Chapter 7
Periodic Properties
of the Elements

Development of Periodic Table

- Elements in the same group generally have similar chemical properties.
- 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.

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_{eff}, is found this way:

$Z_{eff} = Z - S$

where Z is the atomic number and S is a screening constant, usually close to the number of inner electrons.

Sizes of Atoms

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

Bonding atomic radius tends to…

…decrease from left to right across a row due to increasing Z_{eff}.

…increase from top to bottom of a column due to increasing value of n

Sizes of Ions

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

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*.

Sizes of Ions

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

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.

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_{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_{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.

Electron Affinity

Energy change accompanying addition of electron to gaseous atom:

$Cl + e^- \longrightarrow Cl^-$

Trends in Electron Affinity

In general, electron affinity becomes more exothermic as you go from left to right across a row.

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.
  - ➢Properties of Metal, Nonmetals,

and Metalloids

Metals versus Nonmetals

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

Metals versus Nonmetals

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

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.
- Metal oxides tend to be basic.

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.
- Substances containing only nonmetals are molecular compounds.
- Most nonmetal oxides are acidic.

Metalloids

- Have some characteristics of metals, some of nonmetals.
- For instance, silicon looks shiny, but is brittle and fairly poor conductor.

Group Trends

Alkali Metals

- Soft, metallic solids.
- Name comes from Arabic word for ashes.
- Found only as compounds in nature.
- Have low densities and melting points.
- Also have low ionization energies.

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Their reactions with water are famously exothermic.

- Alkali metals (except Li) react with oxygen to form peroxides.
- K, Rb, and Cs also form superoxides:

$K + O_2 \longrightarrow KO_2$

- Produce bright colors when placed in flame.

Alkaline Earth Metals

- Have higher densities and melting points than alkali metals.
- Have low ionization energies, but not as low as alkali metals.
- Be does not react with water, Mg reacts only with steam, but others react readily with water.
- Reactivity tends to increase as go down group.

Group 6A

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

Oxygen

- Two allotropes:
  - ➢O_2
  - ➢O_3, ozone
- Three anions:
  - ➢O^{2-}, oxide
  - ➢O_2^{2-}, peroxide
  - ➢O_2^{1-}, superoxide
- Tends to take electrons from other elements (oxidation)

Sulfur

- Weaker oxidizing agent than oxygen.
- Most stable allotrope is S_8, a ringed molecule.

Group VIIA: Halogens

- 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 VIIIA: Noble Gases
- Astronomical ionization energies
- Positive electron affinities
  - Therefore, relatively unreactive
- Monatomic gases

Group VIIIA: Noble Gases

- Xe forms three compounds:
  - XeF_2
  - XeF_4 (at right)
  - XeF_6
- Kr forms only one stable compound:
  - KrF_2
- The unstable HArF was synthesized in 2000.