

Chapter 7. Periodic Properties of the Elements

Lecture Outline

7.1 Development of the Periodic Table

- The periodic table is the most significant tool that chemists use for organizing and recalling chemical facts.
- Elements in the same column contain the same number of outer-shell electrons or **valence electrons**.
- How do we organize the different elements in a meaningful way that will allow us to make predictions about undiscovered elements?
 - Arrange elements to reflect the trends in chemical and physical properties.
- The periodic table arises from the periodic patterns in the electronic configurations of the elements.
 - Elements in the same column contain the same number of valence electrons.
 - The trends within a row or column form patterns that help us make predictions about chemical properties and reactivity.
- In the first attempt Mendeleev and Meyer arranged the elements in order of increasing atomic weight.
 - Certain elements were missing from this scheme.
 - For example, in 1871 Mendeleev noted that As properly belonged underneath P and not Si, which left a missing element underneath Si. He predicted a number of properties for this element.
 - In 1886 Ge was discovered; the properties of Ge match Mendeleev's predictions well.
- In the modern periodic table, elements are arranged in order of *increasing atomic number*.

7.2 Effective Nuclear Charge

- **Effective nuclear charge** (Z_{eff}) is the charge experienced by an electron on a many-electron atom.
- The effective nuclear charge is not the same as the charge on the nucleus because of the effect of the inner electrons.
- The electron is attracted to the nucleus, but repelled by electrons that shield or screen it from the full nuclear charge.
 - This shielding is called the screening effect.
- The nuclear charge experienced by an electron depends on its distance from the nucleus and the number of electrons in the spherical volume out to the electron in question.
- As the average number of screening electrons (S) increases, the effective nuclear charge (Z_{eff}) decreases.

$$Z_{\text{eff}} = Z - S$$

- As the distance from the nucleus increases, S increases and Z_{eff} decreases.
 - S is called the *screening constant* which represents the portion of the nuclear charge that is screened from the valence electron by other electrons in the atom.
 - The value of S is usually close to the number of core electrons in an atom.

7.3 Sizes of Atoms and Ions

- Consider a collection of argon atoms in the gas phase.
 - When they undergo collisions, they ricochet apart because electron clouds cannot penetrate each other to a significant extent.
 - The *apparent* radius is determined by the closest distances separating the nuclei during such collisions.
 - This radius is the *nonbonding radius*.
- Now consider a simple diatomic molecule.
 - The distance between the two nuclei is called the **bonding atomic radius**.
 - It is shorter than the nonbonding radius.

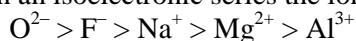
- If the two atoms that make up the molecule are the same, then half the bond distance is called the covalent radius of the atom.

Periodic Trends in Atomic Radii

- Atomic size varies consistently through the periodic table.
 - As we move down a group the atoms become larger.
 - As we move across a period atoms become smaller.
 - There are two factors at work:
 - the principal quantum number, n , and
 - the effective nuclear charge, Z_{eff} .
 - As the principal quantum number increases (i.e., we move down a group), the distance of the outermost electron from the nucleus becomes larger. Hence the atomic radius increases.
 - As we move across the periodic table, the number of core electrons remains constant, however, the nuclear charge increases. Therefore, there is an increased attraction between the nucleus and the outermost electrons. This attraction causes the atomic radius to decrease.

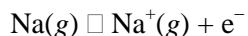
Periodic Trends in Ionic Radii

- Ionic size is important:
 - in predicting lattice energy.
 - in determining the way in which ions pack in a solid.
- Just as atomic size is periodic, ionic size is also periodic.
- In general:
 - Cations are smaller than their parent atoms.
 - Electrons have been removed from the most spatially extended orbital.
 - The effective nuclear charge has increased.
 - Therefore, the cation is smaller than the parent atom.
 - Anions are larger than their parent atoms.
 - Electrons have been added to the most spatially extended orbital.
 - This means total electron-electron repulsion has increased.
 - Therefore, anions are larger than their parent atoms.
- For ions with the same charge, ionic size increases down a group.
- All the members of an **isoelectronic series** have the same number of electrons.
 - As nuclear charge increases in an isoelectronic series the ions become smaller:



7.4 Ionization Energy

- The **ionization energy** of an atom or ion is the minimum energy required to remove an electron from the ground state of the isolated gaseous atom or ion.
- The first ionization energy, I_1 , is the amount of energy required to remove an electron from a gaseous atom:



- The second ionization energy, I_2 , is the energy required to remove the second electron from a gaseous ion:



- The larger the ionization energy, the more difficult it is to remove the electron.
- There is a sharp increase in ionization energy when a core electron is removed.

Variations in Successive Ionization Energies

- Ionization energies for an element increase in magnitude as successive electrons are removed.
 - As each successive electron is removed, more energy is required to pull an electron away from an increasingly more positive ion.
- A sharp increase in ionization energy occurs when an inner-shell electron is removed.

Periodic Trends in First Ionization Energies

- Ionization energy generally increases across a period.
 - As we move across a period, Z_{eff} increases, making it more difficult to remove an electron.
 - Two exceptions are removing the first p electron and removing the fourth p electron.
 - The s electrons are more effective at shielding than p electrons. So, forming the s^2p^0 configuration is more favorable.
 - When a second electron is placed in a p orbital, the electron-electron repulsion increases. When this electron is removed, the resulting s^2p^3 configuration is more stable than the starting s^2p^4 configuration. Therefore, there is a decrease in ionization energy.
- Ionization energy decreases down a group.
 - This means that the outermost electron is more readily removed as we go down a group.
 - As the atom gets bigger, it becomes easier to remove an electron from the most spatially extended orbital.
 - Example: for the noble gases, the ionization energies follow the order $\text{He} > \text{Ne} > \text{Ar} > \text{Kr} > \text{Xe}$
- The representative elements exhibit a larger range of values for I_1 than transition metals.

Electron Configurations of Ions

- These are derived from the electron configurations of elements with the required number of electrons added or removed from the most accessible orbital.
 - Li: $[\text{He}]2s^1$ becomes Li^+ : $[\text{He}]$
 - F: $[\text{He}]2s^22p^5$ becomes F^- : $[\text{He}]2s^22p^6 = [\text{Ar}]$
- Transition metals tend to lose the valence shell electrons first and then as many d electrons as are required to reach the desired charge on the ion.
 - Thus electrons are removed from $4s$ **before** the $3d$, etc.

7.5 Electron Affinities

- **Electron affinity** is the energy change when a gaseous atom gains an electron to form a gaseous ion.
- Electron affinity and ionization energy measure the energy changes of opposite processes.
 - Electron affinity: $\text{Cl}(g) + e^- \rightarrow \text{Cl}^-(g) \quad \infty E = -349 \text{ kJ/mol}$
 - Ionization energy: $\text{Cl}(g) \rightarrow \text{Cl}^+(g) + e^- \quad \infty E = 1251 \text{ kJ/mol}$
- Electron affinity can either be exothermic (as the above example) or endothermic:

$$\text{Ar}(g) + e^- \rightarrow \text{Ar}^-(g) \quad \infty E > 0$$
- Look at electron configurations to determine whether electron affinity is positive or negative.
 - The extra electron in Ar needs to be placed in the $4s$ orbital which is significantly higher in energy than the $3p$ orbital.
 - The added electron in Cl is placed in the $3p$ orbital to form the stable $3p^6$ electron configuration.
 - Electron affinities do not change greatly as we move down in a group.

7.6 Metals, Nonmetals and Metalloids

- **Metallic character** refers to the extent to which the element exhibits the physical and chemical properties of metals.
 - Metallic character increases down a group.
 - Metallic character decreases from left to right across a period.

Metals

- Metals are shiny and lustrous, as well as malleable and ductile.
- Metals are solids at room temperature and have very high melting temperatures (exceptions: mercury is liquid at room temperature; gallium and cesium melt just above room temperature).
- Metals tend to have low ionization energies and tend to form cations easily.
- Metals tend to be oxidized when they react.

- Compounds of metals with nonmetals tend to be ionic substances.
- Metal oxides form basic ionic solids.
 - Most metal oxides are basic:

$$\text{Metal oxide} + \text{water} \rightarrow \text{metal hydroxide}$$

$$\text{Na}_2\text{O}(s) + \text{H}_2\text{O}(l) \rightarrow 2\text{NaOH}(aq)$$
 - Metal oxides are able to react with acids to form salts and water:

$$\text{Metal oxide} + \text{acid} \rightarrow \text{salt} + \text{water}$$

$$\text{NiO}(s) + 2\text{HCl}(aq) \rightarrow \text{NiCl}_2(aq) + \text{H}_2\text{O}(l)$$

Nonmetals

- Nonmetals are more diverse in their behavior than metals.
- In general, nonmetals are nonlustrous, are poor conductors of heat and electricity, and exhibit lower melting points than metals.
- Seven nonmetallic elements exist as diatomic molecules under ordinary conditions:
 - $\text{H}_2(g)$, $\text{N}_2(g)$, $\text{O}_2(g)$, $\text{F}_2(g)$, $\text{Cl}_2(g)$, $\text{Br}_2(l)$, $\text{I}_2(s)$
- When nonmetals react with metals, nonmetals tend to gain electrons:

$$\text{Metal} + \text{nonmetal} \rightarrow \text{salt}$$

$$2\text{Al}(s) + 3\text{Br}_2(l) \rightarrow 2\text{AlBr}_3(s)$$
- Compounds composed entirely of nonmetals are molecular substances.
- Most nonmetal oxides are acidic:

$$\text{Nonmetal oxide} + \text{water} \rightarrow \text{acid}$$

$$\text{CO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{CO}_3(aq)$$

$$\text{P}_4\text{O}_{10}(s) + 6\text{H}_2\text{O}(l) \rightarrow 4\text{H}_3\text{PO}_4(aq)$$
- Nonmetal oxides react with bases to form salts and water:

$$\text{Nonmetal oxide} + \text{base} \rightarrow \text{salt} + \text{water}$$

$$\text{CO}_2(g) + 2\text{NaOH}(aq) \rightarrow \text{Na}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l)$$

Metalloids

- Metalloids have properties that are intermediate between those of metals and nonmetals.
 - Example: Si has a metallic luster but it is brittle.
- Metalloids have found fame in the semiconductor industry.

7.7 Group Trends for the Active Metals

- The **alkali metals** (group 1A) and the **alkaline earth metals** (group 2A) are often called the active metals.

Group 1A: The Alkali Metals

- The alkali metals are in Group 1A.
- Alkali metals are all soft.
- Their chemistry is dominated by the loss of their single *s* electron:

$$\text{M} \rightarrow \text{M}^+ + \text{e}^-$$
- Reactivity increases as we move down the group.
- Alkali metals react with hydrogen to form hydrides.
 - In hydrides, the hydrogen is present as H^- , called the **hydride ion**.

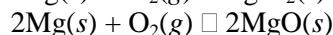
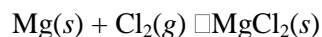
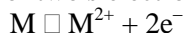
$$2\text{M}(s) + \text{H}_2(g) \rightarrow 2\text{MH}(s)$$
- Alkali metals react with water to form MOH and hydrogen gas:

$$2\text{M}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{MOH}(aq) + \text{H}_2(g)$$
- Alkali metals produce different oxides when reacting with O_2 :
 - $4\text{Li}(s) + \text{O}_2(g) \rightarrow 2\text{Li}_2\text{O}(s)$ (*oxide*)
 - $2\text{Na}(s) + \text{O}_2(g) \rightarrow \text{Na}_2\text{O}_2(s)$ (*peroxide*)
 - $\text{K}(s) + \text{O}_2(g) \rightarrow \text{KO}_2(s)$ (*superoxide*)
- Alkali metals emit characteristic colors when placed in a high-temperature flame.

- The s electron is excited by the flame and emits energy when it returns to the ground state.
- The Na line occurs at 589 nm (yellow), characteristic of the $3p \rightarrow 3s$ transition.
- The Li line is crimson red.
- The K line is lilac.

Group 2A: The Alkaline Earth Metals

- Alkaline earth metals are harder and more dense than the alkali metals.
- Their chemistry is dominated by the loss of two s electrons:



- Reactivity increases down the group.
 - Be does not react with water.
 - Mg will only react with steam.
 - Ca and the elements below it react with water at room temperature as follows:



7.8 Group Trends for Selected Nonmetals

Hydrogen

- Hydrogen is a unique element.
- It most often occurs as a colorless diatomic gas, H_2 .
- Reactions between hydrogen and nonmetals can be very exothermic:

$$2H_2(g) + 2O_2(g) \rightarrow 2H_2O(l) \quad \Delta H^\circ = -571.7 \text{ kJ}$$
- It can either gain another electron to form the hydride ion, H^{-} , or lose its electron to become H^{+} :

$$2Na(s) + H_2(g) \rightarrow 2NaH(s)$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$
- H^{+} is a proton.
- The aqueous chemistry of hydrogen is dominated by $H^{+}(aq)$.

Group 6A: The Oxygen Group

- As we move down the group the metallic character increases.
 - O_2 is a gas, Te is a metalloid, Po is a metal.
- There are two important forms of oxygen: O_2 and **ozone**, O_3 .
 - O_2 and O_3 are allotropes.
 - Allotropes are different forms of the same element in the same state (in this case, gaseous).
 - Ozone can be prepared from oxygen:

$$3O_2(g) \rightarrow 2O_3(g) \quad \Delta H^\circ = +284.6 \text{ kJ}$$
 - Ozone is pungent and toxic.
 - Oxygen (or dioxygen, O_2) is a potent oxidizing agent since the O^{2-} ion has a noble gas configuration.
- There are two oxidation states for oxygen: -2 (e.g., H_2O) and -1 (e.g., H_2O_2).
- Sulfur is another important member of this group.
 - The most common form of sulfur is yellow S_8 .
 - Sulfur tends to form S^{2-} in compounds (sulfides).

Group 7A: The Halogens

- Group 7A elements are known as the **halogens** ("salt formers").
- The chemistry of the halogens is dominated by gaining an electron to form an anion:

$$X_2 + 2e^{-} \rightarrow 2X^{-}$$
- Fluorine is one of the most reactive substances known:

$$2F_2(g) + 2H_2O(l) \rightarrow 4HF(aq) + O_2(g) \quad \Delta H = -758.9 \text{ kJ}$$
- All halogens consist of diatomic molecules, X_2 .

- Chlorine is the most industrially useful halogen.
- The reaction between chlorine and water produces hypochlorous acid (HOCl), which is used to disinfect swimming pool water:



- Halogens react with hydrogen to form gaseous hydrogen halide compounds:
$$\text{H}_2(g) + \text{X}_2 \rightleftharpoons 2\text{HX}(g)$$
- Hydrogen compounds of the halogens are all strong acids with the exception of HF.

Group 8A: The Noble Gases

- The group 8A elements are known as the **noble gases**.
 - These are all nonmetals and monoatomic.
 - They are notoriously unreactive because they have completely filled *s* and *p* subshells.
- In 1962 the first compounds of the noble gases were prepared: XeF₂, XeF₄, and XeF₆.