Chapter 7
Periodic Properties of the Elements

- The periodic table is one of the most useful tools available to chemists.
- Elements are arranged to emphasize the similarities and variations in properties.
- We will examine some of the properties of the elements and see how these properties are related to the electron configurations of the elements.

7.1 Development of the Periodic Table

- There were 114 elements known by 1999.
- The majority of the elements were discovered between 1735 and 1843.
- How do we organize 114 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.
- First attempt (Mendeleev and Meyer) arranged the elements in order of increasing atomic weight.

Periodic Trends

- KC? Discoverer: investigation of trends (available in the Learning Resource Center)
  density
  melting point
  atomic volume
  atomic radius

7.2 Electron Shells and the Sizes of Atoms

- As the principal quantum number increases, the size of the orbital increases.
- All s orbitals are spherical and increase in size as n increases.
- The distribution of electrons in an atom can be represented with a radial electron density graph, which shows the probability of finding an electron at a particular distance from the nucleus.

Electron Shells in Atoms

- The ns orbitals all have the same shape, but have different sizes and different numbers of nodes.
- Consider:
  He: $1s^2$
  Ne: $1s^2\ 2s^2 2p^6$
  Ar: $1s^2\ 2s^2 2p^6\ 3s^2 3p^6$

Radial Electron-Density Graphs

- The radial electron density is the probability of finding an electron at a given distance.
- For He there is only one maximum (for the two 1s electrons).
- For Ne there are two maxima: one largely for the 1s electrons (close to the nucleus) and one largely for the n = 2 electrons (further from the nucleus).

- For Ar there are three maxima: one each largely for n = 1, 2, and 3.
- The maxima give the distance where it is most likely to find electrons with the different principal quantum number (shells).
- These electron shells are diffuse and overlap a great deal.
- These graphs illustrate one of the factors that affect the properties of the elements - the nuclear charge.

Periodic Properties of the Elements

- Properties of atoms correlate with three properties related to electronic configuration:
  - Nuclear Charge
  - Pairing Energy
  - Shielding Effect: effective nuclear charge is essentially the nuclear charge less the number of inner electrons

Atomic Sizes

- The edges of atoms are fuzzy, so size is difficult to measure. Can measure interatomic distances in molecules or between molecules during collisions. These give somewhat different results.
  - bonding or covalent radius
  - metallic radius
  - nonbonding radius

Atomic and Ionic Size

- Measure metallic or covalent radii by diffraction of X-rays

Trends in Size

- What trends would be expected in atomic or ionic size?
- Decreases across a period, increases down a group (See KC? Discoverer)
- Explain in terms of the three factors

Trends in Atomic Radius

- Which member of each pair has the greater atomic radius? Why?
  - F or Cl
  - N or O
  - O or F
  - Na or Mg
  - K or Na

Trends in Ionic Radius (pm)

- See Section 8.3
- Compare isoelectronic series of ions to see the effect of the factors
- Which is larger?
  - Be^{2+} or B^{3+}
  - Al^{3+} or P^{3-}

- Ca^{2+} or Mg^{2+}
- K or Ca
- O^{2-} or F^{-}

7.3 Ionization Energy
- El(g) → El^{+}(g) + e^{-} 1st IE
- El^{+}(g) → El^{2+}(g) + e^{-} 2nd IE
- Which would require the most energy? Why?
- See values in Table 7.2
- Note that there is a sudden jump after some of the electrons are removed. At which electron will this occur for a specific element? Why?

Trends in Ionization Energy
- The 2nd ionization energy is greater than the 1st ionization energy by nearly a constant proportion. Certain elements show a much greater increase. Which elements are these?
- See KC Discoverer
- Which elements have an unusually high ratio of 3rd IE to 2nd IE? ... 3rd IE to 1st IE?

Which element is this?
- Ionization energy plotted against the number of electrons removed.
- Explain trends in terms of three factors

Trends in First Ionization Energy
- Trends mirror trends in metallic character
- Which member of each pair has the greater first ionization energy? Why?
  - Na or Na^{+}
  - F or Cl
  - N or O
  - O or F
  - Na or Mg
  - K or Na

7.4 Electron Affinities
- El(g) + e^{-} → El^{-}(g)
- Also can have successive values for addition of more electrons
- Negative values indicate that energy is released
- The largest negative values occur for the halogens
- The most non-metallic elements have the most negative values

7.5 Metals, Nonmetals, and Metalloids
- Elements can be grouped into three broad categories: metals, nonmetals, and metalloids.
- These categories are primarily established by the electrical conductivity of the elements:
  - metals: electrical conductors

  - nonmetals: electrical insulators
  - metalloids: semiconductors
- Elements of a type are grouped together in the periodic table

Metals

- Metallic character refers to the properties of metals (shiny or lustrous, malleable and ductile, oxides form basic ionic solids, and tend to form cations in aqueous solution).
- Metallic character increases down a group and decreases across a period.
- Metals have low ionization energies.
- Most neutral metals are oxidized rather than reduced.
- When metals are oxidized they tend to form characteristics cations.
  - All group 1A metals form M^+ ions.
  - All group 2A metals form M^{2+} ions.
  - Most transition metals have variable charges.
- Most metal oxides are basic:
  - Metal oxide + water $\rightarrow$ metal hydroxide
  - $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$

Nonmetals

- Nonmetals are more diverse in their behavior than metals.
- When nonmetals react with metals, nonmetals tend to gain electrons:
  - metal + nonmetal $\rightarrow$ salt
  - $2Al(s) + 3Br_2(l) \rightarrow 2AlBr_3(s)$
- Most nonmetal oxides are acidic:
  - nonmetal oxide + water $\rightarrow$ acid
  - $P_4O_{10}(s) + H_2O(l) \rightarrow 4H_3PO_4(aq)$

Metalloids

- Example: Si has a metallic luster but it is brittle.
- Metalloids are useful in the semiconductor industry.

7.6 Group Trends for the Active Metals

- Correlates with position in periodic table, electronic configuration, ionization energy, electron affinity
- Alkali Metals: Group 1A in the periodic table
- Alkali metals are all soft.
- Their chemistry is characterized by loss of one electron: $M \rightarrow M^+ + e^-$
- They combine directly with most nonmetals: $2Na + Cl_2 \rightarrow 2NaCl$
- They react with water to form MOH and H_2: $2Na + 2H_2O \rightarrow 2NaOH + H_2$
- Reaction with oxygen gives oxides (Li), peroxides (Na, K, Rb, Cs) and superoxides (K, Rb, Cs)
- What trends would be predicted for the reaction of the alkali metals with air or water?

Alkaline Earth Metals

- Harder and denser than the alkali metals
- Their chemistry is characterized by loss of two electrons: $M \rightarrow M^{2+} + 2e^-$
- Be does not react with water. Mg will only react with steam. Ca, Sr, Ba react with water:
  $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$

7.7 Group Trends for Selected Nonmetals

- <u>Hydrogen</u>
- Hydrogen is a unique element.
- Most often occurs as a colorless diatomic gas, H_2.
- It can either gain another electron to form the hydride ion, H^-, or lose its electron to become H^+:
  $2Na(s) + H_2(g) \rightarrow 2NaH(s)$
  $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

Group 6A: The Oxygen Group

- <u>O, S, Se, Te, Po</u>
- Trend that affects other properties is the increase in metallic character down the group, indicated by the decreases in ionization energy and electronegativity
- Nonmetallic character dominates in this group
- Nonmetallic O exists as diatomic molecules (O_2) and as ozone (O_3)
- Nonmetallic S exists as various covalently bonded polyatomic forms
- Metalloids Se and Te are more metallic than S, but bear some resemblance to S, which exists primarily as S_8
- Po is even more metallic, but its behavior is not well known since it is a rare, radioactive element

Group 7A: The Halogens

- 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:
  $2F_2(g) + 2H_2O(l) \rightarrow 4HF(aq) + O_2(g) \quad \Delta H = -758.7 \text{ kJ}$.
- All halogens consists of diatomic molecules, X_2.
- Chlorine is the most industrially useful halogen. It is produced by the electrolysis of brine (NaCl):
  $2NaCl(aq) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) + Cl_2(g)$.
- The reaction between chlorine and water produces hypochlorous acid (HOCl) which disinfects pool water:
  $Cl_2(g) + H_2O(l) \rightarrow HCl(aq) + HOCl(aq)$.
- Hydrogen compounds of the halogens are all strong acids with the exception of HF.

Group 8A: The Noble Gases

- These are all nonmetals and monatomic.
- They are notoriously unreactive because they have completely filled s and p subshells.
- In 1962 the first compound of the noble gases was prepared: XeF_2, XeF_4, and XeF_6.
- To date the only other noble gas compound known is KrF_2.