

Lecture Outline - Chapter 7.

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.
- 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. **SHOW SLIDE**

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*.
 - Nonbonding atomic radii are also called *van der Waals radii*.
 - These are used in space-filling models to represent the sizes of different elements.

SHOW ACS website.

- Now consider a simple diatomic molecule. Br_2
 - 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 bond distance is called the covalent radius of the atom.

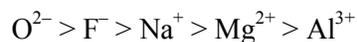
Periodic Trends in Atomic Radii

- Atomic size varies consistently through the periodic table.

- As we move down a group the atoms become larger. **Slide 4**
- 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 **Slide 5**

- Ionic size is important:
 - in predicting lattice energy and
 - 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:



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 (slide 8)

- 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:
He > Ne > Ar > Kr > Xe
- The representative elements exhibit a larger range of values for I_1 than transition metals.

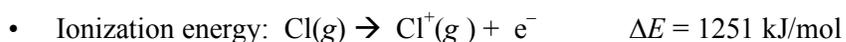
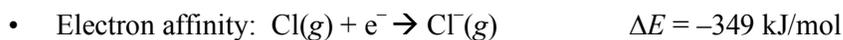
Electron Configurations of Ions

- 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.
- In other words, when writing electron configurations of transition metal cations, the order of removal of electrons is **not** exactly opposite to the order in which subshells were occupied when an electron configuration of the parent atom was written.

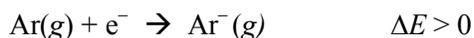
Draw and Aufbau diagram for electron configuration or ions and Electron Affinities

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 can either be exothermic (as the above example) or endothermic:



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