Chapter 8
Basic Concepts of Chemical Bonding

- Why do $TiCl_4$ and $TiCl_3$ have different colors? ... different chemical properties? ... different physical states?

Chemical Bonding and Properties

- Difference in colors is due to differences in electronic configuration for $TiCl_3$ and $TiCl_4$
- 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:

  CaF_2
  $CuCl_2$
  NCl_3
  H_2O
  NH_4Cl
  K_2SO_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	[He]$2s^1$	Li·
Be	[He]$2s^2$	·Be·
B	[He]$2s^22p^1$	·Ḃ·
C	[He]$2s^22p^2$	·Ċ·
N	[He]$2s^22p^3$	·N̈:
O	[He]$2s^22p^4$	:Ö:
F	[He]$2s^22p^5$	·F̤̈:
Ne	[He]$2s^22p^6$	:N̤̈e:

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 $1s^22s^22p^63s^1$
- Na^+ $1s^22s^22p^6$
- H $1s^1$
- H^+ or H^- $1s^0$ or $1s^2$
- Cl $1s^22s^22p^63s^23p^5$
- Cl^- $1s^22s^22p^63s^23p^6$
- O $1s^22s^22p^4$
- O^{2-} $1s^22s^22p^6$
- H + O $1s^1 + 1s^22s^22p^4$
- H_2O $1s^22s^22p^6$ for O, $1s^2$ for H
- Na + O $1s^22s^22p^63s^1 + 1s^22s^22p^4$
- Na_2O $1s^22s^22p^6$ for Na and O
- C + H $1s^22s^22p^2 + 1s^2$
- CH_4 $1s^22s^22p^6$ for C, $1s^2$ for H
- C + Cl $1s^22s^22p^2 + 1s^22s^22p^63s^23p^5$
- CCl_4 $1s^22s^22p^6$ for C,
  $1s^22s^22p^63s^23p^6$ for Cl
- C + O $1s^22s^22p^2 + 1s^22s^22p^4$
- CO_2 $1s^22s^22p^6$ for C and O

Elements can violate the octet rule

- S can form SH_2 with 8 electrons
- S can form SCl_4 with 10 electrons
- S can form SCl_6 with 12 electrons

8.2 Ionic Bonding

- Ionic bonds result from electron transfer
  $Na \rightarrow Na^+ + e^-$
  $Cl + e^- \rightarrow Cl^-$
  $Na^+ + Cl^- \rightarrow NaCl$
- 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 → gaseous atoms → gaseous ions → crystal
- Application of Hess's Law
- Heat of Atomization
  $Na(s) \rightarrow Na(g)$ $\Delta H_{atom} = 108$ kJ
  $Cl_2(g) \rightarrow 2\ Cl(g)$ $\Delta H_{atom} = 122$ kJ
- Ionization Energy
  $Na(g) \rightarrow Na^+(g)$ IE = 496 kJ
- Electron Affinity
  $Cl(g) \rightarrow Cl^-(g)$ EA = - 349 kJ
- The energy change is still positive up to this point.
- Lattice Energy, U
  $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ U = -788 kJ
- The lattice energy must be sufficiently negative to cause the overall energy change to be negative:
  $Na(s) + 1/2\ Cl_2(g) \rightarrow NaCl(s)$ $\Delta H = -411$ kJ

Relative Lattice Energies

- What factors are involved in determining the value of the lattice energy?
- Charge and size: $$\mathbf{U = -A\frac{Z_+\ Z_-}{d_\pm}}$$
- 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
- $H^{\cdot} + {}^{\cdot}H \rightarrow H{:}H$
- Single bond represented as H:H or H-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

- 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?

  H-C≡C-H
  $H_2C{=}CH_2$
  $H_3C{-}CH_3$
  CH_4

More examples to consider:

O_2	O=O
H_2O_2	H-O-O-H
H_2O	H-O-H
N_2	N≡N

NH_3
N_2H_4 H_2N-NH_2

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_2 and F_2 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_2, HF
  FCl, Cl_2
  O_2, BO
  OH, CH, HH, HF

8.6 Drawing Lewis Structures

- Procedure to ensure conformance to the octet rule:

❶Write an atomic skeleton
❷Count valence electrons
❸Place electron pairs between bonded atoms
❹Place remaining electrons on the outside atoms, then the central atom
❺Shift electrons, as necessary, to make multiple bonds and satisfy the octet rule

Write Lewis formulas for the following molecules or ions:

NH_3
NH_4^+
CCl_2F_2
$SOCl_2$
SO_2
CO_2
CO_3^{2-}
SO_3^{2-}
H_2SO_4
HCN
CN^-
NCS^-

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?

SO_2	SO_3
H_2SO_4	CO_3^{2-}
NO_3^-	HNO_3
NCS^-	

- 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_2
- Why does NO_2 combine with itself to form N_2O_4?
- **Incomplete Octets**
- Write a Lewis formula for BH_3
- 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
- $BH_3 + NH_3 \rightarrow H_3BNH_3$
- Draw a Lewis formula for each molecule.
- Why is BH_4^- more stable than BH_3?
- Why is BF_4^- more stable than BF_3?
- Why does aluminum chloride exist in the gaseous state as $Cl_2AlCl_2AlCl_2$ (that is, Al_2Cl_6) instead of $AlCl_3$?
- **Expanded Valence Shells**
- What do you do if there are too many electrons to be accommodated by octets?
- Write Lewis formulas for the following:

SF_4	SF_6	IF_4^+	XeF_4	XeF_2
PF_5	BrF_3	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

- $\Delta H_{rxn} = \underset{\text{reactants}}{\Sigma D_{broken}} - \underset{\text{products}}{\Sigma D_{made}}$
- 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: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
- $\Delta H_{rxn} = D_{N \equiv N} + 3D_{H\text{-}H} - 6D_{N\text{-}H}$
  $\Delta H_{rxn} = 942 + 3(432) - 6(386) = -78$ 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:

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
$D_{C \equiv O} = 1072$ kJ
$D_{O = O} = 492$ kJ
$D_{C = O} = 799$ kJ

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