

Chapter 8 – Bonding: General Concepts

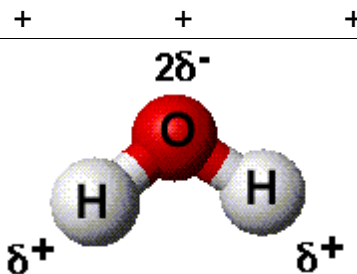
1. Types of Chemical Bonds
 - a. Ionic Bonding
 - i. Electrons are transferred
 - ii. Metals reaction with non-metals
 - iii. Ions paired to have lower energy (greater stability) than separated ions
 - b. Coulombs Law

$$E = 2.31 \times 10^{-19} \text{ J} \cdot \text{nm} \left(\frac{Q_1 Q_2}{r} \right)$$

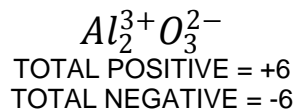
- a. E = Energy in Joules
 - b. Q_1 and Q_2 are numerical ion charges
 - c. r = distance between ion center in nanometers
 - d. Negative sign indicates an attractive force
- c. Bond Length
 - i. Distance at which the system energy is at a minimum
 - ii. Forces at work
 1. Attractive forces (proton-electron)
 2. Repulsion forces (electron-electron, proton-proton)
 - iii. Energy is given off (bond energy) when two atoms achieve greater stability together than apart
 - d. Covalent Bonds
 - i. Electrons are shared by nuclei
 - ii. Pure covalent (non-polar covalent)
 1. Electrons are shared evenly
 - iii. Polar covalent bonds
 1. Electrons are shared unevenly
 2. Atoms end up with fractional charges
 - a. (1) δ^+ and δ^-
2. Electronegativity
 - a. Electronegativity
 - i. The ability of an atom in a molecule to attract shared electrons to itself
 - b. Electronegativity Trends
 - i. Electronegativity generally increases across a period (why?)
 - ii. Electronegativity generally decrease within a family (why?)
 - c. Characterizing bonds
 - i. Greater electronegativity difference between two elements means less covalent character and greater ionic character
 - ii. We will not use subtraction of electronegativities to determine ionic character

Any compound that conducts an electric current when melted is an ionic compound.

3. Bond Polarity and Dipole Moments
 - a. Dipolar Molecules
 - i. Molecules with a somewhat negative end and a somewhat positive end (a dipole moment)
 - ii. Molecules with preferential orientation in an electric field
 - iii. All diatomic molecules with a polar covalent bond are dipolar



- b. Molecules with Polar Bonds but no Dipole Moment
 - i. Linear, radial or tetrahedral symmetry of charge distribution
 - 1. CO₂ – linear
 - 2. CCl₄ – tetrahedral
 - ii. See table 8.6 in your text
4. Ions: Electron Configurations and Sizes
- a. Bonding and Noble Gas Electron Configurations
 - i. Ionic bonds
 - 1. Electrons are transferred until each species attains a noble gas electron configuration
 - ii. Covalent bonds
 - 1. Electrons are shared in order to complete the valence configurations of both atoms
 - b. Predicting Formulas of Ionic Compounds
 - i. Placement of elements on the periodic table suggests how many electrons are lost or gained to achieve a noble-gas configuration
 - 1. Group I loses one electron, Group II loses two, Group VI gains two, Group VII gains one...
 - ii. Formulas for compounds are balanced so that the total positive ionic charge is equal to the total negative ionic charge



- c. Sizes of Ions
 - i. Anions are larger than the parent atom
 - ii. Cations are smaller than the parent atom
 - iii. Ion size increases within a family
 - iv. Isoelectronic ions
 - 1. Ions with the same number of electrons
 - 2. Size decreases as the nuclear charge Z increases

5. Formation of Binary Ionic Compounds

- a. Lattice Energy
 - i. The change in energy that takes place when separated gaseous ions are packed together to form an ionic solid - $M^+(g) + X^-(g) \rightarrow MX(s)$
 - ii. Energy change is exothermic (negative sign)

Example: Formation of lithium fluoride

Process	Description	Energy Change (kJ)
Li(s) → Li(g)	Sublimation energy	161
Li(g) → Li ⁺ (g) + e ⁻	Ionization energy	520
1/2 F ₂ → F(g)	Bond energy (1/2 mole)	77
F(g) + e ⁻ → F ⁻ (g)	Electron affinity	-328
Li ⁺ (g) + F ⁻ (g) → LiF(s)	Lattice energy	-1047
Li(s) + 1/2 F ₂ (g) → LiF(s)	ΔH	-617

- iii. The formation of ionic compounds is endothermic until the formation of the lattice
- iv. The lattice formed by alkali metals and halogens (1:1 ratio) is cubic except for cesium salts
- b. Lattice Energy Calculations
 - i. $Lattice\ Energy = k \left(\frac{Q_1 Q_2}{r} \right)$
 - a. k = a proportionality constant dependent on the solid structure and the electron configuration
 - b. Q_1 and Q_2 are charges on the ions
 - c. r = shortest distance between centers of the cations and the anion
 - ii. Lattice energy increases as the ionic charge increases and the distance between anions and cations decreases

6. Partial Ionic Character of Covalent Bonds

- a. Calculating Percent Ionic Character

$$\text{Percent Ionic Character} = \left(\frac{\text{measured dipole moment } f X - Y}{\text{calculated dipole moment of } X^+ - Y^-} \right)$$

- b. Ionic vs. Covalent
 - i. Ionic compounds generally have greater than 50% ionic character
 - ii. Ionic compounds generally have electronegativity differences greater than 1.6
 - iii. Percent ionic character is difficult to calculate for compounds containing polyatomic ions

7. The Covalent Chemical Bond: A Model

- a. Strengths of the Bond Model
 - i. Associates quantities of energy with the formation of bonds between elements
 - ii. Allows the drawing of structures showing the spatial relationship between atoms in a molecule
 - iii. Provides a visual tool to understanding chemical structure
- b. Weaknesses of the Bond Model
 - i. Bonds are not actual physical structures
 - ii. Bonds can not adequately explain some phenomena
 - 1. Resonance

8. Covalent Bond Energies and Chemical Reactions

a. Average Bond Energies

Process	Energy Required (kJ/mol)
$\text{CH}_4(\text{g}) \rightarrow \text{CH}_3(\text{g}) + \text{H}(\text{g})$	435
$\text{CH}_3(\text{g}) \rightarrow \text{CH}_2(\text{g}) + \text{H}(\text{g})$	453
$\text{CH}_2(\text{g}) \rightarrow \text{CH}(\text{g}) + \text{H}(\text{g})$	425
$\text{CH}(\text{g}) \rightarrow \text{C}(\text{g}) + \text{H}(\text{g})$	339
Total	1652
Average	413

b. Multiple Bonds

- i. Single bonds - 1 pair of shared electrons
- ii. Double bonds - 2 pairs of shared electrons
- iii. Triple bonds - 3 pairs of shared electrons

Multiple Bonds, Average Energy (kJ/mole)			
C=C	614	N=O	607
C≡C	839	N=N	418
O=O	495	N≡N	941
C=O	745	C≡N	891
C≡O	1072	C=N	615

- iv. As the number of shared electrons increases, the bond length shortens

c. Bond Energy and Enthalpy (using bond energy to calculate approximate energies for rxns)

- i. $\Delta H = \text{sum of the energies required to break old bonds (endothermic)}$

$$+ \text{sum of the energies released in forming new bonds (exothermic)}$$
- ii. $\Delta H = \sum D(\text{Bonds broken}) - \sum D(\text{Bonds formed})$
 - 1. D always has a positive sign

9. The Localized Electron Bonding Model

- a. Lone electron pairs
 - i. Electrons localized on an atom (unshared)
- b. Bonding electron pairs
 - i. Electrons found in the space between atoms (shared pairs)
- c. Localized Electron Model
 - i. "A molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms"
- d. Derivations of the Localized Model
 - i. Valence electron arrangement using Lewis structures
 - ii. Prediction of molecular geometry using VSEPR (valence shell electron pair repulsion)
 - iii. Description of the type of atomic orbitals used to share or hold lone pairs of electrons

10. Lewis Structures

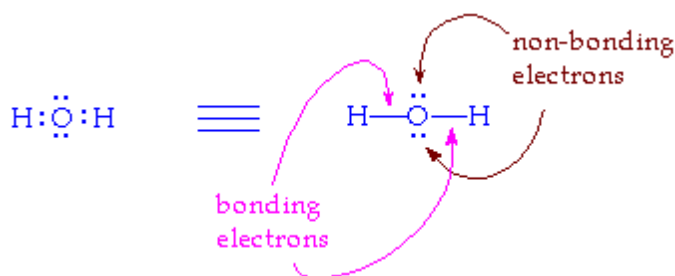
a. Electrons and Stability

- "the most important requirement for the formation of a stable compound is that the atoms achieve noble gas configurations
- Duet rule
 - Hydrogen, lithium, beryllium, and boron form stable molecules when they share two electrons (helium configuration)
- Octet Rule
 - Elements carbon and beyond form stable molecules when they are surrounded by eight electrons

b. Writing Lewis Structures

i. Rules

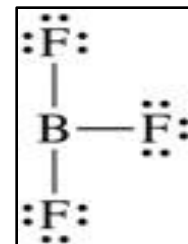
- Add up the TOTAL number of valence electrons from all atoms
- Use a pair of electrons to form a bond between each pair of bound atoms. Lines instead of dots are used to indicate each pair of bonding electrons
- Arrange the remaining atoms to satisfy the duet rule for hydrogen and the octet rule for the second row elements



11. Exceptions to the Octet Rule

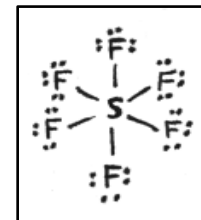
a. Boron Trifluoride

- Note that boron only has six electrons around it
- BF₃ is electron deficient and acts as a Lewis acid (electron pair acceptor)
- Boron often forms molecules that obey the octet rule



b. Sulfur Hexafluoride

- Note that sulfur has 12 electrons around it, exceeding the octet rule
- Sulfur hexafluoride is very stable
- SF₆ fills the 3s and 3p orbitals with 8 of the valence electrons, and places the other 4 in the higher energy 3d orbital



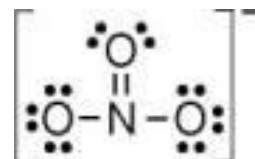
c. More About the Octet Rule

- Second row elements C, N, O and F should always obey the octet rule
- B and Be (second row) often have fewer than eight electrons around them, and form electron deficient, highly reactive molecules
- Second row elements never exceed the octet rule
- Third row and heavier elements often satisfy (or exceed) the octet rule
- Satisfy the octet rule first. If extra electrons remain, place them on elements having available d orbitals
 - When necessary to exceed the octet rule for one of several third row elements, assume that the extra electrons be placed on the central atom

12. Resonance

a. Nitrate ion

- Experiments show that all N-O bonds are equal
- A single Lewis structure cannot represent the nitrate ion
- A resonance structure is drawn by writing the three variant structures, connected by a double-headed arrow



b. Resonance

- When more than one valid Lewis structure can be written for a particular molecule
- The actual structure is an average of the depicted resonance structures

c. Odd Electron Molecules

- Molecules in which there is not an even number of electrons
- Does not fit localized electron model

d. Formal Charge

- Number of valence electrons on the free atom

minus

Number of valence electrons assigned to the atom in the molecule

- Lone pair (unshared) electrons belong completely to the atom in question

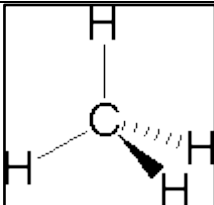
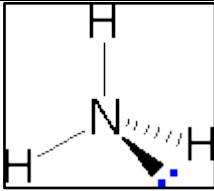
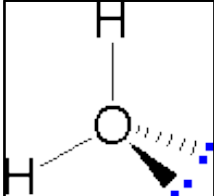
1. Shared electrons are divided equally between the sharing atoms
- iii. The sum of the formal charges of all atoms in a given molecule or ion must equal the overall charge on that species
 1. If the charge on an ion is -2, the sum of the formal charges must be -2
- e. Using Formal Charge to Evaluate Lewis Structures
 - i. If nonequivalent Lewis structures exist for a species, those with the formal charges closest to zero, and with negative formal charges on the most electronegative atoms are considered the best candidates
 - ii. Only experimental evidence can conclusively determine the correct bonding situation in a molecule

13. Molecular Structure: The VSEPR Model

- a. Valence Shell Electron Pair Repulsion (VSEPR)
 - i. The structure around a given atom is determined principally by minimizing electron-pair repulsions
 - ii. Non-bonding and bonding electron pairs will be as far apart as possible

Arrangement of Electron Pairs Around an Atom Yielding Minimum Repulsion		
# of Electron Pairs	Shape	Arrangement of Electron Pairs
2	Linear	Bond Angle = 180 degrees
3	Trigonal Planar	Bond Angle = 120 degrees
4	Tetrahedral	Bond Angle = 109.5 degrees
5	Trigonal bipyramidal	Bond Angles = 90 degrees and 120 degrees
6	Octahedral	Bond Angles = 90 degrees

- b. Effect on unshared electron pairs
 - i. The ideal tetrahedral angle is 109.5°

Comparison of Tetrahedral Bond Angles		
Compound	Structure	Angle between Hydrogens
Methane		109.5°
Ammonia		107°
Water		104.5°

- ii. Lone (unshared) electron pairs require more room than bonding pairs (they have greater repulsive forces) and tend to compress the angles between bonding pairs
 - iii. Lone pairs do not cause distortion when bond angles are 120° or greater
- c. VSEPR and Multiple Bonds
 - i. For the VSEPR model, multiple bonds count as one effective electron pair
 - ii. When a molecule exhibits resonance, ANY of the resonance structures can be used to predict the molecular structure using the VSEPR model
- d. Molecules Containing No Single Central Atom
 - i. Apply the principle of distancing shared and unshared electron pairs
 - ii. Look at real 3-dimensional, rotatable models to develop predictive skills
- e. How Well Does VSEPR Work?
 - i. For non-ionic compounds, VSEPR works in most cases