

7.1 Development of the Periodic Table

- The majority of the elements were discovered between 1735 and 1843.
 - Discovery of new elements in an ongoing process.
- How do we organize the different elements in a meaningful way so that we 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.
 - 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.
- Modern periodic table: Elements are arranged in order of *increasing atomic number*.

7.2 Electron Shells and the Sizes of Atoms

Electron Shells in Atoms

- As we move down the periodic table, the principal quantum number (n) of the valence shell increases.
- The distribution of electrons in an atom may be represented with a *radial electron density graph*.
 - Radial electron density is the probability of finding an electron at a particular distance from the nucleus.
 - The maxima in the plot of radial electron density against distance give the distance where it is most likely to find electrons.
 - The electron shells are diffuse and overlap a great deal.
- Look at a few elements:
 - He: $1s^2$
 - Ne: $1s^22s^22p^6$
 - Ar: $1s^22s^22p^63s^23p^6$
 - The radial plots show one maximum for He (1 s electrons), two for Ne (one due to 1 s electron and one for both 2 s and 2 p electrons), and three for Ar (one for 1 s electrons, one for 2 s and 2 p electrons, and one for 3 s and 3 p electrons).

Atomic Sizes

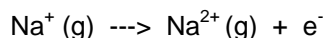
- Consider a collection of argon atoms in the gas phase.
 - When they undergo collisions, they ricochet apart because electron clouds cannot penetrate one another to a significant extent.
 - The *apparent* radii are determined by the closest distances separating the nuclei during such collisions.
 - This radius is the *nonbonding radius*.
- Now consider a simple diatomic molecule.
 - The distance between the two nuclei is called the bond distance.
 - If the two atoms making up the molecules are the same, then half the bond distance is called the *bonding atomic radius* of the atom.
 - It is shorter than the nonbonding radius.
- Atomic size varies consistently through the periodic table.
 - As we move down a group the atoms become larger (increased shielding effect).
 - As we move across a period atoms become smaller (greater coulombic attraction).
 - 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.

7.3 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 an electron from a gaseous ion:



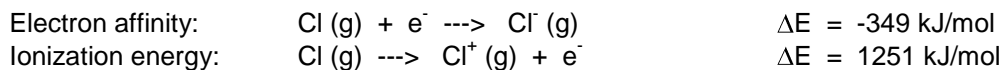
- The larger the ionization energy, the more difficult it is to remove the electron.
- There is a sharp increase in ionization energy when a core electron is removed.

Periodic Trends in Ionization Energy

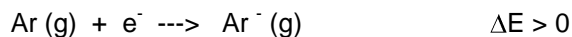
- Ionization energy decreases down a group.
 - This means that the outermost electron is more readily removed as we go down a group.
 - As the atom gets bigger, it becomes easier to remove an electron from the most spatially extended orbital.
 - Example: For the noble gases the ionization energies follow the order $\text{He} > \text{Ne} > \text{Ar} > \text{Kr} > \text{Xe}$
- 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: 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 becomes more favorable.
 - When a second electron is placed in a p orbital, the electron-electron repulsion increases. When this electron is removed, there is less electron-electron repulsion in the resulting s^2p^3 configuration than in the starting s^2p^4 configuration. Therefore, there is a decrease in ionization energy.

7.4 Electron Affinities

- **Electron affinity** is the energy change when a gaseous atom gains an electron to form a gaseous ion.
- The ionization energy required to remove an electron from the ground state of a gaseous atom while the electron affinity is the energy required to add an electron to a gaseous atom.



- Electron affinity can either be exothermic (as the above example) or endothermic.



- Look at the 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 3p⁶ electron configuration.
- Electron affinities do not change greatly as we move down a group.

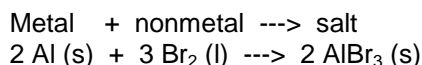
7.5 Metals, Nonmetals, and Metalloids

Metals

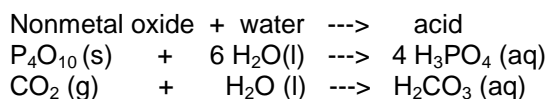
- **Metallic character** refers to the extent to which the element exhibits the physical and chemical properties of metals.
 - Metallic character increases down a group.
 - Metallic character decreases from left to right across a period.
- In general,
 - Metals are shiny and lustrous, malleable, and ductile.
 - Their oxides form basic ionic solids.
 - Most metal oxides are basic:
Metal oxide + water \rightarrow 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:
metal oxide + acid \rightarrow salt + water
 $\text{MgO (s)} + 2 \text{HCl (aq)} \rightarrow \text{MgCl}_2 \text{ (aq)} + \text{H}_2\text{O (l)}$
- Most neutral metals are oxidized rather than reduced.
 - When metals are oxidized they tend to form characteristic cations.
 - All group 1A metals form M^{1+} ions.
 - All group 2A metals form M^{2+} ions.
 - Most transition metals have variable charges.
 - Metals have low ionization energies.

Nonmetals

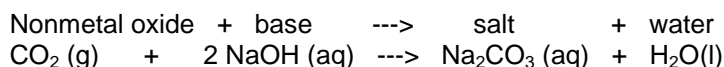
- Nonmetals are more diverse in their behavior than metals.
- In general, nonmetals are nonlustrous, are poor conductors of heat and electricity, and exhibit lower melting points than those of metals.
- Seven nonmetallic elements exist as diatomic molecules under ordinary conditions:
 $\text{H}_2 \text{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



- Most nonmetal oxides are acidic.



- Nonmetal oxides react with bases to form salts and water:



Metalloids

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

7.6 Group Trends for 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 the single s electron:
$$M \rightarrow M^+ + e^-$$
- Reactivity increases down the group.
- Alkali metals react with hydrogen to form hydrides.
 - In hydrides, the hydrogen is present as H^- , called the **hydride ion**.
$$2 M (s) + H_2 (g) \rightarrow 2 MH (s)$$
- Alkali metals react with water to form MOH and hydrogen gas:
$$2 M (s) + 2 H_2O (l) \rightarrow 2 MOH (aq) + H_2 (g)$$
- Alkali metals produce different oxides when reacting with O_2 :
 - Lithium reacts with oxygen to form the oxide:
$$4 Li (s) + O_2 (g) \rightarrow 2 Li_2O (s)$$
 - Sodium, potassium, rubidium and cesium react with oxygen to give peroxides:
$$2 Na (s) + O_2 (g) \rightarrow Na_2O_2 (s)$$
 - Potassium, rubidium and cesium also react with oxygen to give superoxides:
$$K (s) + O_2 (g) \rightarrow KO_2 (s)$$
- 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 ($2p \rightarrow 2s$ transition).
 - The K line is lilac ($4p \rightarrow 4s$ transition).

Group 2A: The Alkaline Earth Metals

- Alkaline earth metals are harder and denser than the alkali metals.
- Their chemistry is dominated by the loss of two s electrons:
$$M \rightarrow M^{2+} + 2e^-$$

$$Mg (s) + Cl_2 (g) \rightarrow MgCl_2 (s)$$

$$2 Mg (s) + O_2 (g) \rightarrow 2 MgO (s)$$
- Reactivity increases down the group.
 - Be does not react with water.
 - Mg will react only with steam.
 - Ca and the elements below it react with water at room temperature as follows:
$$Ca (s) + 2 H_2O (l) \rightarrow Ca(OH)_2 (aq) + H_2 (g)$$

7.7 Group Trends for Selected Nonmetals

Hydrogen

- Hydrogen is a unique element.
- It most often occurs as a colorless diatomic gas, H₂.
- It can gain another electron to form the hydride ion, H¹⁻, or lose its electron to become H¹⁺:
$$2 \text{Na (s)} + \text{H}_2 \text{(g)} \rightarrow 2 \text{NaOH (s)}$$
$$2 \text{H}_2 \text{(g)} + \text{O}_2 \text{(g)} \rightarrow 2 \text{H}_2\text{O (l)}$$
- H¹⁺ is a proton.
- The aqueous chemistry of hydrogen is dominated by H¹⁺(aq).

Group 6A: The Oxygen Group

- As we move down the group the metallic character increases
 - O₂ is a gas, Te is a metalloid, Po is a metal
- There are two important forms of oxygen: O₂ and O₃.
 - O₂ and O₃ are allotropes.
 - Allotropes are different forms of the same element in the same state (in this case, gaseous)
 - Ozone can be prepared from oxygen
$$3 \text{O}_2 \text{(g)} \rightarrow 2 \text{O}_3 \text{(g)} \quad \Delta H = +284.6 \text{ kJ}$$
 - Ozone is pungent and toxic.
 - Oxygen (or dioxygen, O₂) is a potent oxidizing agent because the O²⁻ ion has a noble gas configuration.
- Oxygen has two oxidation states: -2 (e.g., H₂O) and -1 (e.g., H₂O₂).
- Sulfur is another important member of this group.

Group 7A: The Halogens

- Group 7A elements are known as the **halogens**.
- The chemistry of the halogens is dominated by the gain of an electron to form an anion:
$$\text{X}_2 + 2\text{e}^- \rightarrow 2 \text{X}^{1-}$$
- Fluorine is one of the most reactive substances known:
$$2 \text{F}_2 \text{(g)} + 2 \text{H}_2\text{O (l)} \rightarrow 4 \text{HF (aq)} + \text{O}_2 \text{(g)} \quad \Delta H = -758.7 \text{ kJ}$$
- All halogens consist of diatomic molecules, X₂.
- Chlorine is the most industrially useful halogen. It is produced by the electrolysis of brine (NaCl):
$$2 \text{NaCl (aq)} + 2 \text{H}_2\text{O (l)} \rightarrow 2 \text{NaOH (aq)} + \text{H}_2 \text{(g)} + \text{Cl}_2 \text{(g)}$$
- The reaction between chlorine and water produces hypochlorous acid (HOCl), which is used to disinfect swimming pool water:
$$\text{Cl}_2 \text{(g)} + \text{H}_2\text{O (l)} \rightarrow \text{HCl (aq)} + \text{HOCl (aq)}$$
- 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**.
 - They are all nonmetals and monatomic.
 - 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.