Chapter 6 Notes Chemistry; 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 3D 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).

Ionic Bonding

- Consider the reaction between sodium and chlorine:

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

- 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 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- in three dimensions.
  - 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.

Energies of Ionic Bond formation

- The energy required to separate one mole of a solid ionic compound into gaseous ions is called the **lattice energy**.
- 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.

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 how each electron pair shard 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 is a **double bond** (e.g., O_2);
- Three shared pairs of electrons is a **triple bond** (e.g., N_2).
- 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.
      - Example: 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).

Dipole Moments

- Molecules like HF have centers of positive and negative charge that do not coincide.
- The 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 "&+" and the negative pole with a "&-".
- 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 (u).

Bond Types and Nomenclature

- Previously we used two different approaches to naming binary compounds.
  - One for ionic compounds and another 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.

Drawing Lewis Structures

- 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.

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

- 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

- This is the largest class of exceptions.
- Atoms from the third period on 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.
  - Expanding octets occur often when the atoms bound to the central atom are the smallest and most electronegative (e.g., F, Cl, O).

Resonance Structures

- Some molecules are not well described by a single Lewis structure.
  - Typically, structures with multiple bonds can have similar structures with the multiple bonds between different pairs of atoms.

- **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.

Molecular Shapes

- Lewis structures give atomic connectivity: they tell us which atoms are physically connected to which atoms.
- The shape of a molecule is determined by its **bond angles.**
  - The angles made by the lines joining the nuclei of the atoms in a molecule are the bond angles.
- Consider CCl_4:
  - Experimentally we find all Cl-C-Cl bond angles are 109.5 degrees.
  - Therefore, the molecule cannot be planar.
  - All Cl atoms are located at the vertices of a tetrahedron with the C at its center.
- In order to predict molecular shape, we assume that the valence electrons repel each other.
  - Therefore, the molecule adopts the three dimensional geometry that minimizes this repulsion.
  - We call this model the **V**alence **S**hell **E**lectron **P**air **R**epulsion (**VSEPR**) model.

The VSEPR Model

- A covalent bond forms between two atoms when a pair of electrons defines an electron domain located principally on one atom.
  - This is a **bonding pair** of electrons.
  - Such a region is an **electron domain.**
- A **nonbonding pair** or *lone pair* of electrons defines an electron domain located principally on one atom.
- Example: NH_3 has three bonding pairs and one lone pair.
- VSEPR predicts that the best arrangement of electron domains is the one that minimizes the repulsions among them.
  - The arrangement of electron domains about the central atom of an AB_n molecule is its **electron-domain geometry.**
- There are five different electron-domain geometries:
  - Linear (two electron domains), trigonal planar(three domains), tetrahedral (four domains), trigonal bipyramidal (five domains), and octahedral (six domains).
- The **molecular geometry** is the arrangement of the atoms in space.
  - To determine the shape of a molecule we distinguish between lone pairs and bonding pairs.
  - We use the electron domain geometry to help us predict the molecular geometry.
    - Draw the Lewis structure.
    - Count the total number of electron pairs around the central atom.
    - Arrange the electron pairs in one of the above geometries to minimize electron-electron repulsion.
- Next, determine the three-dimensional structure of the molecule:
  - We ignore lone pairs in the molecular geometry.
  - Describe the molecular geometry in terms of the angular arrangement of the bonded atoms.
  - Multiple bonds are counted as one electron domain.