Chemistry: The Central Science

Chapter 8: Basic Concepts of Chemical Bonding

- The properties of substances are determined in large part by the chemical bonds that hold their atoms together

8.1: Chemical bonds, Lewis Symbols, and the Octet Rule

- Chemical bond – The attraction that causes two atoms or ions to be strongly attached to each other
  - Ionic bond – electrostatic forces that exist between ions of opposite charge
  - Covalent bond – bond formed by the sharing of electrons between two atoms
  - Metallic bond – bond found in metal that allow the bonding electrons to move freely throughout the three-dimensional structure of the metal
- Lewis Symbols
  - G. N. Lewis suggested a simple way of showing valence electron, now known as Lewis electron-dot symbols or merely Lewis symbol
    - Lewis symbol for an element consists of the atomic symbol for the element plus a dot for each valence electron
    - The dots are placed on four sides of the atomic symbol: top, bottom, left, and right.
    - Each side can hold up to two electrons
- The Octet Rule
  - Atoms want to achieve the same state as the noble gas, which have eight valence electron
  - Octet rule – Atoms tend to gain, lose, or share electrons until they are surrounded by eight valence electrons
  - There are many exceptions to the octet rule, but it provides a useful framework for introducing many important concepts of bonding

8.2: Ionic Bonding

- Electrons can be transfer from one atom to the other to form ion
  - This depends of one atom’s ionization energy and the other atom’s electron affinity
- A bracket [ ] is needed around the ion that gained the electron to emphasize that all eight electrons are located on that ion
- Energetics of Ionic Bond Formation
Lattice energy – the energy required to completely separate a mole of a solid ionic compound into its gaseous stage
  - The lattice energy is high for ionic substances because the bond strength is strong
  - Conversely, ionic bond formation is highly exothermic because of the same reason as the lattice energy

Electron Configurations of Ions of the s- and p-Block Elements
  - Metal loses electrons until they reach the noble gas configuration of the previous energy level
    - A lot of energy is needed to remove the electron from the previous energy level so the lattice energy is not enough to compensate for it
  - Addition of electron to the nonmetal stops after they gain the noble gas configuration
    - If more electron is added, it is highly unfavorable
  - Base on these concepts, it is expected that ionic compounds of the representative metals will have the charge according to its group and vice versa

Transition-Metal Ions
  - Transition metal have the d orbitals so even after removing the valence electrons, they generally do not form ions with noble gas configuration
    - Octet rule is clearly limited in extent
  - In forming ions, transition metals lose the valence-shell s electrons first, then as many d electrons as are required to reach the charge of the ion

8.3: Covalent Bonding

- The nuclei repel each other and the electrons repel each other but the nuclei attract the electrons
  - Because the molecule such as H₂ is stable, it means that the attraction must exceed the repulsion

Lewis Structures
- Structures that show how the valence electron are shared between two atoms
  - Usually show the electron pair shared between atoms as a line and the unshared electron pair as dots

Multiple Bonds
- Atoms can share more than one pair of electrons
  - Double bond = share two pairs
  - Triple bond = share three pairs
The more shared electron pairs increases, the distance between bonded atoms nuclei decreases

- The distance between nuclei of the atoms involved in a bond is called the bond length

8.4: Bond Polarity and Electronegativity

- Bond polarity – describe the sharing of electrons between atoms
- Nonpolar covalent bond – one in which the electrons are shared equally between two atoms (Cl₂, H₂, N₂, etc.)
- Polar covalent bond – one of the atoms exerts a greater attraction for the bonding electrons than the other
  - If the difference in relative ability to attract electrons is large enough, an ionic bond is formed (does not matter whether it’s metal to nonmetal or nonmetal to nonmetal)
- Electronegativity – the ability of an atom in a molecule to attract electrons to itself
  - Relate to the ionization energy and electron affinity
  - Atom with high ionization energy and very negative electron affinity have high electronegativity
  - Electronegativity is a diagonal trend
    - Increase from left to right and decrease from up to down
    - Increase from bottom left to top right
- Electronegativity and Bond Polarity
  - In polar covalent bond, it causes the electron to be around the atom with greater electronegativity more often than around the atom with lower electronegativity
    - This cause the atom with lower electronegativity to be partially positive (δ+) and the atom with greater electronegativity to be partially negative (δ-)
  - The greater the difference in electronegativity between two atoms, the more polar their bond
- Dipole Moments
  - Polar molecule – the molecule in which the centers of positive and negative charge do not match
  - Positive end of the dipole molecule attract the negative ion and likewise
  - Whenever a distance separates two electrical charges of equal magnitude but opposite in sign, a dipole is created
  - Dipole moment – the quantitative measure of the magnitude of a dipole
    - \( M = Qr \)
- Usually reported in debyes (D), a unit equals to $3.34 \times 10^{-30}$ coulomb-meters (C-m)
- For molecules, we usually measure charge in units of the electronic charge $e$, $1.60 \times 10^{-19}$ C, and a distance in units of angstroms (Å)
  o As electronegativity differences decreases, the bond length increases.

- Differentiating Ionic and Covalent Bonding
  o When covalent bonding is dominant, it usually have a relatively low melting and boiling points and non-electrolyte behavior when dissolved in water
  o When ionic bonding is dominant, it tend to be brittle, high-melting solids with extended lattice structures and they exhibit strong electrolyte behavior when dissolved in water
  o Electronegativity differences can also show which type of bond the atoms have
    - $0 \sim 0.5 = $ nonpolar covalent
    - $0.5 \sim 1.6-1.9 = $ polar covalent
      - $1.6-1.9$ is polar covalent for nonmetal with nonmetal while ionic for metal and nonmetal
    - $\Delta EN > 1.9 = $ ionic
  o As general principle, whenever the oxidation state of the metal increases, it will lead to an increase in the degree of covalent character in bonding

8.5: Drawing Lewis Structures

- Guide to making a Lewis structures
  o Sum the valence electrons from all atoms
  o Write the symbols for the atoms to show which atoms are attached to which, and connect them with a single bond
  o Complete the octets around all the atoms bonded to the central atom
  o Place any leftover electrons on the central atom (even if doing so results in more than an octet of electrons around the atom
  o If there are not enough electrons to give the central atom an octet, try multiple bonds

- Formal Charge
  o The formal charge of any atom in a molecule is the charge the atom would have if all the atoms in the molecule had the same electronegativity
  o Formal charge is use to determine which Lewis structure of the molecule is the most reasonable
  o To calculate the formal charge on any atom in a Lewis structure, we assign the electrons to the atom as follows
• All unshared (nonbonding) electrons are assigned to the atom on which they are found
• For any bond—single, double, or triple—half of the bonding electrons are assigned to each atom in the bond
  • E.g. CN\(^-\) have 2 nonbonding electrons and 3 electrons from the 6 in the triple bond \((6 \times \frac{1}{2} = 3)\) so \(2 + 3 = 5\)
    - The formal charge on C is \(4 - 5 = -1\)
    - The formal charge on N is \(5 - 5 = 0\)
  • The sum of the formal charge is equal to the charge on the molecule
• To find the most reasonable Lewis structure, we use a guideline
  • We generally choose the Lewis structure in which the atoms bear formal charges closest to zero
  • We generally choose the Lewis structure in which any negative charges reside on the more electronegative atoms
  • Formal charges do not represent real charges on atoms

8.6: Resonance Structures
• There are molecules and ions which cannot be describe by a single Lewis structure
  - E.g. O\(_3\)
• Resonance structures – Lewis structure that is completely equivalent but have different placement of electrons
  - Describe by drawing all the resonance structure and drawing a double-headed arrow between the resonance structures
• Resonance in Benzene
  - Resonance is an extremely important concept in describing the bonding in organic molecules, particularly in the ones called aromatic molecules
    - Aromatic organic molecules include the hydrocarbon called benzene, which has the formula C\(_6\)H\(_6\)
  - The C of benzene molecule form hexagon with three single bond and three double bond
  - All C of benzene are have equal bond length
  - It’s commonly represented by omitting the hydrogen atoms and showing only the carbon to carbon framework with no label
    - Can be represented as a hexagon with 3 line along 3 sides of the hexagon to show the double or a hexagon with a circle in it

8.7: Exceptions to the Octet Rule
• Three main types of octet rule exceptions:
• Molecule and polyatomic ions containing an odd number of electrons
• Molecules and polyatomic ions in which an atom has fewer than an octet of valence electrons
• Molecules and polyatomic ions in which an atom has more than an octet of valence electrons

● Odd Number of Electrons
  o In vast majority of molecule and polyatomic ions, the total number of valence electrons is even, and complete pairing of electrons occurs
  o In some molecules and polyatomic ions, such as ClO₂, NO, NO₂, and O₂⁻, the number of electrons is odd so the complete pairing of these electrons is impossible

● Less than an Octet of Valence Electrons
  o Most of the exceptions are found in compounds of boron and beryllium
  o In the Lewis structure of BF₃, there are only 6 electrons around beryllium
    ▪ It could be solve by boron forming a double bond with a fluorine but that is unfavorable because it would cause the boron to have a formal charge of 1⁻ while fluorine have 1+
    ▪ The Lewis structure of BF₃ is represented with Lewis structure that boron that has 6 valence electrons
    ▪ BF₃ is reacts very energetically with molecules having an unshared pair of electrons that can be used to form a bond with boron

● More than an Octet of Valence Electrons
  o Largest of the exceptions
  o Can only form with the center element as an element from energy level 3 or higher because of the empty d orbital
  o Amount of expansion depends on the size of the atom
  o Expanded valence shells occur most often with the surrounding atoms as F, Cl, and O
  o In general, when choosing between alternative Lewis structures, it is possible to draw a Lewis structure where the octet rule is satisfied

8.8: Strengths of Covalent Bonds

● Bond enthalpy is the enthalpy change for the breaking of a particular bond in one mole of a gaseous substance
  o The designation D(bond type) is use to represent bond enthalpies
● Many important bonds such as C—H bond only exist in polyatomic molecule
  o For these type of bond, we use the average bond enthalpies
  o E.g. The enthalpy of CH₄ methane is 1660 kJ so D(C—H) = 1660/4 = 415 kJ
The bond enthalpy for a given set of atoms such as C—H depends on the rest of the molecule of which the atom pair is a part of.

- The variation from one molecule to another is generally small.

- The bond enthalpy is always a positive quantity; energy is always required to break the chemical bond.
  - Conversely, energy is always released when a bond forms between two gaseous atoms or molecular fragments.

- A molecule with strong chemical bonds generally has less tendency to undergo chemical change.

**Bond Enthalpies and the Enthalpies of Reactions**

- Bond enthalpies can be used to find the enthalpy of reaction even if the enthalpy of formation is not known.

\[ \Delta H_{\text{rxn}} = \sum (\text{bond enthalpies of bonds broken}) - \sum (\text{bond enthalpies of bonds formed}) \]

- E.g., reaction of methane and chlorine gas to produce methyl chloride and hydrogen chloride:
  \[ \text{H}--\text{CH}_3(g) + \text{Cl}--\text{Cl}(g) \rightarrow \text{Cl}--\text{CH}_3(g) + \text{H}--\text{Cl}(g) \]
  \[ \Delta H_{\text{rxn}} = \] ?

  - Bonds broken: 1 mol C—H, 1 mol Cl—Cl
  - Bonds made: 1 mol C—Cl, 1 mol H—Cl

  \[ \Delta H_{\text{rxn}} = [D(\text{C—H}) + D(\text{Cl—Cl})] - [D(\text{C—Cl}) + D(\text{H—Cl})] \]
  \[ = (413 \text{ kJ} + 242 \text{ kJ}) - (328 \text{ kJ} + 431 \text{ kJ}) = -104 \text{ kJ} \]

  - The enthalpy of reaction from the enthalpy of formation is approximately 
    -99.8 kJ

  - The use of bond enthalpy provides a reasonably accurate estimate of the actual enthalpy of change.

- Bond enthalpies are derived for gaseous molecules and that they are often averaged values.

**Bond Enthalpy and Bond Length**

- As the number of bonds between two atoms increases, the bond grows shorter and stronger.