

*Chapter 8*  
*Basic Concepts of Chemical Bonding*

- Why do  $\text{TiCl}_4$  and  $\text{TiCl}_3$  have different colors? ... different chemical properties? ... different physical states?

*Chemical Bonding and Properties*

- Difference in colors is due to differences in electronic configuration for  $\text{TiCl}_3$  and  $\text{TiCl}_4$
- Differences in chemical behavior are due to differences in the types of bonds
- Bond: forces that hold atoms together in molecules or ionic compounds.

*8.1 Chemical Bonds and Electronic Configuration*

- Types of bonds and types of substances
  - Ionic
  - Covalent
  - Metallic
- The type of bond between atoms is partially responsible for the properties of the substance.

*Types of Bonds*

- Bonds tend to form to give more stable electronic configurations by losing, gaining, or sharing electrons.
- Ionic Bonding: complete transfer of electrons with resultant electrostatic attractions between ions of opposite charge
- Covalent Bonding: sharing of electron pairs
- Metallic Bonding: sharing of loosely held electrons
- How do these bonding models explain the properties of substances ?
- Which elements will combine together to give each type of bond?
- How many bonds will form between given atoms?
- Classify the following substances by the type of bond:

$\text{CaF}_2$   
 $\text{CuCl}_2$   
 $\text{NCl}_3$   
 $\text{H}_2\text{O}$   
 $\text{NH}_4\text{Cl}$   
 $\text{K}_2\text{SO}_4$

*Lewis Symbols and the Octet Rule*

- Lewis Symbols: The number of valence electrons available for bonding are indicated by unpaired dots.
- The Octet Rule: atoms and ions tend to have eight valence electrons (many exceptions)
- These symbols are called Lewis symbols
- We generally place the electrons on four sides of a square around the

**TABLE 8.1 Lewis Symbols**

Element	Electron Configuration	Electron-Dot Symbol
Li	$[\text{He}]2s^1$	$\text{Li}\cdot$
Be	$[\text{He}]2s^2$	$\cdot\text{Be}\cdot$
B	$[\text{He}]2s^22p^1$	$\cdot\overset{\cdot}{\text{B}}\cdot$
C	$[\text{He}]2s^22p^2$	$\cdot\overset{\cdot}{\underset{\cdot}{\text{C}}}\cdot$
N	$[\text{He}]2s^22p^3$	$\cdot\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{N}}}}\cdot$
O	$[\text{He}]2s^22p^4$	$\cdot\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{O}}}}}\cdot$
F	$[\text{He}]2s^22p^5$	$\cdot\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{F}}}}}}\cdot$
Ne	$[\text{He}]2s^22p^6$	$\cdot\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Ne}}}}}}}\cdot$

element symbol.

### *Octet Rule*

- Octet rule: we know that  $s^2p^6$  is a noble gas configuration. We assume that an atom is stable when surrounded by 8 electrons (4 electron pairs).
- What ion or compound is formed from the following to approximate a noble gas electronic configuration? What is the configuration?
- Na  $1s^22s^22p^63s^1$
- $\text{Na}^+$   $1s^22s^22p^6$
- H  $1s^1$
- $\text{H}^+$  or  $\text{H}^-$   $1s^0$  or  $1s^2$
- Cl  $1s^22s^22p^63s^23p^5$
- $\text{Cl}^-$   $1s^22s^22p^63s^23p^6$
- O  $1s^22s^22p^4$
- $\text{O}^{2-}$   $1s^22s^22p^6$
- $\text{H} + \text{O}$   $1s^1 + 1s^22s^22p^4$
- $\text{H}_2\text{O}$   $1s^22s^22p^6$  for O,  $1s^2$  for H
- $\text{Na} + \text{O}$   $1s^22s^22p^63s^1 + 1s^22s^22p^4$
- $\text{Na}_2\text{O}$   $1s^22s^22p^6$  for Na and O
- $\text{C} + \text{H}$   $1s^22s^22p^2 + 1s^2$
- $\text{CH}_4$   $1s^22s^22p^6$  for C,  $1s^2$  for H
- $\text{C} + \text{Cl}$   $1s^22s^22p^2 + 1s^22s^22p^63s^23p^5$
- $\text{CCl}_4$   $1s^22s^22p^6$  for C,  
 $1s^22s^22p^63s^23p^6$  for Cl
- $\text{C} + \text{O}$   $1s^22s^22p^2 + 1s^22s^22p^4$
- $\text{CO}_2$   $1s^22s^22p^6$  for C and O

### *Elements can violate the octet rule*

- S can form  $\text{SH}_2$  with 8 electrons
- S can form  $\text{SCL}_4$  with 10 electrons
- S can form  $\text{SCL}_6$  with 12 electrons

### 8.2 *Ionic Bonding*

- Ionic bonds result from electron transfer  
 $\text{Na} \rightarrow \text{Na}^+ + e^-$   
 $\text{Cl} + e^- \rightarrow \text{Cl}^-$   
 $\text{Na}^+ + \text{Cl}^- \rightarrow \text{NaCl}$
- Loss of electrons from metals to give a noble gas configuration gives different charges and different compositions for various metals.

### *Structures of Ionic Crystals*

- Crystal lattice is an arrangement of ions of opposite charge surrounding one another in three dimensions.
- Several ways of doing this, depending on the sizes and charges of the ions .
- Coordination number: number of ions of opposite charge that surround a given ion.

- What are the coordination numbers in the following structures?

#### *Structure and Properties*

- Why are crystalline solids brittle, whereas metallic solids are malleable?

#### *Strength of Ionic Bonds*

- Ionic bonds are very strong, so separating ions requires much energy
- High melting points, boiling points
- High heats of fusion and vaporization
- Crystals are hard and brittle
- Electrical insulators when solid, electrical conductors when molten or dissolved in water

#### *Born-Haber Cycle*

- Used to understand the stability of ionic compounds
- elements  $\rightarrow$  gaseous atoms  $\rightarrow$  gaseous ions  $\rightarrow$  crystal
- Application of Hess's Law
- Heat of Atomization
  - $\text{Na(s)} \rightarrow \text{Na(g)} \quad \Delta H_{\text{atom}} = 108 \text{ kJ}$
  - $\text{Cl}_2\text{(g)} \rightarrow 2 \text{Cl(g)} \quad \Delta H_{\text{atom}} = 122 \text{ kJ}$
- Ionization Energy
  - $\text{Na(g)} \rightarrow \text{Na}^+\text{(g)} \quad \text{IE} = 496 \text{ kJ}$
- Electron Affinity
  - $\text{Cl(g)} \rightarrow \text{Cl}^-\text{(g)} \quad \text{EA} = -349 \text{ kJ}$
- The energy change is still positive up to this point.
- Lattice Energy, U
  - $\text{Na}^+\text{(g)} + \text{Cl}^-\text{(g)} \rightarrow \text{NaCl(s)} \quad U = -788 \text{ kJ}$
- The lattice energy must be sufficiently negative to cause the overall energy change to be negative:
  - $\text{Na(s)} + 1/2 \text{Cl}_2\text{(g)} \rightarrow \text{NaCl(s)} \quad \Delta H = -411 \text{ kJ}$

#### *Relative Lattice Energies*

- What factors are involved in determining the value of the lattice energy?
- Charge and size:

$$U = -A \frac{Z_+ Z_-}{d_{\pm}}$$

- The crystal is more stable (bond strength is greater) if the charges are greater, or if the sizes are smaller. The factor A varies with the structure.

#### *8.4 Covalent Bonding*

- Molecules arise from localized attractive forces between atoms, which we call covalent bonds
- Atoms are connected strongly, but molecules are not strongly held together
- Molecules are usually gases or liquids unless they are very large

- Solids are usually soft  
low melting points  
low boiling points  
low heats of fusion  
low heats of vaporization
- Properties arise because molecules are not strongly held together
- Usually found with nonmetals

### *Single Covalent Bonds*

- Sharing of 1 pair of electrons
- Each atom has one half-filled valence orbital that overlap one another
- $\text{H} \cdot + \cdot \text{H} \rightarrow \text{H}:\text{H}$
- Single bond represented as  $\text{H}:\text{H}$  or  $\text{H}-\text{H}$   
Called a Lewis formula or electron-dot formula

### *Single bonds between like atoms*

- Halogens  
Why do they all have the same Lewis formula?

### *Single bonds between unlike atoms*

- HF  
*Some atoms can form bonds with more than one atom*
- $\text{CCl}_4$   
How many valence electrons are supplied by each atom?

### *Multiple Bonds*

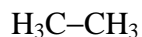
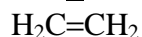
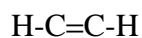
- Can share more than one pair of electrons to form double or triple bonds

### *Comparison of Bonds*

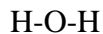
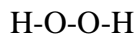
- Bond Energy (bond strength):  
single bond < double bond < triple bond
- Bond Length (distance between atom centers):  
single bond > double bond > triple bond

### *Valence Electrons and Number of Bonds*

- How is the number of bonds formed by a given atom related to its number of valence electrons?



### *More examples to consider:*





### *Structures of Covalent Molecules*

- Various structures, such as a tetrahedral arrangement around carbon, are common. These will be considered in Chapter 9.

### 8.5 *Bond Polarity and Electronegativity*

- Polar and Nonpolar Covalent Bonds
- How do we predict whether atoms will transfer or share electrons when forming a bond?
- Do electrons in every covalent bond have to be shared equally? Does the average location of the shared electron pair have to be half-way between the atoms?

### *Polarity of Covalent Bonds*

- Unequal sharing of electrons in a bond leads to the development of partial charges separated from one another - this phenomenon is called polarity.
- The greater the charge separation, the more like an ionic bond the covalent bond becomes. We speak of the relative ionic and covalent character of the bond.

### *Bonds: Ionic, Polar Covalent, Non-Polar Covalent*

- Bonds can be found with a range of polarities, from completely ionic to completely covalent.
- When will a bond be polar?

### *Electronegativity*

- How do we measure the tendency of an atom to share its electrons in a bond?
- Pauling found that HF has a stronger bond than the average of the H<sub>2</sub> and F<sub>2</sub> bonds; he attributed this extra strength to partial ionic character.
- From the bond strengths, he assigned values of electronegativity - the ability of an atom to attract electrons in a bond to itself.

### *Trends in Electronegativity*

- See KC Discoverer
- What do these trends remind you of ?
- Which combinations of elements are more likely to form ionic bonds? ... covalent bonds?

### *Polarity and Electronegativity*

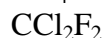
- What is the relative polarity of the bonds in the following sets?  
F<sub>2</sub>, HF  
FCl, Cl<sub>2</sub>  
O<sub>2</sub>, BO  
OH, CH, HH, HF

8.6 *Drawing Lewis Structures*

- Procedure to ensure conformance to the octet rule:

- ① Write an atomic skeleton
- ② Count valence electrons
- ③ Place electron pairs between bonded atoms
- ④ Place remaining electrons on the outside atoms, then the central atom
- ⑤ Shift electrons, as necessary, to make multiple bonds and satisfy the octet rule

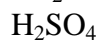
Write Lewis formulas for the following molecules or ions:

*Formal Charge*

- Can be used to decide between alternate Lewis structures
- Will not consider this concept further since there is considerable controversy as to whether the concept of formal charge dictating electron distribution is in fact correct.

8.7 *Resonance Structures*

- Lewis formulas don't always accurately represent bonds. Sometimes it takes two formulas to adequately represent the bonds.
- How many different valid Lewis formulas can you write for the following molecules or ions? How do they differ?



- The different resonance forms represent delocalized bonding.

8.8 *Exceptions to the Octet Rule*

- **Odd-Electron Molecules**
  - Write a Lewis formula for NO and for NO<sub>2</sub>
  - Why does NO<sub>2</sub> combine with itself to form N<sub>2</sub>O<sub>4</sub>?
- **Incomplete Octets**
  - Write a Lewis formula for BH<sub>3</sub>
  - How can the octet rule be satisfied for molecules with incomplete octets?
- Coordinate Covalent Bonding

- Molecules with too few electron pairs can bond with molecules with unshared electron pairs to form a new shared-electron-pair bond
- $\text{BH}_3 + \text{NH}_3 \rightarrow \text{H}_3\text{BNH}_3$
- Draw a Lewis formula for each molecule.
- Why is  $\text{BH}_4^-$  more stable than  $\text{BH}_3$ ?
- Why is  $\text{BF}_4^-$  more stable than  $\text{BF}_3$ ?
- Why does aluminum chloride exist in the gaseous state as  $\text{Cl}_2\text{AlCl}_2\text{AlCl}_2$  (that is,  $\text{Al}_2\text{Cl}_6$ ) instead of  $\text{AlCl}_3$ ?
- **Expanded Valence Shells**
- What do you do if there are too many electrons to be accommodated by octets?
- Write Lewis formulas for the following:  

$\text{SF}_4$	$\text{SF}_6$	$\text{IF}_4^+$	$\text{XeF}_4$	$\text{XeF}_2$
$\text{PF}_5$	$\text{BrF}_3$	$\text{BrF}_5$		

### 8.9 Strengths of Covalent Bonds

- Bond Energy or Bond Dissociation Energy - energy require to break a bond in a gaseous molecule
- Reactions generally proceed to form compounds with more stable bonds (greater bond energy)
- Values in Table 8.4

#### Average Bond Energy

- Bond energy varies somewhat from one molecule to another, or even within one molecule, so we use an average bond energy (D)

H-OH	502 kJ/mol
H-O	427 kJ/mol
H-OOH	431 kJ/mol

Average = 459 kJ/mol for O-H

#### Bond Energies and Heats of Reaction

- $$\Delta H_{\text{rxn}} = \sum \text{D}_{\text{broken}} - \sum \text{D}_{\text{made}}$$

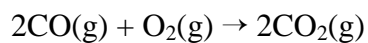
reactants
products
- Use only when heats of formation are not available, since bond energies are average values for gaseous molecules.
- Why is this a problem?
- Break all reactant bonds, then make product bonds
- Use bond energies to calculate the enthalpy change for the following reaction:  

$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$$
- $$\Delta H_{\text{rxn}} = \text{D}_{\text{N}\equiv\text{N}} + 3\text{D}_{\text{H-H}} - 6\text{D}_{\text{N-H}}$$

$$\Delta H_{\text{rxn}} = 942 + 3(432) - 6(386) = -78 \text{ kJ}$$
 measured value = -92.2 kJ
- Why are the values different?

#### Sample Problem

- Use bond energies to calculate the enthalpy change for the following reaction:



$$D_{\text{C}\equiv\text{O}} = 1072 \text{ kJ}$$

$$D_{\text{O}=\text{O}} = 492 \text{ kJ}$$

$$D_{\text{C}=\text{O}} = 799 \text{ kJ}$$

- $\Delta H_{\text{rxn}} = 2D_{\text{C}\equiv\text{O}} + D_{\text{O}=\text{O}} - 4D_{\text{C}=\text{O}}$   
 $\Delta H_{\text{rxn}} = 2(1072) + 492 - 4(799)$   
 $= -560 \text{ kJ}$

### *Bond Energy and Bond Length*

- The distance between the nuclei of the atoms involved in a bond is called the bond length.
- Multiple bonds are shorter than single bonds.
- Multiple bonds are also stronger than single bonds.
- As the number of bonds between two atoms increases, the atoms are held closer and more tightly together.