Chapter 8. Basic Concepts of Chemical Bonding

Lecture Outline

8.1 Chemical Bonds, Lewis Symbols, and the Octet Rule
- The properties of many materials can be understood in terms of their microscopic properties.
- Microscopic properties of molecules include:
  - the connectivity between atoms and
  - the 3-D shape of the molecule.
- When atoms or ions are strongly attracted to one another, we say that there is a **chemical bond** between them.
  - In chemical bonds, electrons are shared or transferred between atoms.
- Types of chemical bonds include:
  - **ionic bonds** (electrostatic forces that hold ions together, e.g., NaCl);
  - **covalent bonds** (result from sharing electrons between atoms, e.g., Cl_2);
  - **metallic bonds** (refers to metal nuclei floating in a sea of electrons, e.g., Na).

Lewis Symbols
- The electrons involved in bonding are called *valence electrons*.
  - Valence electrons are found in the incomplete, outermost shell of an atom.
- As a pictorial understanding of where the electrons are in an atom, we represent the electrons as dots around the symbol for the element.
  - The number of valence electrons available for bonding are indicated by unpaired dots.
  - These symbols are called **Lewis symbols**, or Lewis electron-dot symbols.
  - We generally place the electrons on four sides of a square around the element's symbol.

The Octet Rule
- Atoms tend to gain, lose, or share electrons until they are surrounded by eight valence electrons; this is known as the **octet rule**.
  - An octet consists of full *s* and *p* subshells.
  - We know that s^2p^6 is a noble gas configuration.
  - We assume that an atom is stable when surrounded by eight electrons (four electron pairs).

8.2 Ionic Bonding
- Consider the reaction between sodium and chlorine:
$$Na(s) + \tfrac{1}{2}Cl_2(g) \rightarrow NaCl(s) \qquad \infty H\square_f = -410.9 \text{ kJ/mol}$$
  - The reaction is violently exothermic.
  - We infer that the NaCl is more stable than its constituent elements.
    - Sodium has lost an electron to become Na^+ and chlorine has gained the electron to become Cl^-.
    - Note that Na^+ has an Ne electron configuration and Cl^- has an Ar configuration.
    - That is, both Na^+ and Cl^- have an octet of electrons.
- NaCl forms a very regular structure in which each Na^+ ion is surrounded by six Cl^- ions.
  - Similarly each Cl^- ion is surrounded by six Na^+ ions.
  - There is a regular arrangement of Na^+ and Cl^-.
  - Note that the ions are packed as closely as possible.
  - Note that it is not easy to find a molecular formula to describe the ionic lattice.

Energetics of Ionic Bond Formation
- The heat of formation of NaCl(*s*) is exothermic:
$$Na(s) + \tfrac{1}{2}Cl_2(g) \rightarrow NaCl(s) \qquad \infty H\square_f = -410.9 \text{ kJ/mol}$$
- Separation of the NaCl into sodium and chloride ions is endothermic:
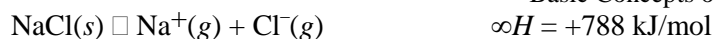
$$NaCl(s) \rightarrow Na^+(g) + Cl^-(g) \qquad \infty H = +788 \text{ kJ/mol}$$
- The energy required to separate one mole of a solid ionic compound into gaseous ions is called the **lattice energy**, $\infty H_{lattice}$.
- Lattice energy depends on the charge on the ions and the size of the ions.
- The stability of the ionic compound comes from the attraction between ions of unlike charge.
- The specific relationship is given by Coulomb's equation:

$$E = k \frac{Q_1 Q_2}{d}$$

- where E is the potential energy of the two interacting charged particles, Q_1 and Q_2 are the charges on the particles, d is the distance between their centers, and k is a constant (8.99 x 10^9 J $|$ M/C^2).
  - As Q_1 and Q_2 increase, E increases; and as d increases, E decreases.

Calculation of Lattice Energies: The Born-Haber Cycle
- The **Born-Haber cycle** is a thermodynamic cycle that analyzes lattice energy precisely.
- Consider a Born-Haber cycle for the formation of $NaCl(s)$ from $Na(s)$ and $Cl_2(g)$.
- The direct route is:

$$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s) \qquad \infty H\Box_f = -411 \text{ kJ}$$

- Alternatively, we can form:
  - sodium gas (108 kJ; *endothermic*), then
  - chlorine atoms (122 kJ; *endothermic*), then
  - sodium ions (ionization energy for Na, 496 kJ; *endothermic*), then
  - chloride ions (electron affinity for Cl, –349 kJ; *exothermic*), then
  - form the ionic lattice (*exothermic*).
- The sum of the above enthalpies is –411 kJ.
- The lattice energy is +788 kJ.

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 cannot 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 4s **before** the 3d, etc..

Polyatomic Ions
- Polyatomic ions are formed when there is an overall charge on a compound containing covalent bonds.
  - Examples are NH_4^+ and CO_2^{2-}.
- In polyatomic ions, two or more atoms are bound together by predominantly covalent bonds.
  - The stable grouping carries a charge.

8.3 Covalent Bonding

- The majority of chemical substances do not have characteristics of ionic compounds.
- We need a different model for bonding between atoms.
- A chemical bond formed by sharing a pair of electrons is called a *covalent* bond.
- Both atoms acquire noble-gas electronic configurations.
- This is the "glue" that binds atoms together.

Lewis Structures

- Formation of covalent bonds can be represented using Lewis symbols.
  - The structures are called **Lewis structures**.
  - We usually show each electron pair shared between atoms as a line and show unshared electron pairs as dots.
  - Each pair of shared electrons constitutes one chemical bond.
  - Example: H $|$ + H $|$ □ H⟨H has electrons on a line connecting the two H nuclei (H–H).

Multiple Bonds

- It is possible for more than one pair of electrons to be shared between two atoms (e.g., **multiple bonding**).
- One shared pair of electrons is a **single bond** (e.g., H_2).
- Two shared pairs of electrons form a **double bond** (e.g., O_2).
- Three shared pairs of electrons form a **triple bond** (e.g., N_2).
- **Bond length** is the distance between the nuclei of the atoms in a bond.
- Generally, bond distances decrease as we move from single through double to triple bonds.

8.4 Bond Polarity and Electronegativity

- The electron pairs shared between two different atoms are usually unequally shared.
- **Bond polarity** describes the sharing of the electrons in a covalent bond.
  - There are two extremes:
    - In a **nonpolar covalent bond** the electrons are shared equally.
      - An example is bonding between identical atoms (example: Cl_2).
    - In a **polar covalent bond**, one of the atoms exerts a greater attraction for bonding electrons than the other (example: HCl)
  - If the difference is large enough, an ionic bond forms (example: NaCl).

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.
- The Pauling electronegativity scale ranges 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 is between two atoms, the more polar the bond (polar covalent bonds) is.
- There is no sharp distinction between bonding types.

Dipole Moments

- Molecules like HF have centers of positive and negative charge that do not coincide.
- These are **polar molecules**.
- We indicate the polarity of molecules in two ways:

- • The positive end (or pole) in a polar bond may be represented with a "δ+" and the negative pole with a "δ−".
- We can also place an arrow over the line representing the bond.
  - • The arrow points toward the more electronegative element and shows the shift in electron density toward that atom.
- We can quantify the polarity of the molecule.
  - • When charges are separated by a distance, a **dipole** is produced.
  - • The **dipole moment** is the quantitative measure of the magnitude of the dipole (μ)

$$\mu = Q\, r$$

  - • The magnitude of the dipole moment is given in *debyes* (D).

Bond Types and Nomenclature

- • Previously, we used two different approaches to naming binary compounds.
  - • One is for ionic compounds and another is for molecular compounds.
  - • In both systems the less electronegative element is given first.
    - • The other element follows with the ending *-ide*.
- Both approaches are sometimes used with the same substance!
  - • Metals with higher oxidation numbers tend to be molecular rather than ionic.
  - • for example: TiO_2
    - • The names titanium(IV) oxide and titanium dioxide are used but titanium dioxide is more commonly used.

8.5 Drawing Lewis Structures

- • Here are some simple guidelines for drawing Lewis structures:
  - • Add up all of the valence electrons on all atoms.
    - • For an anion, add electrons equal to the negative charge.
    - • For a cation, subtract electrons equal to the positive charge.
  - • Identify the central atom.
    - • When a central atom has other atoms bound to it, the central atom is usually written first.
      - • Example: In CO_3^{2-} the central atom is carbon.
  - • Place the central atom in the center of the molecule and add all other atoms around it.
  - • Place one bond (two electrons) between each pair of atoms.
  - • Complete the octets for all atoms connected to the central atom (exception: hydrogen can only have two electrons).
  - • Complete the octet for the central atom; use multiple bonds if necessary.

Formal Charge

- • Sometimes it is possible to draw more than one Lewis structure with the octet rule obeyed for all the atoms.
- • To determine which structure is most reasonable, we use formal charge.
- • The **formal charge** of an atom is the charge that an atom (in a molecule) would have if all of the atoms had the same electronegativity.
- • To calculate formal charge, electrons are assigned as follows:
  - • All nonbonding (unshared) electrons are assigned to the atom on which they are found.
  - • Half of the bonding electrons are assigned to each atom in a bond.
  - • Formal charge is the number of valence electrons in the isolated atom, minus the number of electrons assigned to the atom in the Lewis structure.
- • For example: consider CN^- (cyanide ion):
  - • For carbon:
    - • There are four valence electrons (from the periodic table).
    - • In the Lewis structure there are two nonbonding electrons and three electrons from the triple bond.

- • There are five electrons from the Lewis structure.
- • Formal charge: $4 - 5 = -1$.
  - • For nitrogen:
    - • There are five valence electrons.
    - • In the Lewis structure there are two nonbonding electrons and three from the triple bond.
    - • There are five electrons from the Lewis structure.
    - • Formal charge $= 5 - 5 = 0$.
- • Use formal charge calculations to distinguish between alternative Lewis structures:
  - • the most stable structure has the smallest formal charge on each atom and
  - • the most negative formal charge on the most electronegative atoms.
- • It is important to keep in mind that formal charges do NOT represent REAL charges on atoms!

8.6 Resonance Structures

- • Some molecules are not adequately described by a single Lewis structure.
  - • Typically, structures with multiple bonds can have similar structures with the multiple bonds between different pairs of atoms.
    - • Example: Experimentally, ozone has two identical bonds whereas the Lewis structure requires one single (longer) and one double bond (shorter).
- • **Resonance structures** are attempts to represent a real structure that is a mix between several extreme possibilities.
  - • Resonance structures are Lewis structures that differ only with respect to placement of the electrons.
  - • The "true" arrangement is a blend or hybrid of the resonance structures.
  - • Example: In ozone the extreme possibilities have one double and one single bond.
    - • The resonance structure has two identical bonds of intermediate character.
  - • We use a double headed arrow ($\leftrightarrow$) to indicate resonance.
  - • Common examples are O_3, NO_3^-, SO_3, NO_2, and benzene.

Resonance in Benzene

- • Benzene belongs to an important category of organic molecules called *aromatic* compounds.
- • Benzene (C_6H_6) is a cyclic structure.
  - • It consists of six carbon atoms in a hexagon.
  - • Each carbon atom is attached to two other carbon atoms and one hydrogen atom.
  - • There are alternating double and single bonds between the carbon atoms.
  - • Experimentally, the C−C bonds in benzene are all the same length.
  - • Experimentally, benzene is planar.
- • To emphasize the resonance between the two Lewis structures (hexagons with alternating single and double bonds), we often represent benzene as a hexagon with a circle in it.

8.7 Exceptions to the Octet Rule

- • There are three classes of exceptions to the octet rule:
  - • molecules with an odd number of electrons,
  - • molecules in which one atom has less than an octet, and
  - • molecules in which one atom has more than an octet.

Odd Number of Electrons

- • Most molecules have an even number of electrons and complete pairing of electrons occurs although some molecules have an odd number of electrons.
  - • Examples are ClO_2, NO, and NO_2.

Less than an Octet of Valence Electrons

- • Molecules with less than an octet are also relatively rare.

- They are most often encountered in compounds containing boron or beryllium.
  - A typical example is BF_3.

More than an Octet of Valence Electrons

- This is the largest class of exceptions.
- Atoms from the third period and beyond can accommodate more than an octet.
  - Examples are PCl_5, SF_4, AsF_6^-, and ICl_4^-.
- Elements from the third period and beyond have unfilled d orbitals that can be used to accommodate the additional electrons.
- Size also plays a role.
  - The larger the central atom, the larger the number of atoms that can surround it.
  - The size of the surrounding atoms is also important.
  - Expanded octets occur often when the atoms bound to the central atom are the smallest and most electronegative (e.g., F, Cl, O).

8.8 Strengths of Covalent Bonds

- The energy required to break a covalent bond is called the **bond enthalpy**, D.
  - That is, for the Cl_2 molecule, $D(Cl–Cl)$ is given by ∞H for the reaction:

$$Cl_2(g) \,\square\, 2Cl(g).$$

- When more than one bond is broken:

$$CH_4(g) \,\square\, C(g) + 4H(g) \qquad\qquad \infty H = 1660 \text{ kJ}$$

  - The bond enthalpy is a fraction of ∞H for the atomization reaction:

$$D(C–H) = \tfrac{1}{4}\,\infty H = \tfrac{1}{4}(1660 \text{ kJ}) = 415 \text{ kJ}.$$

- Bond enthalpy is always a positive quantity.

Bond Enthalpies and the Enthalpies of Reactions

- We can use bond enthalpies to calculate the enthalpy for a chemical reaction.
- We recognize that in any chemical reaction bonds need to be broken and then new bonds form.
- The enthalpy of the reaction is given by:
  - the sum of bond enthalpies for bonds broken less the sum of bond enthalpies for bonds formed.
- Where ∞H_{rxn} is the enthalpy for a reaction,

$\infty H_{rxn} = \times D(\text{bonds broken}) - \times D(\text{bonds formed})$

- We illustrate the concept with the reaction between methane, CH_4, and chlorine:

$$CH_4(g) + Cl_2(g) \,\square\, CH_3Cl(g) + HCl(g)$$

  - In this reaction one C–H bond and one Cl–Cl bond are broken while one C–Cl bond and one H–Cl bond are formed.
  - So $\infty H_{rxn} = [D(C–H) + D(Cl–Cl)] - [D(C–Cl) + D(H–Cl)] = -104 \text{ kJ}$.
  - The overall reaction is exothermic which means than the bonds formed are stronger than the bonds broken.
  - The above result is consistent with Hess's law.

Bond Enthalpy and Bond Length

- The distance between the nuclei of the atoms involved in a bond is called the **bond length**.
- Multiple bonds are shorter than single bonds.
  - We can show that multiple bonds are stronger than single bonds.
  - As the number of bonds between atoms increases, the atoms are held closer and more tightly together.