

Chapter 8 Notes - Bonding: General Concepts

8.1 Types of Chemical Bonds

A. Ionic Bonding

1. Electrons are transferred
2. Metals react with nonmetals
3. Ions paired have lower energy (greater stability) than separated ions

B. Coulomb's Law

$$1. \quad E = 2.31 \times 10^{-19} \text{ J} \cdot \text{nm} \left(\frac{Q_1 Q_2}{r} \right)$$

- 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 (covalent)

1. Distance at which the system energy is at a minimum
2. Forces at work
 - a. Attractive forces (proton - electron)
 - b. Repulsive forces (electron - electron, proton - proton)
3. Energy is given off (bond energy) when two atoms achieve greater stability together than apart

D. Covalent Bonds

1. Electrons are shared by nuclei
2. Pure covalent (non-polar covalent)
 - a. Electrons are shared evenly
3. Polar covalent bonds
 - a. Electrons are shared unequally
 - b. Atoms end up with fractional charges
(1) $\delta+$ or $\delta-$

8.2 Electronegativity

A. Electronegativity

1. The ability of an atom in a molecule to attract shared electrons to itself

B. Electronegativity Trends

1. Electronegativity generally increases across a period (why?)
2. Electronegativity generally decrease within a family (why?)

C. Characterizing bonds

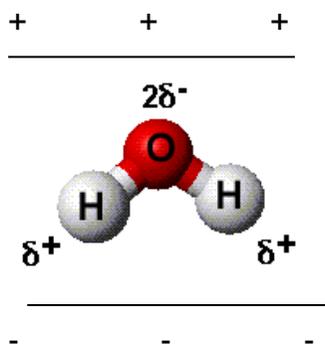
1. Greater electronegativity difference between two elements means less covalent character and greater ionic character
2. We will not use the subtraction of electronegativities to determine ionic character. This text uses a practical definition to identify ionic compounds:

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

8.3 Bond Polarity and Dipole Moments

A. Dipolar Molecules

1. Molecules with a somewhat negative end and a somewhat positive end (a dipole moment)
2. Molecules with preferential orientation in an electric field



3. All diatomic molecules with a polar covalent bond are dipolar

B. Molecules with Polar Bonds but no Dipole Moment

1. Linear, radial or tetrahedral symmetry of charge distribution
 - a. CO₂ - linear
 - b. CCl₄ - tetrahedral
2. See table 8.2 in your text

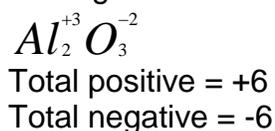
8.4 Ions: Electron Configurations and Sizes

A. Bonding and Noble Gas Electron Configurations

1. Ionic bonds
 - a. Electrons are transferred until each species attains a noble gas electron configuration
2. Covalent bonds
 - a. Electrons are shared in order to complete the valence configurations of both atoms

B. Predicting Formulas of Ionic Compounds

1. Placement of elements on the periodic table suggests how many electrons are lost or gained to achieve a noble-gas configuration
 - a. Group I loses one electron, Group II loses two, Group VI gains two, Group VII gains one....
2. Formulas for compounds are balanced so that the total positive ionic charge is equal to the total negative ionic charge



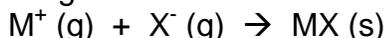
C. Sizes of Ions

1. Anions are larger than the parent atom
2. Cations are smaller than the parent atom
3. Ion size increases within a family
4. Isoelectronic ions
 - a. Ions with the same number of electrons
 - b. Size decreases as the nuclear charge Z increases

8.5 Energy Effects in Binary Ionic Compounds

A. Lattice Energy

1. The change in energy that takes place when separated gaseous ions are packed together to form an ionic solid



2. Energy change is exothermic (negative sign)

Example: Formation of lithium fluoride

Process	Description	Energy Change (kJ)
$Li(s) \rightarrow Li(g)$	Sublimation energy	161
$Li(g) \rightarrow Li^+(g) + e^-$	Ionization energy	520
$1/2F_2 \rightarrow F(g)$	Bond energy (1/2 mole)	77
$F(g) + e^- \rightarrow F^-(g)$	Electron affinity	-328
$Li^+(g) + F^-(g) \rightarrow LiF(s)$	Lattice energy	-1047
$Li(s) + 1/2F_2(g) \rightarrow LiF(s)$	ΔH	-617

3. The formation of ionic compounds is endothermic until the formation of the lattice
4. The lattice formed by alkali metals and halogens (1:1 ratio) is cubic except for cesium salts

B. Lattice Energy Calculations

1. $Lattice\ Energy = k \left(\frac{Q_1 Q_2}{r} \right)$

- 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 anions
2. Lattice energy increases as the ionic charge increases and the distance between anions and cations decreases

8.6 Partial Ionic Character of Covalent Bonds

A. Calculating Percent Ionic Character

$$\text{Percent ionic character} = \left(\frac{\text{measured dipole moment of } X-Y}{\text{calculated dipole moment of } X^+Y^-} \right) \times 100\%$$

B. Ionic vs. Covalent

1. Ionic compounds generally have greater than 50% ionic character
2. Ionic compounds generally have electronegativity differences greater than 1.6
3. Percent ionic character is difficult to calculate for compounds containing polyatomic ions

8.7 The Covalent Chemical Bond: A Model

A. Strengths of the Bond Model

1. Associates quantities of energy with the formation of bonds between elements
2. Allows the drawing of structures showing the spatial relationship between atoms in a molecule
3. Provides a visual tool to understanding chemical structure

B. Weaknesses of the Bond Model

1. Bonds are not actual physical structures
2. Bonds can not adequately explain some phenomena
 - a. resonance

8.8 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

1. Single bonds - 1 pair of shared electrons
2. Double bonds - 2 pairs of shared electrons
3. 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

4. As the number of shared electrons increases, the bond length shortens (see table 8.5)

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

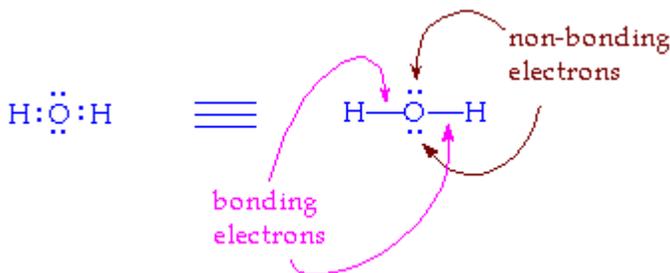
1. $\Delta H = \text{sum of the energies required to break old bonds (endothermic)}$
+
 $\text{sum of the energies released in forming new bonds (exothermic)}$
2. $\Delta H = \sum D(\text{Bonds broken}) - \sum D(\text{Bonds formed})$
 - a. D always has a positive sign

8.9 The Localized Electron Bonding Model

- A. Lone electron pairs
 - 1. Electrons localized on an atom (unshared)
- B. Bonding electron pairs
 - 1. Electrons found in the space between atoms (shared pairs)
- C. Localized Electron Model
 - 1. "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
 - 1. Valence electron arrangement using Lewis structures
 - 2. Prediction of molecular geometry using VSEPR (valence shell electron pair repulsion)
 - 3. Description of the type of atomic orbitals used to share or hold lone pairs of electrons

8.10 Lewis Structures

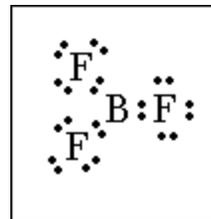
- A. Electrons and Stability
 - 1. "the most important requirement for the formation of a stable compound is that the atoms achieve noble gas configurations"
 - 2. Duet rule
 - a. Hydrogen, lithium, beryllium, and boron form stable molecules when they share two electrons (helium configuration)
 - 3. Octet Rule
 - a. Elements carbon and beyond form stable molecules when they are surrounded by eight electrons
- B. Writing Lewis Structures
 - 1. Rules
 - a. Add up the TOTAL number of valence electrons from all atoms
 - b. 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
 - c. Arrange the remaining atoms to satisfy the duet rule for hydrogen and the octet rule for the second row elements



8.11 Exceptions to the Octet Rule

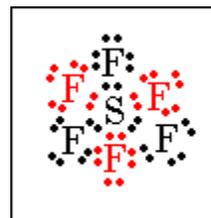
A. Boron Trifluoride

1. Note that boron only has six electrons around it
2. BF_3 is electron deficient and acts as a Lewis acid (electron pair acceptor)
3. Boron often forms molecules that obey the octet rule



B. Sulfur Hexafluoride

1. Note that sulfur has 12 electrons around it, exceeding the octet rule
2. Sulfur hexafluoride is very stable
3. SF_6 fills the 3s and 3p orbitals with 8 of the valence electrons, and places the other 4 in the higher energy 3d orbital



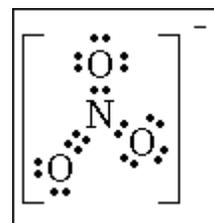
C. More About the Octet Rule

1. Second row elements C, N, O and F should always obey the octet rule
2. B and Be (second row) often have fewer than eight electrons around them, and form electron deficient, highly reactive molecules
3. Second row elements never exceed the octet rule
4. Third row and heavier elements often satisfy (or exceed) the octet rule
5. Satisfy the octet rule first. If extra electrons remain, place them on elements having available d orbitals
 - a. 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

8.12 Resonance

A. Nitrate ion

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



B. Resonance

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

C. Odd Electron Molecules

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

D. Formal Charge

1. Number of valence electrons on the free atom

minus

Number of valence electrons assigned to the atom in the molecule

- a. Lone pair (unshared) electrons belong completely to the atom in question
- b. Shared electrons are divided equally between the sharing atoms

2. The sum of the formal charges of all atoms in a given molecule or ion must equal the overall charge on that species
 - a. If the charge on an ion is -2, the sum of the formal charges must be -2

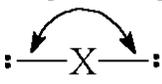
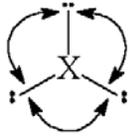
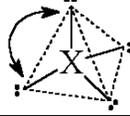
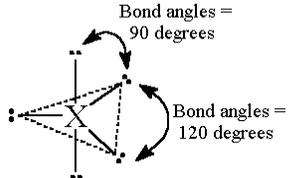
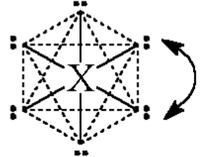
E. Using Formal Charge to Evaluate Lewis Structures

1. 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
2. Only experimental evidence can conclusively determine the correct bonding situation in a molecule

8.13 Molecular Structure: The VSEPR Model

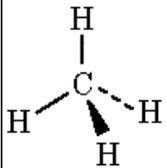
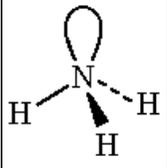
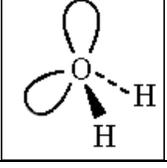
A. Valence Shell Electron Pair Repulsion (VSEPR)

1. The structure around a given atom is determined principally by minimizing electron-pair repulsions
2. 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	All bond angles = 120 degrees 
4	Tetrahedral	All bond angles = 109.5 degrees 
5	Trigonal bipyramidal	Bond angles = 90 degrees Bond angles = 120 degrees 
6	Octahedral	All bond angles = 90 degrees or 180 degrees 

B. Effect of Unshared Electron Pairs

1. 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°

2. Lone (unshared) electron pairs require more room than bonding pairs (they have greater repulsive forces) and tend to compress the angles between bonding pairs
3. Lone pairs do not cause distortion when bond angles are 120° or greater

C. VSEPR and Multiple Bonds

1. For the VSEPR model, multiple bonds count as one effective electron pair
2. 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

1. Apply the principal of distancing shared and unshared electron pairs
2. Look at real 3-dimensional, rotatable models to develop predictive skills

E. How Well Does VSEPR Work?

1. For non-ionic compounds, VSEPR works in most cases