1577</td>
<td>3232</td>
<td>4356</td>
<td>16,091</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>1012</td>
<td>1907</td>
<td>2914</td>
<td>4964</td>
<td>6274</td>
<td>21,267</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>1000</td>
<td>2252</td>
<td>3357</td>
<td>4556</td>
<td>7004</td>
<td>8496</td>
<td>27,107</td>
</tr>
<tr>
<td>Cl</td>
<td>1251</td>
<td>2298</td>
<td>3822</td>
<td>5159</td>
<td>6542</td>
<td>9362</td>
<td>11,018</td>
</tr>
<tr>
<td>Ar</td>
<td>1521</td>
<td>2666</td>
<td>3931</td>
<td>5771</td>
<td>7238</td>
<td>8781</td>
<td>11,995</td>
</tr>
</tbody>
</table>
Trends in First Ionization Energies

- As one goes down a column, less energy is required to remove the first electron.

  For atoms in the same group, $Z_{\text{eff}}$ is essentially the same, but the valence electrons are farther from the nucleus.
Trends in First Ionization Energies

- Generally, as one goes across a row, it gets harder to remove an electron.
  - As you go from left to right, $Z_{\text{eff}}$ increases.
Trends in First Ionization Energies

However, there are two apparent discontinuities in this trend.
Trends in First Ionization Energies

• The first occurs between Groups IIA and IIIA.

• Electron removed from $p$-orbital rather than $s$-orbital
  ➢ Electron farther from nucleus
  ➢ Small amount of repulsion by $s$ electrons.
Trends in First Ionization Energies

- The second occurs between Groups VA and VIA.
  - Electron removed comes from doubly occupied orbital.
  - Repulsion from other electron in orbital helps in its removal.
Practice

• Referring to a periodic table, arrange the following atoms in order of increasing first ionization energy:

  ➢ Ne, Na, P, Ar, K
Answer

- Ionization energy increases as we move left to right across a row.
- It decreases as we move from the top of a group to the bottom.
- Na, P and Ar are in the same row, we expect $I_1$ to vary in the order Na < P < Ar.
- Because Ne is above Ar in group 8A, we expect Ne to have a greater $I_1$: Ar < Ne. Similarly K is below Na so K < Na
- $K < Na < P < Ar < Ne$
Practice

• Which has the lowest first ionization energy?
  ➢ B, Al, C or Si?

• Which has the highest first ionization energy?
  ➢ B, Al, C or Si?
Answer

- Al has the lowest, C has the highest.
Electron Configurations of Ions

- Write the electron configuration for
  - Calcium ion
  - Cobalt III ion
  - Sulfide Ion
Answer

- **Ca Atom**
  - [Ar] 4s²
- **Ca Ion**
  - [Ar]
- **Co Atom**
  - [Ar] 3d⁷ 4s²
- **Cobalt III Ion**
  - [Ar] 3d⁶
- **Sulfur Atom**
  - [Ne] 3s² 3p⁴
- **Sulfide Ion**
  - [Ne] 3s² 3p⁶ = [Ar]
7.5 Electron Affinity

Energy change accompanying addition of electron to gaseous atom:

\[ \text{Cl} + e^- \rightarrow \text{Cl}^- \quad \Delta E = -349 \text{ kJ/mol} \]
In general, electron affinity becomes more **exothermic** as you go from left to right across a row. The more negative the electron affinity, the greater the attraction of the atom for an electron.
Periodic Properties of the Elements

Trends in Electron Affinity

There are again, however, **two** discontinuities in this trend.
Trends in Electron Affinity

• The first occurs between Groups **IA and IIA**.
  - Added electron must go in $p$-orbital, not $s$-orbital.
  - Electron is farther from nucleus and feels repulsion from $s$-electrons.
Trends in Electron Affinity

- The second occurs between Groups IVA and VA.
  - Group VA has no empty orbitals.
  - Extra electron must go into occupied orbital, creating repulsion.
7.6 Properties of Metal, Nonmetals, and Metalloids
# Metals versus Nonmetals

<table>
<thead>
<tr>
<th>Metals</th>
<th>Nonmetals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Have a shiny luster; various colors, although most are silvery</td>
<td>Do not have a luster; various colors</td>
</tr>
<tr>
<td>Solids are malleable and ductile</td>
<td>Solids are usually brittle; some are hard, some are soft</td>
</tr>
<tr>
<td>Good conductors of heat and electricity</td>
<td>Poor conductors of heat and electricity</td>
</tr>
<tr>
<td>Most metal oxides are ionic solids that are basic</td>
<td>Most nonmetal oxides are molecular substances that form acidic solutions</td>
</tr>
<tr>
<td>Tend to form cations in aqueous solution</td>
<td>Tend to form anions or oxyanions in aqueous solution</td>
</tr>
</tbody>
</table>

Differences between metals and nonmetals tend to revolve around these properties.
Metals versus Nonmetals

- Metals tend to form **cations**.
- Nonmetals tend to form **anions**.

<table>
<thead>
<tr>
<th>1A</th>
<th>2A</th>
<th>3A</th>
<th>4A</th>
<th>5A</th>
<th>6A</th>
<th>7A</th>
<th>8A</th>
</tr>
</thead>
<tbody>
<tr>
<td>H+</td>
<td>2A</td>
<td>N3-</td>
<td>O2-</td>
<td>F-</td>
<td>H-</td>
<td>H-</td>
<td>H-</td>
</tr>
<tr>
<td>Li+</td>
<td></td>
<td>Al3+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na+</td>
<td>Mg2+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K+</td>
<td>Ca2+</td>
<td>Cr3+</td>
<td>Mn2+</td>
<td>Fe2+</td>
<td>Fe3+</td>
<td>Co2+</td>
<td>Ni2+</td>
</tr>
<tr>
<td>Rb+</td>
<td>Sr2+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs+</td>
<td>Ba2+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Periodic Properties of the Elements**
Metals

Tend to be lustrous, malleable, ductile, and good conductors of heat and electricity.
Metals

- Compounds formed between metals and nonmetals tend to be ionic.
- Example: $\text{NaCl}$
- Metal oxides tend to be basic.
- Example:
  - $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2 \text{NaOH}$
Nonmetals

- Dull, brittle substances that are poor conductors of heat and electricity.
- Tend to gain electrons in reactions with metals to acquire noble gas configuration.
Nonmetals

• Substances containing only nonmetals are molecular compounds.
  ➢ Example: $\text{CO}_2$

• Most nonmetal oxides are acidic.
  ➢ Example: $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$
Metalloids

• Have some characteristics of metals, some of nonmetals.

• For instance, silicon looks shiny, but is brittle and fairly poor conductor.
7.7 Group Trends
Alkali Metals

- Soft, metallic solids.
- Name comes from Arabic word for ashes.
Alkali Metals

- Found only as **compounds** in nature.
- Have low **densities and melting points**.
- Also have low ionization energies.

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron Configuration</th>
<th>Melting Point (°C)</th>
<th>Density (g/cm³)</th>
<th>Atomic Radius (Å)</th>
<th>$I_1$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>[He]2s¹</td>
<td>181</td>
<td>0.53</td>
<td>1.34</td>
<td>520</td>
</tr>
<tr>
<td>Sodium</td>
<td>[Ne]3s¹</td>
<td>98</td>
<td>0.97</td>
<td>1.54</td>
<td>496</td>
</tr>
<tr>
<td>Potassium</td>
<td>[Ar]4s¹</td>
<td>63</td>
<td>0.86</td>
<td>1.96</td>
<td>419</td>
</tr>
<tr>
<td>Rubidium</td>
<td>[Kr]5s¹</td>
<td>39</td>
<td>1.53</td>
<td>2.11</td>
<td>403</td>
</tr>
<tr>
<td>Cesium</td>
<td>[Xe]6s¹</td>
<td>28</td>
<td>1.88</td>
<td>2.25</td>
<td>376</td>
</tr>
</tbody>
</table>
Alkali Metals

Their reactions with water are famously **exothermic**.
Alkali Metals

- Alkali metals (except Li) react with oxygen to form peroxides.
- K, Rb, and Cs also form superoxides:
  \[ K + O_2 \rightarrow KO_2 \]
- Produce bright colors when placed in flame.
## Alkaline Earth Metals

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron Configuration</th>
<th>Melting Point (°C)</th>
<th>Density (g/cm³)</th>
<th>Atomic Radius (Å)</th>
<th>I₁ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beryllium</td>
<td>[He]2s²</td>
<td>1287</td>
<td>1.85</td>
<td>0.90</td>
<td>899</td>
</tr>
<tr>
<td>Magnesium</td>
<td>[Ne]3s²</td>
<td>650</td>
<td>1.74</td>
<td>1.30</td>
<td>738</td>
</tr>
<tr>
<td>Calcium</td>
<td>[Ar]4s²</td>
<td>842</td>
<td>1.55</td>
<td>1.74</td>
<td>590</td>
</tr>
<tr>
<td>Strontium</td>
<td>[Kr]5s²</td>
<td>777</td>
<td>2.63</td>
<td>1.92</td>
<td>549</td>
</tr>
<tr>
<td>Barium</td>
<td>[Xe]6s²</td>
<td>727</td>
<td>3.51</td>
<td>1.98</td>
<td>503</td>
</tr>
</tbody>
</table>

- Have **higher** densities and melting points than alkali metals.
- Have **low** ionization energies, but not as low as alkali metals.
Alkaline Earth Metals

- Be does not react with water, Mg reacts only with steam, but others react readily with water.
- Example: \( \text{Ca} + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{H}_2 \)
- Reactivity tends to increase as you go down group.
### Group 6A

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron Configuration</th>
<th>Melting Point (°C)</th>
<th>Density</th>
<th>Atomic Radius (Å)</th>
<th>$I_1$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>[He]2$s^2$2$p^4$</td>
<td>−218</td>
<td>1.43 g/L</td>
<td>0.73</td>
<td>1314</td>
</tr>
<tr>
<td>Sulfur</td>
<td>[Ne]3$s^2$3$p^4$</td>
<td>15</td>
<td>1.96 g/cm³</td>
<td>1.02</td>
<td>1000</td>
</tr>
<tr>
<td>Selenium</td>
<td>[Ar]3$d^{10}$4$s^2$4$p^4$</td>
<td>221</td>
<td>4.82 g/cm³</td>
<td>1.16</td>
<td>941</td>
</tr>
<tr>
<td>Tellurium</td>
<td>[Kr]4$d^{10}$5$s^2$5$p^4$</td>
<td>450</td>
<td>6.24 g/cm³</td>
<td>1.35</td>
<td>869</td>
</tr>
<tr>
<td>Polonium</td>
<td>[Xe]4$f^{14}$5$d^{10}$6$s^2$6$p^4$</td>
<td>254</td>
<td>9.20 g/cm³</td>
<td>—</td>
<td>812</td>
</tr>
</tbody>
</table>

- Oxygen, sulfur, and selenium are nonmetals.
- Tellurium is a **metalloid**.
- The radioactive polonium is a metal.
Oxygen

- Two allotropes:
  - $\text{O}_2$
  - $\text{O}_3$, ozone

- Three anions:
  - $\text{O}^{2-}$, oxide
  - $\text{O}_2^{2-}$, peroxide
  - $\text{O}_2^{1-}$, superoxide

- Tends to take electrons from other elements (oxidation)
Sulfur

- Weaker oxidizing agent than oxygen.
- Most stable allotrope is $\text{S}_8$, a ringed molecule.
Group VIIA: Halogens

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron Configuration</th>
<th>Melting Point (°C)</th>
<th>Density</th>
<th>Atomic Radius (Å)</th>
<th>$I_1$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>[He]2$s^2$2$p^5$</td>
<td>−220</td>
<td>1.69 g/L</td>
<td>0.71</td>
<td>1681</td>
</tr>
<tr>
<td>Chlorine</td>
<td>[Ne]3$s^2$3$p^5$</td>
<td>−102</td>
<td>3.21 g/L</td>
<td>0.99</td>
<td>1251</td>
</tr>
<tr>
<td>Bromine</td>
<td>[Ar]3$d^{10}$4$s^2$4$p^5$</td>
<td>−7.3</td>
<td>3.12 g/cm³</td>
<td>1.14</td>
<td>1140</td>
</tr>
<tr>
<td>Iodine</td>
<td>[Kr]4$d^{10}$5$s^2$5$p^5$</td>
<td>114</td>
<td>4.94 g/cm³</td>
<td>1.33</td>
<td>1008</td>
</tr>
</tbody>
</table>

- Prototypical nonmetals
- Name comes from the Greek *halos* and *gennao*: “salt formers”
Group VIIA: Halogens

- **Large**, negative electron affinities
  - Therefore, tend to oxidize other elements easily
- React directly with metals to form metal halides
- Chlorine added to water supplies to serve as disinfectant
**Group VIII A: Noble Gases**

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron Configuration</th>
<th>Boiling Point (K)</th>
<th>Density (g/L)</th>
<th>Atomic Radius* (Å)</th>
<th>$I_I$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>$1s^2$</td>
<td>4.2</td>
<td>0.18</td>
<td>0.32</td>
<td>2372</td>
</tr>
<tr>
<td>Neon</td>
<td>[He]$2s^22p^6$</td>
<td>27.1</td>
<td>0.90</td>
<td>0.69</td>
<td>2081</td>
</tr>
<tr>
<td>Argon</td>
<td>[Ne]$3s^23p^6$</td>
<td>87.3</td>
<td>1.78</td>
<td>0.97</td>
<td>1521</td>
</tr>
<tr>
<td>Krypton</td>
<td>[Ar]$3d^{10}4s^24p^6$</td>
<td>120</td>
<td>3.75</td>
<td>1.10</td>
<td>1351</td>
</tr>
<tr>
<td>Xenon</td>
<td>[Kr]$4d^{10}5s^25p^6$</td>
<td>165</td>
<td>5.90</td>
<td>1.30</td>
<td>1170</td>
</tr>
<tr>
<td>Radon</td>
<td>[Xe]$4f^{14}5d^{10}6s^26p^6$</td>
<td>211</td>
<td>9.73</td>
<td>1.45</td>
<td>1037</td>
</tr>
</tbody>
</table>

*Only the heaviest of the noble-gas elements form chemical compounds. Thus, the atomic radii for the lighter noble-gas elements are estimated values.

- Astronomical ionization energies
- Positive electron affinities
  - Therefore, relatively **unreactive**
- Monatomic gases
Group VIII A: Noble Gases

• Xe forms three compounds:
  ➢ $\text{XeF}_2$
  ➢ $\text{XeF}_4$ (at right)
  ➢ $\text{XeF}_6$

• Kr forms only one stable compound:
  ➢ $\text{KrF}_2$

• The unstable $\text{HArF}$ was synthesized in 2000.