Chapter 8: Basic Concepts of Chemical Bonding

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What is a Bond?

- Force of attraction between two atoms in a molecule
- Why are compounds formed?
  - Gives the atoms more stability/lower energy state due to full octet in valence shell

Types of Bonds

- **Three Main Types (INTRA-molecular Forces)**
  - **Ionic Bond**
  - **Covalent Bond**
  - **Metallic Bond**

Types of Bonds

- **Three Main Types (INTRA-molecular Forces)**
  - **Ionic Bond:**
    - Formed by complete transfer of electrons
    - Transfer results in electrostatic attraction between oppositely charged ions

Types of Bonds

- **Three Main Types (INTRA-molecular Forces)**
  - **Covalent Bond:**
    - Sharing of electrons between two atoms

Types of Bonds

- **Three Main Types (INTRA-molecular Forces)**
  - **Metallic Bond:**
    - Found in metals
    - Electrons are free and delocalized
    - "Sea of electrons" or "electron soup"

Lewis Dot Symbols

- A way to keep track of valence electrons
- A Lewis Dot symbol consists of the element's symbol and one dot for each valence electron in an atom of the element

TABLE 8.1 ■ Lewis Symbols

Element	Electron Configuration	Lewis Symbol	Element	Electron Configuration	Lewis Symbol
Li	$[He]2s^1$	Li·	Na	$[Ne]3s^1$	Na·
Be	$[He]2s^2$	·Be·	Mg	$[Ne]3s^2$	·Mg·
B	$[He]2s^22p^1$	·Ḃ·	Al	$[Ne]3s^23p^1$	·Ȧl·
C	$[He]2s^22p^2$	·Ċ̣·	Si	$[Ne]3s^23p^2$	·Ṩi·
N	$[He]2s^22p^3$	·Ṅ:	P	$[Ne]3s^23p^3$	·Ṗ:
O	$[He]2s^22p^4$	:Ȯ:	S	$[Ne]3s^23p^4$	:Ṡ:
F	$[He]2s^22p^5$	·F̈:	Cl	$[Ne]3s^23p^5$	·C̈l:
Ne	$[He]2s^22p^6$	:N̈e:	Ar	$[Ne]3s^23p^6$	:Ä̤r:

Octet Rule

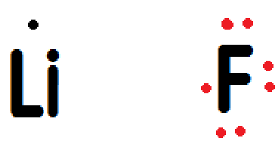
- Elements tend to gain, lose, or share electrons to complete their octet
  – provides the greatest stability
- Helps to explain how and why bonds would form
- The bonding type depends on if an element shares electrons (covalent) or transfers electrons (ionic)

Ionic Bonds

Ionic Bonding

- Ionic bonds result from a **full transfer** of electrons between atoms
- **Electrostatic force (Coulombic Force)** holds the resulting ions together

Example



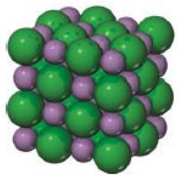
$1s^22s^1$ $1s^22s^12p^5$

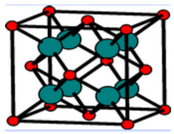
Ionic Bonding

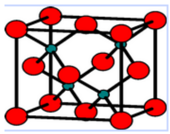
- **Electrostatic force (Coulombic Force)** holds the resulting ions together
- Crystal structures maximize attractive forces and minimize repulsive forces
  – Systematic periodic 3-D array

Crystal Structures

- Create 3-D crystal structure
- For NaCl, which is Na^+ and which is Cl^-?

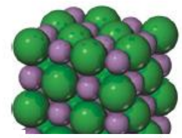


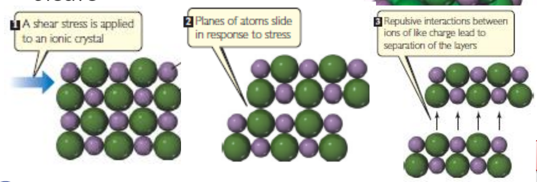




Properties of Ionic Cmpds

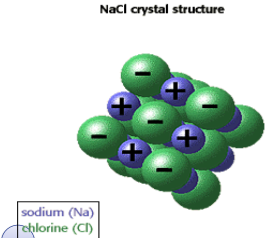
- Crystalline
- Brittle
- High MP and BP
- Cleave

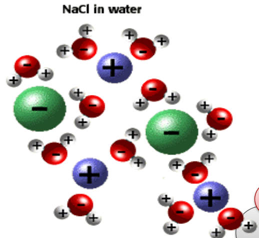




Properties of Ionic Cmpds

- Conduct electricity*





Ionic Bonding

- An atom with a low ionization energy reacts with an atom with high electron affinity
  - *REMEMBER:*
    - **Ionization energy:** the energy required to remove an electron
    - **Electron Affinity:** is the energy change when an electron is added to form an anion

Why are ionic compounds stable?

- Attraction between ions of opposite charge draws ions together and releases energy
  - Endothermic or Exothermic?
- A measure of how much stabilization results from arranging oppositely charged ions in an ionic solid (crystal lattice) is called lattice energy
  - **Lattice Energy:** The energy required to completely **separate** 1 mole of a solid ionic compound into its gaseous ions
    - $NaCl (s) \rightarrow Na^+ (g) + Cl^- (g)$
    - Will the lattice energy be positive or negative?

TABLE 8.2 ■ Lattice Energies for Some Ionic Compounds

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	$MgCl_2$	2326
LiCl	834	$SrCl_2$	2127
LiI	730		
NaF	910	MgO	3795
NaCl	788	CaO	3414
NaBr	732	SrO	3217
NaI	682		
KF	808	ScN	7547
KCl	701		
KBr	671		
CsCl	657		
CsI	600		

NOTE: The positive energy indicates that the ions are strongly attracted to one another in these solids

Lattice Energy

- Lattice energy depends on ion charges, size and arrangement and is equivalent to the electrostatic potential energy between the ions

$$E_{el} = \frac{\kappa q_1 q_2}{r}$$

- Lattice energy increases with charge of ions and with decreasing radii

Example

Arrange the following ionic compounds in order of increasing Lattice Energy: NaF, CsI and CaO

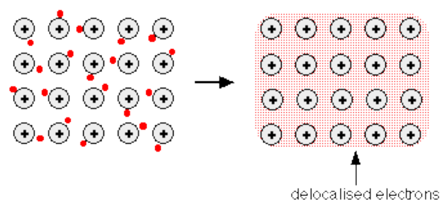
$$E_{el} = \frac{\kappa Q_1 Q_2}{d}$$

CsI < NaF < CaO

Metallic Bonds

Metallic Bonding

- "Sea of electrons"
- Delocalized valence electrons



Properties of metals

- Conduct electricity
- High thermal conductivity
- Malleable
- Ductile
- Crystal structures

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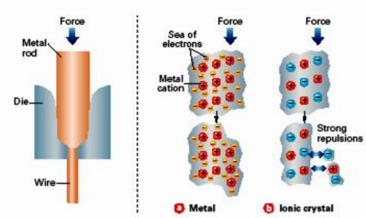
Figure 7.12
Metal Rod Forced Through Die

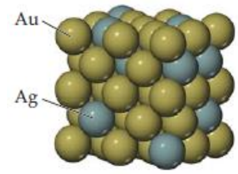


Alloys

- Alloy—contains more than 1 element, still has metallic properties
- Homogeneous mixtures
- Brass, steel, gold in jewelry

Alloys

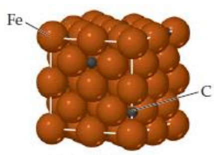
- Substitutional alloy—one atom replaces another
  - 14 k gold
  - Similar radii
  - Similar bonding



Substitutional alloy
14-karat gold

Alloys

- Interstitial alloy—solute atoms fill in "holes"
  - Steel
  - Smaller radius
  - Bonds to metals
  - Stronger, harder, less ductile



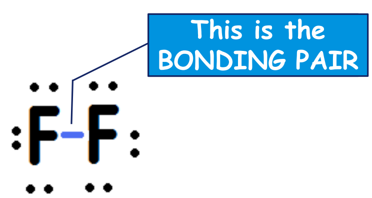
Interstitial alloy
Steel

Covalent Bonds

Covalent Bonding

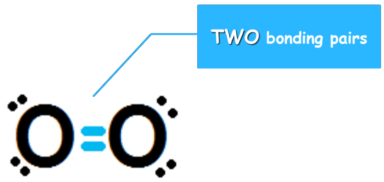
- **Sharing** of electrons to satisfy the octet rule
- Usually between non-metals (including hydrogen)
- Covalent compounds are very different than ionic compounds
  - Much lower melting/boiling points
  - Usually easily vaporize
  - Tend to be pliable

Example



Both of the fluorine atoms will share electrons until they each have a full octet of electrons

Example



Both of the oxygen atoms will share electrons until they each have a full octet of electrons

Multiple Covalent Bonds

Single	C-C	(alkane)
Double	C=C	(alkene)
Triple	C≡C	(alkyne)

- **Which has the shortest bond length?**
- **Which is strongest?**

Bond Length

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Lewis structures for molecules

1. Count the number of total valence electrons in molecule, determine # electron pairs
2. Write the atoms in the order they'll go
   a. Atom with lowest IE in center
   b. H never in center
3. Make a bond (2 e^-) between each atom
4. Complete octet with more bonds or lone pairs of e^-

Incomplete Octet

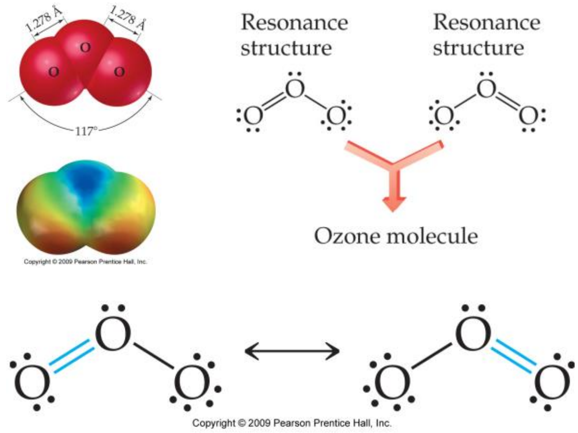
- Some atoms can have less than a full octet
  - Hydrogen
    - 2 e-
  - Beryllium
    - 4 e-
  - Boron
    - 6 e-

Lets try some

- Nitrogen Trifluoride
- Hypochlorite ion
- Carbon dioxide
- Water
- Carbonate ion
- Nitrogen gas

What's Special About Ozone?

- Ozone has a combination of multiple and single bonds, thus a **RESONANCE** structure must be drawn
- Why?
- Since the placement of the double bond could be in two locations, both must be depicted
- What would you expect the bond length in ozone to be most similar to? O-O or O=O

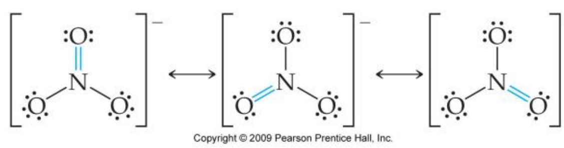


Resonance Structures

- A resonance structure is one of two or more Lewis Structures for a single molecule that cannot be represented accurately by only one Lewis Structure
- A resonance structure is designed to address the limitation of simple bonding models

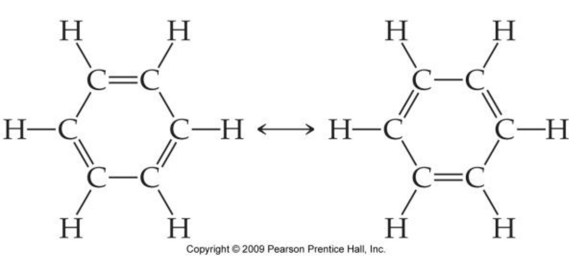
Lets try one!

- Nitrate Ion

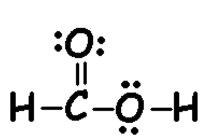


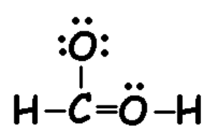
Another Example

- Benzene- C_6H_6 Cyclic Aromatic Compound



Which is the correct Lewis Dot for Formic Acid?





Formal Charge

- Formal charge is the difference between the valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis Structure

$$\text{Formal charge on an atom in a Lewis Structure} = \text{Total number of valence electrons in the free atom} - \text{Total number of nonbonding electrons} - \frac{1}{2}\left[\text{Total number of bonding electrons}\right]$$

Rules for Formal Charge

- Sum of formal charges must add up to charge on molecule
- Neutral molecules, the sum = 0
- Cations and anions, sum = charge

Why does this matter?

- Molecules try to achieve as low a formal charge as possible.
- Negative formal charges should be on electronegative elements.
- For molecules and polyatomic ions that exceed the octet, it helps determine the correct structure

So Which One Is Correct?

Of course there are… EXCEPTIONS!!

- Although most atoms follow the octet rule, there are some important exceptions:
  1. Odd number of valence electrons
  2. Atoms that can have fewer than an octet
  3. Atoms that can have more than an octet

Odd Number Of Valence Electrons

- Some molecules have an odd number of valence electrons
- ClO_2, NO, NO_2 and O_2^-
- Use formal charge to determine best structure

Expanded Octet

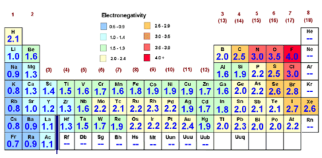
- Some atoms can have more than a full octet
  - Elements in third row or higher
    - Can exceed the octet since the D orbitals are available
- Examples:
  - **Phosphorus** PCl_5
  - **Sulfur** SF_6
  - **Xenon** XeF_4

Types of Covalent Bonds

- Covalent bonds can also be described in terms of their polarity
  - Bond polarity indicates how evenly/unevenly two atoms share electrons
- **Non-Polar Covalent:** Electrons shared equally
- **Polar Covalent:** Electrons shared unequally
  - One atom is better at attracting the shared electrons towards itself
  - What periodic property could cause this?

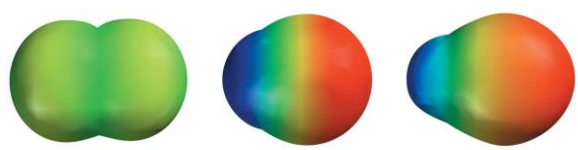
Types of Covalent Bonds

- Bond polarity can be *estimated* from the **difference in electronegativity** between the atoms
  - Non-polar Covalent Bond 0 - 0.5
  - Polar Covalent Bond > 0.5-1.9
  - Ionic Bond > 1.9



Example

Compound	F_2	HF	LiF
Electronegativity difference	4.0 − 4.0 = 0	4.0 − 2.1 = 1.9	4.0 − 1.0 = 3.0
Type of bond	Nonpolar covalent	Polar covalent	Ionic



Polar Molecules

- Electrons are not distributed evenly across compound
- One end is slightly positive, the other slightly negative.
- Indicated using delta (δ)
- An arrow can also be used to indicate electron density

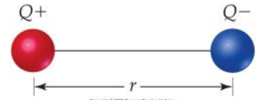
δ+ δ-

H - F

Dipole Moment

- Whenever a distance separates two electric charges of equal magnitude but opposite sign, a dipole forms, measured in debyes (D).

$\mu = Qr$



- Q measured in units of electronic charge (e) = 1.60×10^{-19} Coulombs
- Distance (r) measured in Angstroms (A)
  - 1 Angstrom = 10^{-10} meters
- 1 debye = 3.335×10^{-30} Coulomb-meters

Dipole Moment

- For a non-polar bond, say in F_2, the dipole moment is zero
- So for a dipole moment to form, the bond **must** be polar
- The more polar the bond, the larger the dipole moment

TABLE 8.3 ▪ Bond Lengths, Electronegativity Differences, and Dipole Moments of the Hydrogen Halides

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

Ionic vs Covalent

Ionic Compounds
- Metal and nonmetal
- High melting point
- Brittle
- Strong electrolyte
- Mostly solids

Covalent Compounds
- Nonmetal and nonmetal
- Low melting and boiling points
- Non electrolytes
- More polar bonds- more ionic behavior

Bond Enthalpy

- Amount of energy required to break a particular bond in 1 mole of gaseous substances
- Bond enthalpy indicates bond strength
- Bond enthalpies give a prediction for ΔH_{rxn}

ΔH_{rxn}= Σ(bond enthalpies of bonds broken) - Σ(bond enthalpies of bonds formed)

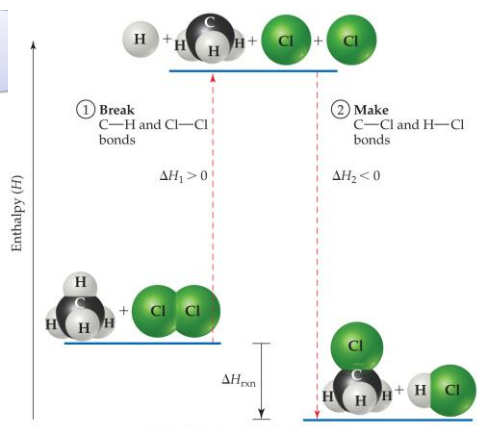
TABLE 8.4 ▪ Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Si—Cl	464						

Multiple Bonds

C=C	614	N=N	418	O_2	495
C≡C	839	N≡N	941		
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				



Bond Enthalpy and Length

- Distance between atoms decreases with increasing number of bonds

TABLE 8.5 ▪ Average Bond Lengths for Some Single, Double, and Triple Bonds

Bond	Bond Length (Å)	Bond	Bond Length (Å)
C—C	1.54	N—N	1.47
C=C	1.34	N=N	1.24
C≡C	1.20	N≡N	1.10
C—N	1.43	N—O	1.36
C=N	1.38	N=O	1.22
C≡N	1.16		
		O—O	1.48
C—O	1.43	O=O	1.21
C=O	1.23		
C≡O	1.13		

Chapter 9

Molecular Geometry and Bonding Theory

Molecular Geometry

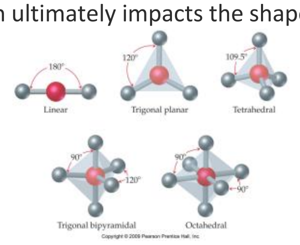
- Lewis Dot structures are a good way to show the placement of electrons but they don't represent a complete picture of a molecules structure
  - Molecules are not 2D, Lewis Dot structures do not provide information about their 3D shape

Molecular Geometry

- REPULSION:
  - Electrons (both shared and unshared) repel each other and will spread out until the distance between them is maximized
- The study of molecular geometry is called the **Valence Shell Electron Pair Repulsion** or **VSEPR**

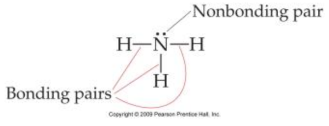
Bond Angles

- As the electrons in these atoms spread out to maximize space, the angles between them change which ultimately impacts the shape of the molecule



Rules that Govern VSEPR

- Two categories of electrons within a molecule:
  - Bonding/Shared Pairs:
    - Electrons that are shared between atoms
  - Non-bonding/Unshared/Lone Pairs
    - Lone pair of electrons on a single atom



Rules that Govern VSEPR

- Single, double or triple bonds all "count" as a **SINGLE bonding pair**
- If a molecule has 2 or more resonance structures, we can apply the VSEPR model to any one of them

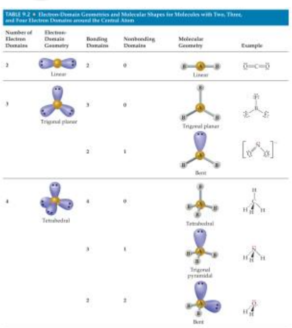
Electron Domain Geometry vs Molecular Geometry

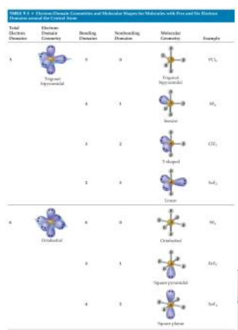
- **Electron Domain Geometry:**
  - Uses all electron domains (shared and unshared) around the central atom to name the VSEPR shape
- **Molecular Geometry:** AP focuses more on this
  - Uses only the shared electron domains to determine the arrangement and shape of atoms around the central atom

Steps for VSEPR Model

1. Draw the Lewis Structure and count total number of electron domains
2. Determine electron domain geometry
3. Determine the molecular geometry by counting bonding and lone pairs
4. Predict bond angles
5. Predict Molecular Polarity

VSEPR OVERVIEW



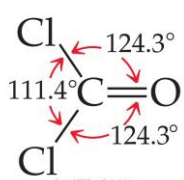


Bond Angles

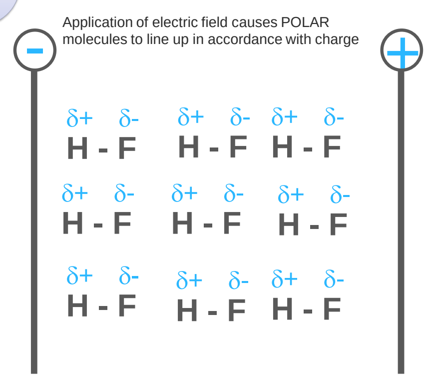
- Lone pairs cause more distortions in shape
- As more lone pairs are present there is a greater tendency to compress bond angles
- More distortions = less symmetry = polarity

Bond Angles

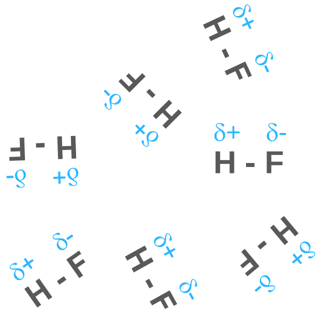
- Multiple bonds also exert more repulsive force and tend to compress other bond angles



Polar Molecules and Electric Fields



Without the field…



Which Molecules Have Dipole Moments?

- Symmetrical Molecules
  - Dipole moments of bonds cancel each other
  - Results in a **non-polar** molecule
- Asymmetrical Molecules
  - Dipole moments of bonds do not cancel each other
  - Results in a **polar** molecule due to different "looking" sides/poles