Chapter 5 Notes Chemistry; The Periodic Law

The Periodic Table

- **The periodic table** is used to organize the elements in a meaningful way.
- As a consequence of this organization, there are periodic properties associated with the periodic table.
- Columns in the periodic table are called **groups.**
  - Several numbering conventions are used(i.e. groups may be numbered from 1 to 18, or from 1A to 8A and 1B to 8B).
- Rows in the periodic table are called **periods.**
- Some of the groups in the periodic table are given special names.
  - These names indicate the similarities between group members.
  - Examples:
    - Group 1A: Alkali metals
    - Group 2A: Alkaline earth metals
    - Groups 3-12: Transition metals
    - Group 17 (7A): Halogens
    - Group 18 (8A): Noble Gases
- **Metallic elements** are located on the left-hand side of the periodic table (most of the elements are metals).
- **Nonmetallic elements** are located in the top right-hand side of the periodic table.
- Elements with properties similar to both metals and nonmetals are called **metalloids** and are located at the interface between the metals and nonmetals.
  - These include the elements B,Si,Ge,As,Sb and Te.
- Metals tend to be malleable, ductile, and lustrous and are good thermal and electrical conductors. Nonmetals generally lack these properties; they tend to be brittle as solids, dull in appearance, and do not conduct heat or electricity well.

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.**
- The majority of the elements were discovered between 1735 and 1843.
  - Discovery of new elements is an ongoing process.
- 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.
  - 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 1186 Ge was discovered; the properties of Ge match Mendeleev's predictions well.
- Modern periodic table: elements are arranged in order of *increasing atomic number.*

Effective Nuclear Charge

- **Effective nuclear charge** is the net positive 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 the inner-shell electrons that shield or screen it from 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.
- As the distance from the nucleus increases, S increases and (Z_{eff}) decreases. (Z_{eff}) = Z – S

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 simply 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 which make up the molecule are the same, then half the bonding 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 causes the atomic radius to decrease.

Trends in the Sizes of Ions

- 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 (positive ions) are smaller than their parent atom.

        - Electrons have been removed from the most spatially extended orbital.
        - The effective nuclear charge has been increased.
        - Therefore, the cation is smaller than the parent atom.
    - Anions (negative ions) are larger then their parent atom.
        - 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 members of an **isoelectric series** have the same number of electrons.
    - As nuclear charge increases in an isoelectronic series the ions become smaller:
      O^{-2}>F->Na+>Mg+2>Al+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: Na(g) → Na+(g) + e-
- The second ionization energy, I_2, is the energy required to remove the second electron from a gaseous ion: Na+(g) → Na+2 (g) + e-
- 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 First Ionization Energies

- 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 get 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
          He > Ne > Ar > Kr > 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.

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 = [He]$2s^1$ becomes Li- = [He]
    - F = [He] $2s^2$ $2p^5$ becomes F- = [He] $2s^2$ $2p^6$ =[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 4*s* **before** the 3*d*, etc.

Electron Configuration of Ions of the Representative Elements

- These are derived from the electron configuration of elements with the required number of electrons added or removed from the most accessible orbital.
- Electron configuration of ions can predict stable ion formation:
    - Na = [Ne] $3s^1$
    - Na+ = [Ne]
    - Cl = [Ne] $3s^2$ $3p^5$
    - Cl- = [Ne] $3s^2$ $3p^6$ = [Ar]

Transition-Metal Ions

- Lattice energies compensate for the loss of up to three electrons.
- We often encounter cations with charges of 1+, 2+, or 3+ in ionic compounds.
- However, transition metals can't attain a noble gas conformation (>3 electrons beyond a noble gas core).
  - 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 4*s* **before** the 3*d*, etc.

Polyatomic Ions

- Polyatomic ions are formed when there is an overall charge on a compound containing covalent bonds.
  - Examples: $SO_{4\,(-2)}$, NO_3-
- In polyatomic ions, two or more atoms are bound together by predominantly covalent bonds.
  - The stable grouping carries a charge.

Electron Affinities

- **Electron affinity** is the energy change when a gaseous atom gains an electron to form a gaseous ion:
  - Electron affinity: Cl(g) +e- → Cl-(g)
  - Ionization energy: Cl(g) → Cl+(g) + e-
- Electron affinities do not change greatly as we move down in a group.

Electronegativity

- The ability of an atom *in a molecule* to attract electrons to itself is its **electronegativity.**
- The electronegativity of an element is related to its ionization energy and electron affinity.
- Pauling electronegativity scale: from 0.7 (Cs) to 4.0 (F).
- Electronegativity increases across a period and decreases down a group.

Electronegativity and Bond Polarity

- Electronegativity differences close to zero result in nonpolar covalent bonds.
  - The electrons are equally or almost equally shared.
- The greater the difference in electronegativity between two atoms, the more polar the bond (polar covalent bonds).
- There is no sharp distinction between bonding types.

Metal, Nonmetals and Metalloids

Metals

- Metals are shiny and lustrous, malleable and ductile.
- Metals are solids at room temperature (exception: mercury is a liquid at room temperature; gallium and cesium melt just above room temperature) and have very high melting temperatures.
- Metals tend to have low ionization energies and tend to form **cations** easily.
- Compounds of metals and nonmetals tend to be ionic substances.
- Metal oxides form basic ionic solids.

Nonmetals

- Nonmetals are more diverse in their behavior than metals.
- In general, nonmetals are non lustrous, are poor conductors of heat and electricity, and exhibit lower melting points than metals.
- Seven nonmetallic elements exist as diatomic molecules under ordinary conditions:
  - H_2(g), N_2(g), O_2(g), F_2(g), Cl_2(g), Br_2(g), I_2(g)
- Metal + nonmetal → salt

- $2Al(s) + 3Br_2(l) \rightarrow 2AlBr_3(s)$
- Compounds composed entirely of nonmetals are molecular substances (**molecules).**

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.