

## Chemical Bonding I: Lewis Theory

“Theories are nets cast to catch what we call ‘the world’: to rationalize, to explain, and to master it. We endeavor to make the mesh ever finer and finer.”

--Karl Popper (1902-1994)

Chapter 9

## Chapter 9 – Chemical Bonding I Suggested Problems

- 51, 53, 55, 61, 63, 69, 73, 75, 87, and 123
- Also available at <http://www.western.edu/faculty/dorth>

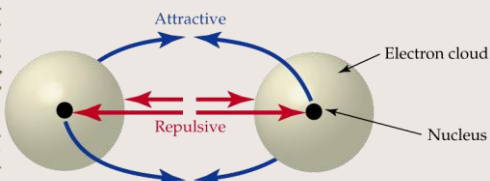
## Chemical Bonding I

- Lewis Structures – simple model of covalent bonding
- Bond Length, formal charge and resonance
- Bond Polarity
- Ionic and Metallic Bonding
  - Lattice energy

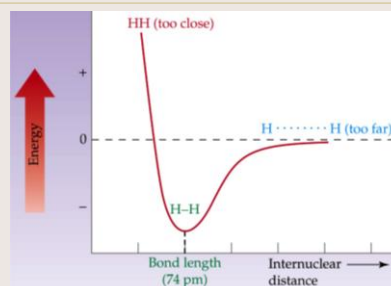
## Covalent Bonding

- Valence electrons are shared between atoms
- Typically occurs between two non-metals
- The atoms are bonded because both nuclei are attracting the same (shared) electrons

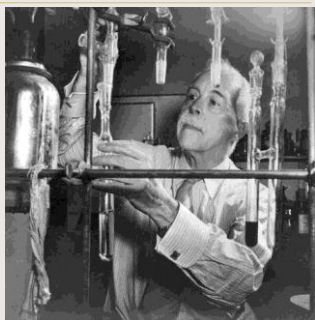
## Competing forces in covalent bond formation



## Potential energy



## Gilbert N. Lewis



## Lewis Model of Covalent Bonding

- Only valence electrons participate
- Valence electrons are shared between atoms as pairs of electrons (bonds)
- Sharing usually results in each atom being surrounded by eight electrons (octet rule)
- Valence electrons are represented as dots
- Pairs of shared electrons (bonds) are represented as lines

## How to Draw Lewis Structures

- Determine total # of valence electrons
  - Add one for each negative charge of anions
  - Subtract one for each + charge of cations
- Decide what atoms are connected and draw a line to represent bonds between them
- Determine the electrons remaining
  - total valence  $e^-$  - 2(# bonds drawn)
  - assign remaining electrons to terminal atoms to obey octet rule
- IF any  $e^-$  remain, assign them to the central atom
- IF central atom still lacks an octet, move one or more lone pairs from terminal atoms to form double or triple bonds to give an octet

## Lewis structure practice

- HCl
  - 8 valence electrons
- CO<sub>2</sub>
  - 16 valence electrons
- CN<sup>-</sup>
  - 10 valence electrons
- O<sub>3</sub>
  - 18 valence electrons

## Multiple bonds

- Consider C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub>
- Double bond
  - 4 shared electrons
  - stronger and shorter than single bond
- Triple bond
  - 6 shared electrons
  - stronger and shorter than double bond

## Which molecule has the stronger oxygen-oxygen bond?

- (A) O<sub>2</sub>
- (B) H<sub>2</sub>O<sub>2</sub>
- (C) both are the same

## Which molecule has the shortest carbon oxygen bond?

- A CO
- B CO<sub>2</sub>
- C CH<sub>3</sub>OH

## Resonance

- Multiple valid Lewis structures
- Reality is some average of the different structures – Resonance hybrid
- Draw all resonance structures linked with double headed arrow  $\leftrightarrow$
- Relative stability of different resonance structures can be compared by considering formal charge

## Assigning Formal Charge

- Formal charge is assigned to each atom in a molecule
- Formal charge =  
(# of valence electrons in free atom)  
- (  $\frac{1}{2}$  # of bonding electrons)  
- (# of nonbonding electrons)
- Sum of total charges = charge on the molecule or ion

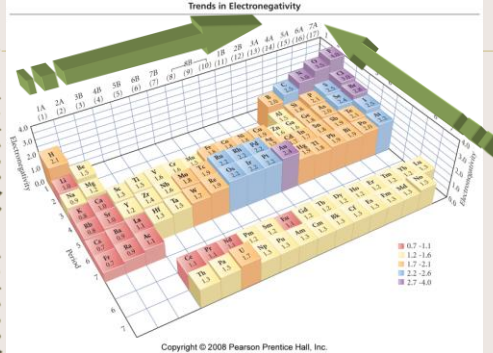
## Using Formal Charge

- Favorable Lewis Structures have
- Minimal (absolute value) formal charges on each atom
- Minimal separation of formal charges
- Appropriate sign of formal charge on atoms
  - more electronegative atom should carry negative formal charge
  - less electronegative atom should carry positive formal charge

## Electronegativity

- The attraction of an atom for bonding electrons
  - Max = 4.0 (fluorine)
  - Min = 0.7 (cesium)
- Increases across a period (row)
- Decreases going down a group (column)

## Electronegativity Scale



Draw correct Lewis structures for the following and assign Formal Charge to each atom

- acetylene,  $C_2H_2$
- hydronium ion,  $H_3O^+$
- sulfur hexafluoride,  $SF_6$
- nitric oxide,  $NO$
- sulfur trioxide,  $SO_3$
- nitrous oxide,  $N_2O$  (connectivity is  $NNO$ )

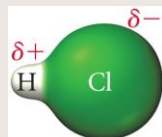
## Polar Covalent Bonding

- The sharing of electrons in most covalent bonds is NOT equal
- The atom which better attracts the bonding electrons attains a partial negative charge
- The other atom attains a partial positive charge

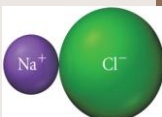
## Bond Polarity



$EN_{Cl} = 3.0$   
 $3.0 - 3.0 = 0$   
 Pure Covalent



$EN_{Cl} = 3.0$   
 $EN_H = 2.1$   
 $3.0 - 2.1 = 0.9$   
 Polar Covalent



$EN_{Cl} = 3.0$   
 $EN_{Na} = 1.0$   
 $3.0 - 0.9 = 2.1$   
 Ionic

## Electronegativity and Bond Polarity

- If difference in electronegativity between bonded atoms is 0, the bond is **pure covalent**  
 – equal sharing
- If difference in electronegativity between bonded atoms is 0.1 to 0.4, the bond is **nonpolar covalent**
- If difference in electronegativity between bonded atoms 0.5 to 1.9, the bond is **polar covalent**
- If difference in electronegativity between bonded atoms larger than or equal to 2.0, the bond is **ionic**

## Dipole Moments

TABLE 9.2 Dipole Moments of Several Molecules in the Gas Phase

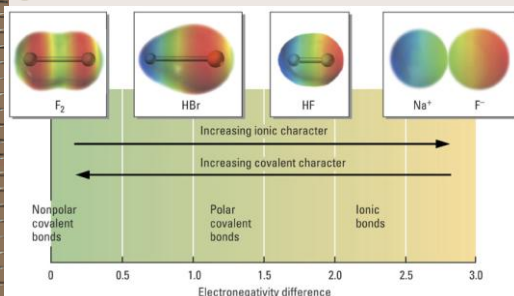
Molecule	$\Delta EN$	Dipole Moment (D)
$Cl_2$	0	0
$ClF$	1.0	0.88
$HF$	1.9	1.82
$LiF$	3.0	6.33

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## Important examples

- Polar bonds
  - Carbon-oxygen
  - Oxygen-hydrogen
- Non-polar bonds
  - Any homonuclear diatomic
  - Carbon-hydrogen

## Bond Characteristics



## Ionic and Metallic bonding

- Lewis theory is only meant for covalent bonding, though some authors try to apply it to ionic bonding.
- Ionic bonding is transfer of electron(s) followed by attraction due to Coulomb's law.

## Lattice Energy

- Tremendous attraction between oppositely charged ions
- Coulomb's Law

$$U = k \frac{q_1 q_2}{d}$$

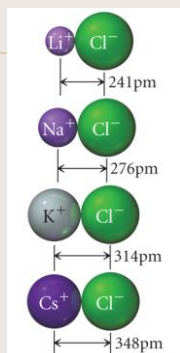
- k depends upon crystal geometry
- Larger for larger charges and smaller ions

## Trends in Lattice Energy Ion Size

- the force of attraction between charged particles is inversely proportional to the distance between them
- larger ions mean the center of positive charge (nucleus of the cation) is farther away from negative charge (electrons of the anion)
  - **larger ion = weaker attraction = smaller lattice energy**

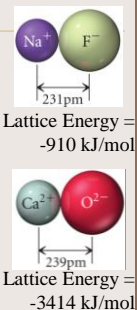
## Lattice Energy vs. Ion Size

Metal Chloride	Lattice Energy (kJ/mol)
LiCl	-834
NaCl	-787
KCl	-701
CsCl	-657



## Trends in Lattice Energy Ion Charge

- the force of attraction between oppositely charged particles is directly proportional to the product of the charges
- larger charge means the ions are more strongly attracted
  - **larger charge = stronger attraction = larger lattice energy**
- of the two factors, ion charge generally more important



Which of the following compounds will have the **highest** lattice energy value?

- (A) KBr
- (B) NaBr
- (C) LiBr
- (D) RbBr

Which of the following has the larger lattice energy?

- A LiF
- B MgS
  
- A CaF<sub>2</sub>
- B CaCl<sub>2</sub>

## Metallic Bonds

- low ionization energy of metals allows them to lose electrons easily
- the simplest theory of metallic bonding involves the metals atoms releasing their valence electrons to be shared by all to atoms/ions in the metal
  - an organization of metal cation islands in a sea of electrons
  - electrons delocalized throughout the metal structure