Basic Concepts of Chemical Bonding

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.
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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 ns^2np^6 is a noble gas configuration.
  - We assume that an atom is stable when surrounded by eight electrons (four electron pairs).

Ionic Bonding

- Consider the reaction between sodium and chlorine:

$$Na(s) + \frac{1}{2} Cl_2(g) \rightarrow NaCl(s) \qquad \Delta H^\circ_f = -410.9 \text{ kJ/mol}$$

  - The reaction is violently exothermic. SHOW YOUTUBE
  - 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.

Energetics of Ionic Bond Formation

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The energy required to separate one mole of a solid ionic compound into gaseous ions is called the **lattice energy**, $\Delta H_{\text{lattice}}$.

- 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:

    $k = 8.99 \times 10^9$ J-m/C^2.
  - As Q_1 and Q_2 increase, E increases, and as d increases, E decreases.

Build the lattice diagram for CaCl2

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" to bind 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).

Drawing Lewis Structures (rules for humans)

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

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 is a **double bond** (e.g., O_2);
- Three shared pairs of electrons is 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.

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.
    - 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.
- Pauling electronegativity scale: from 0.7 (Cs) to 4.0 (F).
- Electronegativity increases across a period and decreases down a group.

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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**.

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 "$\delta+$" and the negative pole with a "$\delta-$".
- 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 d*ebyes* (D).

Differentiating Ionic and Covalent Bonding

- Interactions of metals and nonmetals often yield ionic compounds.
  - When ionic bonding is dominant, we expect compounds to exhibit properties associated with ionic substances (high-melting solids, strong electrolyte behavior when dissolved in water, etc.)
- Interactions of nonmetals with other nonmetals often yield compounds that are covalent.
  - When covalent bonding is dominant, we expect compounds to exist as molecules and exhibit properties associated with molecular substances (low melting and boiling points, nonelectrolyte behavior when dissolved in water, etc.).
- Assigning the labels "ionic" and "covalent" to compounds is not necessarily straightforward.
  - **There is a continuum between the extremes of ionic and covalent bonding.**

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.

Examples SCN^-

Using 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!**

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 arrows (↔) to indicate resonance.
  - Common examples: 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 and 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.

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,
  - 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: ClO_2, NO, and NO_2.

Less than an Octet of Valence Electrons

- Molecules with less than an octet are also relatively rare.
- Most often encountered in compounds of 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: 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).

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 ΔH for the reaction:

$$Cl_2(g) \rightarrow 2Cl(g).$$

- When more than one bond is broken:

$$CH_4(g) \rightarrow C(g) + 4H(g) \qquad \Delta H = 1660 \text{ kJ}$$

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

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

- 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 ΔH_{rxn} is the enthalpy for a reaction,

$$\Delta H_{rxn} = \sum D(\text{bonds broken}) - \sum D(\text{bonds formed})$$

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

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

  - 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 $\Delta H_{rxn} = [D(\text{C–H}) + D(\text{Cl–Cl})] - [D(\text{C–Cl}) + D(\text{H–Cl})] = -104$ 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.