Chapter 8. Basic Concepts of Chemical Bonding

8.1 Chemical Bonds, Lewis Symbols, and the Octet Rule

8.2 Ionic Bonding

- Consider the reaction between sodium and chlorine:
  \[ \text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{NaCl}(s) \quad \Delta H^o_f = -410.9 \text{ kJ/mol} \]
  - The reaction is violently exothermic.
  - We infer that the NaCl is more stable than its constituent elements.
  - Sodium has lost an electron to become Na\(^+\) and chlorine has gained the electron to become Cl\(^-\).
  - Note Na\(^+\) has an Ne electron configuration and Cl\(^-\) has an Ar configuration.
  - That is, both Na\(^+\) and Cl\(^-\) have an octet of electrons.

- NaCl forms a very regular structure in which each Na\(^+\) ion is surrounded by six Cl\(^-\) ions.
  - Similarly each Cl\(^-\) ion is surrounded by six Na\(^+\) ions.
  - There is a regular arrangement of Na\(^+\) and Cl\(^-\) in three dimensions.
  - Note that the ions are packed as closely as possible.
  - Note that it is not easy to find a molecular formula to describe the ionic lattice.

Energetics of Ionic Bond Formation

- The heat of formation of NaCl(s) is exothermic:
  \[ \text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{NaCl}(s) \quad \Delta H^o_f = -410.9 \text{ kJ/mol} \]

- Separation of the NaCl into sodium and chloride ions is endothermic:
  \[ \text{NaCl}(s) \rightarrow \text{Na}^+(g) + \text{Cl}^-(g) \quad \Delta H = +788 \text{ kJ/mol} \]

- The energy required to separate one mole of a solid ionic compound into gaseous ions is called the lattice energy, \( \Delta H_{\text{lattice}} \).
  - Lattice energy depends on the charge on the ions and the size of the ions.
  - The stability of the ionic compound comes from the attraction between ions of unlike charge.
  - The specific relationship is given by Coulomb’s equation:
    \[ E = k \frac{Q_1 Q_2}{d} \]
    - where \( E \) is the potential energy of the two interacting charged particles, \( Q_1 \) and \( Q_2 \) are the charges on the particles, \( d \) is the distance between their centers, and \( k \) is a constant.
    \[ k = 8.99 \times 10^9 \text{ J-m/C}^2. \]
    - As \( Q_1 \) and \( Q_2 \) increase, \( E \) increases, and as \( d \) increases, \( E \) decreases.
Calculation of Lattice Energies: The Born-Haber Cycle

- The **Born-Haber cycle** is a thermodynamic cycle that analyzes lattice energy precisely.

- Consider a Born-Haber cycle for the formation of NaCl(s) from Na(s) and Cl₂(g).
- The direct route is: \( \text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{NaCl}(s) \quad \Delta H_f^o = -411 \text{ kJ} \)

- Alternatively, we can form:
  - Sodium gas (108 kJ; *endothermic*), then
  - Chlorine atoms (122 kJ; *endothermic*), then
  - Sodium ions (ionization energy for Na, 496 kJ; *endothermic*), then
  - Chloride ions (electron affinity for Cl, –349 kJ; *exothermic*), then
  - Form the ionic lattice (*exothermic*).

- The sum of the above enthalpies is –411 kJ.
Sample Exercise 8.1 (p. 302)

Without using Table 8.2 (above), arrange the following ionic compounds in order of increasing lattice energy: NaF, CsI, CaO.

Practice Exercise 8.1

Which substance would you expect to have the greatest lattice energy? MgF$_2$, CaF$_2$ or ZrO$_2$?

Electron Configuration of Ions of the Representative Elements

Sample Exercise 8.2 (p. 303)

Predict the ion generally formed by each of the following atoms:

a) Sr  
b) S  
c) Al

Practice Exercise 8.2

Predict the charges on the ions formed when magnesium reacts with nitrogen.
**Transition-Metal Ions**
- Lattice energies compensate for the loss of up to three electrons.
- We often encounter cations with charges of 1+, 2+ or 3+ in ionic compounds.
- However, transition metals can’t attain a noble gas conformation (>3 electrons beyond a noble gas core).
  - Transition metals tend to lose the valence shell electrons first and then as many $d$ electrons as are required to reach the desired charge on the ion.
  - Thus electrons are removed from 4s **before** the 3$d$, etc.

**Polyatomic Ions**
- Polyatomic ions are formed when there is an overall charge on a compound containing covalent bonds.
  - Examples: $\text{SO}_4^{2-}$, $\text{NO}_3^-$
- In polyatomic ions, two or more atoms are bound together by predominantly covalent bonds.
  - The stable grouping carries a charge.

**8.3 Covalent Bonding**

Read this section, then answer the Sample and Practice Exercises

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**Sample Exercise 8.3 (p. 306)**

Given the Lewis symbols for the elements nitrogen and fluorine shown in Table 8.1, predict the formula of the stable binary compound (a compound composed of two elements) formed when nitrogen reacts with fluorine, and draw its Lewis structure.

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**Practice Exercise 8.3**

Compare the Lewis symbol for neon with the Lewis structure for methane, $\text{CH}_4$.

In what important way are the electron arrangements about neon and carbon alike?

In what important respect are they different?
8.4 Bond Polarity and Electronegativity

Read this section, then answer the following Sample and Practice Exercise:

Sample Exercise 8.4 (p. 309)

Which bond is more polar:
   a) B-Cl or C-Cl?
   b) P-F or P-Cl?

Indicate in each case which atom has the partial negative charge.

Practice Exercise 8.4

Which of the following bonds is most polar:
S-Cl, S-Br, Se-Cl, or Se-Br?

Dipole Moments

- Molecules like HF have centers of positive and negative charge that do not coincide = polar molecules.
- We indicate the polarity of molecules in two ways:
  - The positive end (or pole) in a polar bond may be represented with a “$\delta^+$” and the negative pole with a “$\delta^-$”.
  - We can also place an arrow over the line representing the bond.
    - The arrow points toward the more electronegative element and shows the shift in electron density toward that atom.
- We can quantify the polarity of the molecule.
  - When charges are separated by a distance, a dipole is produced.
  - The dipole moment is the quantitative measure of the magnitude of the dipole ($\mu$)
    \[ \mu = Q \cdot r \]
    - The magnitude of the dipole moment is given in debyes (D).
Sample Exercise 8.5 (p. 311)
The distance between the centers of the H and Cl atoms in the HCl molecule (called its bond length) is 1.27 Å.

a) Calculate the dipole moment, in D, that would result if the charges on the H and Cl atoms were 1+ and 1-, respectively.  (6.08 D)

b) The experimentally measured dipole moment of HCl(g) is 1.08 D.  What magnitude of charge, in units of $e$, on the H and Cl atoms would lead to this dipole moment?

(0.178 e)

Practice Exercise 8.5
The dipole moment of chlorine monofluoride, ClF(g) is 0.88 D.  The bond length of the molecule is 1.63 Å.

a) Which atom is expected to have a negative charge? (F)

b) What is the charge on that atom, in e? (0.11-)

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Length (Å)</th>
<th>Electronegativity Difference</th>
<th>Dipole Moment (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>0.92</td>
<td>1.9</td>
<td>1.82</td>
</tr>
<tr>
<td>HCl</td>
<td>1.27</td>
<td>0.9</td>
<td>1.08</td>
</tr>
<tr>
<td>HBr</td>
<td>1.41</td>
<td>0.7</td>
<td>0.82</td>
</tr>
<tr>
<td>HI</td>
<td>1.61</td>
<td>0.4</td>
<td>0.44</td>
</tr>
</tbody>
</table>

8.5 Drawing Lewis Structures

1. Add up all of the valence electrons on all atoms.
   • For an anion, add electrons equal to the negative charge.
   • For a cation, subtract electrons equal to the positive charge.
2. Identify the central atom.
   • When a central atom has other atoms bound to it, the central atom is usually written first.
     • Example: In CO$_3^{2-}$ the central atom is carbon.
3. Place the central atom in the center of the molecule and add all other atoms around it.
4. Place one bond (two electrons) between each pair of atoms.
5. Complete the octets for all atoms connected to the central atom (exception: hydrogen can only have two electrons).
6. Complete the octet for the central atom; use multiple bonds if necessary.
Sample Exercise 8.6 (p. 314)

Draw the Lewis structure for phosphorus trichloride, PCl₃.

Practice Exercise 8.6

a) How many valence electrons should appear in the Lewis structure for CH₂Cl₂?

b) Draw the Lewis structure.

Sample Exercise 8.7 (p. 315)

Draw the Lewis structure for HCN.

Practice Exercise 8.7

Draw the Lewis structure for

a) NO⁺ ion;

b) C₂H₄
Sample Exercise 8.8 (p. 316)

Draw the Lewis structure for the \( \text{BrO}_3^- \) ion.

Practice Exercise 8.8

Draw the Lewis structure for

a) \( \text{ClO}_2^- \) ion

b) \( \text{PO}_4^{3-} \) ion

Formal Charge

- Sometimes it is possible to draw more than one Lewis structure with the octet rule obeyed for all the atoms.
- To determine which structure is most reasonable, we use formal charge.
- The formal charge of an atom is the charge that an atom (in a molecule) would have if all of the atoms had the same electronegativity.

- To calculate formal charge, electrons are assigned as follows:
  - All nonbonding (unshared) electrons are assigned to the atom on which they are found.
  - Half of the bonding electrons are assigned to each atom in a bond.
  - Formal charge is the number of valence electrons in the isolated atom, minus the number of electrons assigned to the atom in the Lewis structure.
- For example: consider CN\(^-\) (cyanide ion):
  - For carbon:
    - There are four valence electrons (from periodic table).
    - In the Lewis structure there are two nonbonding electrons and three electrons from the triple bond.
    - There are five electrons from the Lewis structure.
    - Formal charge: \( 4 - 5 = -1 \).
• For nitrogen:
  • There are five valence electrons.
  • In the Lewis structure there are two nonbonding electrons and three from the triple bond.
  • There are five electrons from the Lewis structure.
  • Formal charge = 5 – 5 = 0.

\[
\begin{array}{c}
\text{Valence electrons: } & 6 & 4 & 6 & 6 & 4 & 6 \\
-(\text{Electrons assigned to atom): } & 6 & 4 & 6 & 7 & 4 & 5 \\
\text{Formal charge: } & 0 & 0 & 0 & -1 & 0 & +1
\end{array}
\]

Formal charge.

The concept of formal charge can help us choose between alternative Lewis structures. We will consider the CO₂ molecule to see how this is done. As shown in Section 8.3, CO₂ is represented as having two double bonds. However, we can also satisfy the octet rule by drawing a Lewis structure having one single bond and one triple bond. Calculating the formal charge for each atom in these structures is given in the figure.

• Using formal charge calculations to distinguish between alternative Lewis structures:
  • The most stable structure has the smallest formal charge on each atom and
  • The most negative formal charge on the most electronegative atoms.

• It is important to keep in mind that formal charges do NOT represent REAL charges on atoms!

Sample Exercise 8.9 (p. 317)

The following are three possible Lewis structures for the thiocyanate ion, NCS⁻:

\[
\begin{align*}
&[\hat{\text{N}}\equiv\text{C}\equiv\text{S}^-] \quad [\hat{\text{N}}\equiv\text{C}\equiv\text{S}^-] \quad [\text{N}\equiv\text{C}\equiv\text{S}^-]
\end{align*}
\]

a) Determine the formal charges of the atoms in each structure.

b) Which Lewis structure is the preferred one?
Practice Exercise 8.9

The cyanate ion (NCO\textsuperscript{-}), like the thiocyanate ion, has three possible Lewis structures.

a) Draw these three Lewis structures and assign formal charges to the atoms in each structure;

b) Which Lewis structures should be the preferred one?

Oxidation number and formal charge.

(a) The oxidation number for any atom in a molecule is determined by assigning all shared electrons to the more electronegative atom (in this case Cl).

(b) Formal charges are derived by dividing all shared electron pairs equally between the bonded atoms.

(c) The calculated distribution of electron density on an HCl molecule. Regions of relatively more negative charge are red; those of more positive charge are blue. Negative charge is clearly localized on the chlorine atom.
8.6 Resonance Structures

- Some molecules are not well described by a single Lewis structure.
  - Typically, structures with multiple bonds can have similar structures with the multiple bonds between different pairs of atoms.
    - Example: Experimentally, ozone has two identical bonds whereas the Lewis structure requires one single (longer) and one double bond (shorter).
  - Resonance structures are attempts to represent a real structure that is a mix between several extreme possibilities.
    - Resonance structures are Lewis structures that differ only with respect to placement of the electrons.
    - The “true” arrangement is a blend or hybrid of the resonance structures.
    - Example: In ozone the extreme possibilities have one double and one single bond.
      - The resonance structure has two identical bonds of intermediate character.
  - We use a double headed arrows (↔) to indicate resonance.
  - Common examples: O₃, NO₃⁻, SO₃, NO₂, and benzene.

Sample Exercise 8.10 (p. 320)
Which is predicted to have the shorter sulfur-oxygen bonds, SO₃ or SO₃²⁻?

Practice Exercise 8.10
Draw two equivalent resonance structures for the formate ion, HCO₂⁻.
Resonance in Benzene

- Benzene belongs to an important category of organic molecules called aromatic compounds.

- Benzene (C_6H_6) is a cyclic structure, consisting of six carbon atoms in a hexagon.
  - Each carbon atom is attached to two other carbon atoms and one hydrogen atom.
  - There are alternating double and single bonds between the carbon atoms.
  - Experimentally, the C–C bonds in benzene are all the same length.
  - Experimentally, benzene is planar.

- To emphasize the resonance between the two Lewis structures (hexagons with alternating single and double bonds), we often represent benzene as a hexagon with a circle in it.

Resonance in benzene.
We can write two equivalent Lewis structures for benzene, each of which satisfies the octet rule. These two structures are in resonance are shown in the figure.

Benzene is commonly represented by omitting the hydrogen atoms attached to carbon and showing only the carbon–carbon framework with the vertices unlabeled. In this convention, the resonance in the benzene molecule is represented either by two structures separated by a double-headed arrow, as with our other examples, or by a shorthand notation in which we draw a hexagon with a circle in it.
8.7 Exceptions to the Octet Rule

- There are three classes of exceptions to the octet rule:
  - Molecules with an **odd number of electrons**.
  - Molecules in which one atom has less than an octet.
  - Molecules in which one atom has more than an octet.

**Odd Number of Electrons**

- Most molecules have an even number of electrons and complete pairing of electrons occurs although some molecules have an odd number of electrons.
  - Examples: ClO₂, NO, and NO₂.

![Lewis structure for N₂O and N₂O₃](image)

**Less than an Octet**

- Molecules with less than an octet are also relatively rare.

- Most often encountered in compounds of boron or beryllium.
  - A typical example is BF₃.

![Lewis structure for BF₃](image)

Caption: We could complete the octet around boron by forming a double bond (step 5). In so doing, we see that there are three equivalent resonance structures (the formal charges on each atom are shown in red). These Lewis structures force a fluorine atom to share additional electrons with the boron atom, which is inconsistent with the high electronegativity of fluorine. In fact, the formal charges tell us that this is an unfavorable situation.

In each of the Lewis structures, the F atom involved in the double bond has a formal charge of +1, while the less electronegative B atom has a formal charge of −1. Thus, the Lewis structures in which there is a double bond are less important than the one in which there are fewer than an octet of valence electrons around boron.
More than an Octet

- This is the largest class of exceptions.
- Atoms from the third period on can accommodate more than an octet.
  - Examples: PCl₅, SF₄, AsF₆⁻, and ICl₄⁻.

Elements from the third period and beyond have unfilled d orbitals that can be used to accommodate the additional electrons.

[Orbital diagram for P.]

Orbital diagram for P.
Elements from the third period and beyond have ns, np, and unfilled nd orbitals that can be used in bonding. For example, the orbital diagram for the valence shell of a phosphorus atom is shown in the figure. Although third-period elements often satisfy the octet rule, as in PCl₃, they also often exceed an octet by seeming to use their empty d orbitals to accommodate additional electrons.

- Size also plays a role.
  - The larger the central atom, the larger the number of atoms that can surround it.
  - The size of the surrounding atoms is also important.
  - Expanded octets occur often when the atoms bound to the central atom are the smallest and most electronegative (e.g., F, Cl, O).

Sample Exercise 8.11 (p. 324)

Draw the Lewis structure for ICl₄⁻.

Practice Exercise 8.11

a) Which of the following atoms is never found with more than an octet of electrons around it: S, C, P, Br?

b) Draw the Lewis structure for XeF₂.
8.8 Strengths of Covalent Bonds

- The energy required to break a covalent bond is called the bond enthalpy, $D$.
  - That is, for the Cl$_2$ molecule, $D$(Cl-Cl) is given by $\Delta H$ for the reaction:

$$
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\to & \quad 2 \cdot \text{Cl} \\
\end{align*}
$$

- When more than one bond is broken:

$$
\begin{align*}
\text{CH}_4(g) & \rightarrow \text{C}(g) + 4\text{H}(g) & \Delta H = 1660 \text{ kJ} \\
\end{align*}
$$

- The bond enthalpy is a fraction of $\Delta H$ for the atomization reaction:

$$
D(\text{C-H}) = \frac{1}{4} \Delta H = \frac{1}{4}(1660 \text{ kJ}) = 415 \text{ kJ}.
$$

- Bond enthalpy is always a positive quantity.

<table>
<thead>
<tr>
<th>Table 8.4 Average Bond Enthalpies (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Single Bonds</strong></td>
</tr>
<tr>
<td>C$-$H</td>
</tr>
<tr>
<td>C$-$C</td>
</tr>
<tr>
<td>C$-$N</td>
</tr>
<tr>
<td>C$-$O</td>
</tr>
<tr>
<td>C$-$F</td>
</tr>
<tr>
<td>C$-$Cl</td>
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<tr>
<td>C$-$Br</td>
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<tr>
<td>C$-$I</td>
</tr>
<tr>
<td>C$-$S</td>
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<td></td>
</tr>
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<td>Si$-$H</td>
</tr>
<tr>
<td>Si$-$Si</td>
</tr>
<tr>
<td>Si$-$C</td>
</tr>
<tr>
<td>Si$-$O</td>
</tr>
<tr>
<td>Si$-$Cl</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Multiple Bonds</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>C$=$C</td>
</tr>
<tr>
<td>C$=$C</td>
</tr>
<tr>
<td>C$=$N</td>
</tr>
<tr>
<td>C$=$O</td>
</tr>
<tr>
<td>C$=$O</td>
</tr>
<tr>
<td>C$=$O</td>
</tr>
</tbody>
</table>
Bond Enthalpies and the Enthalpies of Reactions

- We can use bond enthalpies to calculate the enthalpy for a chemical reaction.
- We recognize that in any chemical reaction bonds need to be broken and then new bonds form.
- The enthalpy of the reaction is given by:
  - The sum of bond enthalpies for bonds broken less the sum of bond enthalpies for bonds formed.
- Where $\Delta H_{\text{rxn}}$ is the enthalpy for a reaction,
  \[ \Delta H_{\text{rxn}} = \sum D(\text{bonds broken}) - \sum D(\text{bonds formed}) \]
- We illustrate the concept with the reaction between methane, CH$_4$, and chlorine:
  \[ \text{CH}_4(g) + \text{Cl}_2(g) \rightarrow \text{CH}_3\text{Cl}(g) + \text{HCl}(g) \]
- In this reaction one C-H bond and one Cl-Cl bond are broken while one C-Cl bond and one H-Cl bond are formed.
- So $\Delta H_{\text{rxn}} = [D(\text{C-H}) + D(\text{Cl-Cl})] - [D(\text{C-Cl}) + D(\text{H-Cl})] = -104$ kJ.
- The overall reaction is exothermic which means than the bonds formed are stronger than the bonds broken.
- The above result is consistent with Hess’s law.

Using bond enthalpies to calculate $\Delta H_{\text{rxn}}$.

Average bond enthalpies are used to estimate $\Delta H_{\text{rxn}}$ for the reaction in Equation 8.13. Breaking the C—H and Cl—Cl bonds produces a positive enthalpy change ($\Delta H_1$, whereas making the C—Cl and H—Cl bonds causes a negative enthalpy change ($\Delta H_2$). The values of $\Delta H_1$ and $\Delta H_2$ are estimated from the values in Table 8.4. From Hess's law, $\Delta H_{\text{rxn}} = \Delta H_1 + \Delta H_2$. 

- 16 -
Sample Exercise 8.12 (p. 328)

Using Table 8.4, estimate ΔH for the reaction in the figure (where we explicitly show the bonds involved in the reactants and products).

\[
\text{H--C--C--H(g) + } \frac{7}{2} \text{O}_2(g) \rightarrow 2 \text{O==C==O(g) + 3 H--O--H(g)}
\]

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Practice Exercise 8.12

Using Table 8.4, estimate ΔH for the reaction shown.

\[
\text{H--N--N--H(g) } \rightarrow \text{ N==N(g) + 2 H--H(g)}
\]

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Bond Enthalpy 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.
  - We can show that multiple bonds are stronger than single bonds.
  - As the number of bonds between atoms increases, the atoms are held closer and more tightly together.
Sample Integrative Exercise 8

Phosgene, a substance used in poisonous gas warfare in World War I, is so named because it was first prepared by the action of sunlight on a mixture of carbon monoxide and chlorine gases. Its name comes from the Greek words ψός (light) and γένες (born of). Phosgene has the following elemental composition: 12.14% C, 16.17% O, and 71.69% Cl by mass. Its molar mass is 98.9 g/mol.

a) Determine the molecular formula of this compound.

b) Draw three Lewis structures for the molecule that satisfy the octet rule for each atom. (The Cl and O atoms bond to C.)

c) Using formal charges, determine which Lewis structure is the most important one.

d) Using average bond enthalpies, estimate ΔH for the formation of gaseous phosgene from CO(g) and Cl₂(g).