

## CHAPTER 6

### IONIC BONDS AND SOME MAIN-GROUP CHEMISTRY

#### Chapter Learning Goals

- Section 6.1** Predict the ground-state electron configuration for ions.
- Section 6.2** Given a set of atoms and ions, determine which atom or ion is expected to have the largest radius.
- Section 6.3** For any two elements, predict which has the higher first ionization energy.
- Section 6.4** For any two elements, predict which has the higher second, third, fourth, etc. ionization energy.
- Section 6.5** For any two elements, predict which has the more favorable (more negative) electron affinity.
- Section 6.6** Identify the energies involved in a Born-Haber calculation of lattice energy. Know whether these energies are positive or negative, large or small. Given all other energies, use the Born-Haber cycle to calculate the remaining energy in the cycle.
- Section 6.7** On the basis of ionic charges and ionic radii, predict which of two ionic compounds should have the greater lattice energy.
- Section 6.8** Use the octet rule to generalize the chemistry of each family of elements studied in this chapter. Know when to expect the octet rule to be valid and when it can fail. Give the noble gas configuration of cations and anions in ionic compounds. Use the octet rule to determine the number of electrons gained or lost by a given element in a redox reaction.
- Section 6.9** Know which alkali metals form 1) oxides, 2) peroxides, and 3) superoxides upon reaction with oxygen. Assign oxidation numbers to the oxygen atoms in these compounds. Give the formulas of products formed when alkali metals react with halogens, hydrogen, nitrogen, oxygen, water, or ammonia. Balance the equations.
- Section 6.10** Know which alkaline earth metals form 1) oxides, 2) peroxides, and 3) superoxides upon reaction with oxygen. Assign oxidation numbers to the oxygen atoms in these compounds. Give the formulas of products formed when alkaline earth metals react with halogens, hydrogen, oxygen, or water. Balance the equations.
- Section 6.11** Give the formulas of products formed when aluminum reacts with halogens, nitrogen, oxygen, acids, or bases. Balance the equations.
- Section 6.12** Give the formulas of products formed when halogens react with metals, hydrogen, or other halogens.
- Section 6.13** Give the formulas of products formed when noble gases react with metals, hydrogen, or other halogens. Assign oxidation numbers to elements in noble gas compounds. Balance redox equations representing reactions studied throughout this chapter. Identify which species are oxidized and which are reduced and which elements have undergone a change in oxidation state.

## Lecture Outline

### 6.1. Ions and Their Electron Configuration

- A. Main-group elements - Electrons are always lost from orbitals having the highest value of principal quantum number,  $n$ , before they are lost from orbitals with lower values of  $n$ .
  1. Electrons lost by a metal come from the highest-energy occupied orbital
  2. Electrons gained by a nonmetal go into lowest-energy unoccupied orbital
- B. Transition metals – lose valence-shell  $s$  electrons first, then  $d$  electrons

### 6.2. Ionic Radii - The larger the proton-to-electron ratio, the greater the attraction of the nucleus for the valence electrons and the smaller the size of the ion.

- A. Cations have smaller radii than neutral atoms
  1. Electrons removed from larger valence-shell orbitals
  2. Increase in  $Z_{\text{eff}}$  when electrons removed
- B. Anions have larger radii than neutral atoms
  1. Decrease in  $Z_{\text{eff}}$  when electrons added
  2. Increase in electron-electron repulsions

### 6.3. Ionization Energy

- A. Ionization energy ( $E_i$ ) – amount of energy required to remove the outermost electron from an isolated neutral atom in the gaseous state
- B. Periodic trends in ionization energy - Core electrons shield valence electrons effectively; electrons in the same shell shield one another ineffectively.
  1. Minimum  $E_i$  – group 1A alkali metals
  2. Maximum  $E_i$  – group 8A noble gases
  3.  $E_i$  increases across a period
  4.  $E_i$  decreases down a group. The closer an electron is to the nucleus, the higher its ionization energy. Hence, small atoms have high ionization energies. Due to its small size, the first element in every group tends to differ significantly from the other elements in the same group.
- C. Periodicity due to electron configurations
  1. Single  $s$  electron in valence-shell of alkali metals feels low  $Z_{\text{eff}}$ 
    - a. Single valence electron well shielded by the core (inner-shell) electrons.
    - b. Electron loosely held.
    - c. Low energy needed to remove electron
  2. Electrons in filled valence-subshell of noble gas elements feel high  $Z_{\text{eff}}$ 
    - a. Electrons tightly held
    - b. Radius of atom shrinks
    - c. High energy needed to remove electron
  3. Increase in atomic number down a group
    - a. Average distance of the electron from the nucleus increases as the value of  $n$  increases.
    - b. Valence-shell electrons less tightly held than core electrons
    - c.  $E_i$  decreases
- D. Minor irregularities occur from left to right across a row of the periodic table
  1. Group 2A elements –  $E_i(\text{Be}) > E_i(\text{B})$  (due to electron configuration)
    - a.  $2p$  electron of boron shielded somewhat by  $2s$  electrons
    - b. Feels a smaller  $Z_{\text{eff}}$
    - c. More easily removed
  2. Group 6 A elements –  $E_i(\text{N}) > E_i(\text{O})$  (due to electron configuration)
    - a.  $2p$  electron removed from nitrogen removed from a half-filled orbital (stable configuration)
    - b.  $2p$  electron removed from oxygen removed from a filled orbital
      - i. Electrons in filled orbitals forced together and have slightly higher energy
      - ii. Easier to remove electrons from filled orbitals

### 6.4. Higher Ionization Energies

- A. Energy involved with the removal of two, three, or even more electrons sequentially from an atom

- B. Successively larger amounts of energy required for each ionization step – more difficult to remove a negatively charged electron from a positively charged ion
- C. Large jumps in successive ionization energies of the elements – textbook Table 6.2
  - 1. Valence-shell electrons easily lost during ionization
  - 2. Core electrons relatively difficult to remove
- D. Valence-shell electron configuration of an atom controls its chemistry.

### 6.5. Electron Affinity

- A. Electron affinity ( $E_{ea}$ ) – energy change when electron added to an isolated gaseous atom
- B.  $E_{ea}$  usually has a negative value
  - 1. Energy usually released when an atom adds an electron
  - 2. More negative the value,
    - a. greater the tendency of the atom to accept an electron
    - b. more stable the anion
- C.  $E_{ea} > 0$  for atoms that form an unstable anion on addition of an electron
- D. No experimental measurements can be made.
- E. Periodic trends of  $E_{ea}$  related to electron configurations
  - 1. Sign and magnitude of  $E_{ea}$  due to offsetting factors
    - a. Negative  $E_{ea}$  due to attraction between the additional electron and the atomic nucleus
    - b. Positive  $E_{ea}$  due to repulsions between the additional electron and the electrons in the atom
  - 2. Halogens have large, negative  $E_{ea}$ 
    - a. High  $Z_{eff}$
    - b. Room in valence-shell for an additional electron
    - c. High attraction between additional electron and atomic nucleus
  - 3. Noble-gas elements have positive  $E_{ea}$ 
    - a. Filled  $s$  and  $p$  sublevels
    - b. Additional electron goes into the next higher shell – feels a low  $Z_{eff}$
    - c. Small attraction between the additional electron and the atomic nucleus
    - d. High electron-electron repulsions
  - 4. Alkaline earth metals have  $E_{ea} \approx 0$ 
    - a. Filled  $s$  subshell
    - b. Added electron goes into  $p$  subshell of higher energy
    - c. Relatively low  $Z_{eff}$

### 6.6. Ionic Bonds and the Formation of Ionic Solids

- A. Element with low  $E_i$  can transfer an electron to an element with negative  $E_{ea}$ 
  - 1. Produces a cation and an anion
  - 2. Cation and anion mutually attracted by electrostatic forces
  - 3. Ionic bond created - Compounds are usually ionic if formed from reaction of a metal with a nonmetal.
  - 4. Three-dimensional network of ions (ionic solid) formed
    - a. Each cation surrounded by and attracted to many anions
    - b. Each anion surrounded by and attracted to many cations
- B. Ionic bond formation leads to large gain in stability
  - 1. Overcomes unfavorable energy change of electron transfer
  - 2. The ions are stabilized by strong forces arising from electrostatic attraction
  - 3. Formulas for ionic compounds are empirical formulas giving the relative number of cations and anions.
- C. Born-Haber cycle – series of hypothetical steps each of which contributes to the overall energy change during the formation of an ionic compound. It is used to calculate properties that are impossible to measure directly.
  - 1. Net process is the sum of individual steps
  - 2. Typical individual steps
    - a. Sublimation of a metal atom to a gaseous atom
    - b. Dissociation of nonmetal molecules
    - c. Ionization of isolated metal atoms
    - d. Formation of nonmetal anions

- e. Formation of solid ionic compound

### 6.7. Lattice Energies in Ionic Solids

- A. Lattice energy ( $U$ ) – sum of electrostatic interaction energies between ions in a solid
  - 1. Refers to the breakup of a crystal into individual ions
    - a. Positive value
    - b. When using the lattice energy in a Born-Haber cycle must change the sign because last step is the reverse of the breakup of the crystal
  - 2. Lattice energy mostly coulombic
    - Coulomb's law:  $F = k \times \frac{z_1 z_2}{d^2}$
  - 3. Effect of ion charge – compounds of ions with higher charges have greater lattice energies than compounds of ions with lower charges
  - 4. Effect of ion size – compounds of ions with smaller sizes have greater lattice energies than compounds of ions with larger sizes

### 6.8. The Octet Rule

- A. Octet rule – main-group elements tend to undergo reactions that leave them with eight valence electrons
  - 1. Useful for making predictions; provides insights about chemical bonds
  - 2. “Magic number” = 8
    - a. Filled octet –  $s$  and  $p$  subshells both filled
    - b. Can't take electrons away – electrons tightly held by high  $Z_{\text{eff}}$
    - c. No low-energy orbitals available to accept electrons
  - 3. Failure of rule
    - a. Elements on right side of periodic table in third or lower period
    - b. More than eight electrons sometimes accommodated by larger atoms
- B. Factors that determine cation or anion formation
  - 1. Cations
    - a. Electrons highly shielded from nucleus by core electrons
      - i. Feel low  $Z_{\text{eff}}$
      - ii. Easily lost
    - b. Charge based on electronic configuration – energy required unavailable to lose another electron once next-lower noble gas configuration achieved
  - 2. Anions
    - a. Electrons poorly shielded from nucleus by core electrons
      - i. Feel high  $Z_{\text{eff}}$
      - ii. Can gain electrons because of  $Z_{\text{eff}}$
    - b. Charge based on electronic configuration – low-energy orbitals required for additional electrons unavailable once next-higher noble gas configuration achieved

### 6.9. Chemistry of the Alkali Metals (Group 1A)

- A. General properties:
  - 1. Valence-shell electron configuration –  $ns^1$ 
    - a. Common ion  $M^+$  dominates chemistry
    - b. Lowest ionization energies of all elements
    - c. Most powerful reducing agents in the periodic table
  - 2. Low densities and melting points.
  - 3. Metals
    - a. Bright, silvery solids
    - b. Malleable
    - c. Good conductors of electricity
    - d. Soft enough to cut with a knife
  - 4. Very reactive
    - a. Must be stored under oil to prevent instantaneous reaction with oxygen and water
  - 5. Occur in nature as salts

- B. Produced by reaction of their chloride salts
1. Lithium and sodium produced by electrolysis – electric current is passed through molten salt
  2. Potassium, rubidium, and cesium produced by chemical reduction
- C. Reactions of alkali metals
1. Halogens
    - a. General reaction:  $2 M(s) + X_2(g) \rightarrow 2 MX(s)$
    - b. Products are halides, crystalline ionic salts
    - c. Lower the ionization energy, greater the reactivity
  2. Hydrogen
    - a. General reaction:  $2 M(s) + H_2(g) \rightarrow 2 MH(s)$
    - b. Products are hydrides (oxidation number of H = -1)
    - c. Sluggish reaction at room temperature
  3. Nitrogen – only lithium reacts:  $6 Li(s) + N_2(g) \rightarrow 2 Li_3N(s)$
  4. Oxygen
    - a. All react rapidly
    - b. Form different kinds of products
      - i. Li → oxide (oxidation number of O = -2)
      - ii. Na → peroxide (oxidation number of O = -1)
      - iii. K, Rb, Cs → superoxide (oxidation number O = -1/2)
  5. Water
    - a. General reaction:  $2 M(s) + 2 H_2O(l) \rightarrow 2 M^+(aq) + 2 OH^-(aq) + H_2(g)$
    - b. Reactivity increases down the group
    - c. Produces an alkaline solution
    - d. Redox process
  6. Ammonia
    - a. General reaction:  $2 M(s) + 2 NH_3(l) \rightarrow 2 M^+(soln) + 2 NH_2^-(soln) + H_2(g)$
    - b. Analogous to reaction between metal and water
    - c. Metal amide,  $MNH_2$ , solutions have powerful reducing properties

### 6.10. Chemistry of the Alkaline Earth Metals (Group 2A)

- A. General properties
1. Similar to alkali metals
  2. Valence-shell electron configuration –  $ns^2$ 
    - a. Common ion –  $M^{2+}$
    - b. Powerful reducing agents
  3. Soft, silvery metals
  4. Higher melting points and densities than alkali metals
  5. Less reactive toward oxygen and water than alkali metals
  6. Occur in nature as salts
- B. Produced by reduction of their salts
- C. Reactions of alkaline earth metals
1. Same kinds of redox reactions as alkali metals
  2. Less reactive than alkali metals –  $E_i(\text{alkaline earth}) > E_i(\text{alkali})$
  3. Halogens → ionic halide salts,  $MX_2$
  4. Oxygen → oxides, MO; Sr, Ba → peroxides,  $MO_2$
  5. Water → metal hydroxides,  $M(OH)_2$

### 6.11. Chemistry of the Group 3A Elements: Aluminum

- A. General properties
1. Valence-shell electron configuration –  $ns^2np^1$
  2. B – semimetal
  3. Others – silvery metals
    - a. Soft
    - b. Good conductors of electricity
  4. Al – common ion:  $Al^{3+}$ , a reducing agent
- B. Aluminum – most abundant metal in earth's crust

1. Name comes from alum,  $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ , a medicinal salt
  2. Occurs in many common minerals and gemstones
    - a. Sapphire and ruby – impure forms of  $\text{Al}_2\text{O}_3$
    - b. Impurity creates color
  3. Commercially obtained from bauxite,  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$
  4. Reducing agent – loses all three valence electrons
- C. Reactions of aluminum
1. Halogens  $\rightarrow \text{AlX}_3$ 
    - a. Vigorous at room temperature
    - b. Releases large amount of heat
  2. Oxygen  $\rightarrow \text{Al}_2\text{O}_3$  – vigorous at room temperature only on surface
  3. Acids and bases  $\rightarrow \text{Al}^{3+} + \text{H}_2$

### 6.12. Chemistry of the Halogens (Group 7A)

- A. General properties
1. Exist as diatomic molecules
  2. Valence-shell electron configuration –  $ns^2np^5$ 
    - a. Gain electrons
    - b. Powerful oxidizing agents
    - c. Large negative  $E_{\text{ea}}$
  3. Occur in nature as salts and minerals
- B. Produced by oxidation of their anions
- C. Reactions
1. Most reactive elements in the periodic table
  2. Less reactive going down the periodic table
  3. Metals  $\rightarrow$  metal halides,  $\text{MX}_n$
  4. Hydrogen  $\rightarrow$  hydrogen halides,  $\text{HX}$  – behave as acids when dissolved in water
  5. Other halogens  $\rightarrow \text{XY}$ 
    - a. Interhalogen compounds
    - b. Redox process – the lighter, more reactive element is the oxidizing agent and the heavier, less reactive element is the reducing agent
    - c. Properties intermediate between parent elements
    - d. Act as strong oxidizing agents in redox reactions

### 6.13. Chemistry of the Noble Gases (Group 8A)

- A. General properties
1. Colorless, odorless, unreactive gases
  2. Valence-shell electron configuration –  $ns^2np^6$ 
    - a. Stable configuration
    - b. Do not form cations or anions
    - c. Normally do not undergo redox reactions
    - d. Commercial use – applications that require inert atmospheres
- B. Reactions of noble gases
1. Kr and Xe react only with fluorine
    - a. Xenon fluorides – powerful oxidizing agents
  2. Lack of reactivity due to valence-shell configuration
    - a. Large  $E_{\text{i}}$
    - b. Small  $E_{\text{ea}}$