Chemical Bonding -- Lewis Theory  (Chapter 9)

Ionic Bonding

1. Ionic Bond

   Electrostatic attraction of positive (cation) and negative (anion) ions

   \[
   \text{Neutral Atoms} \xrightarrow{\text{e}^- \text{ transfer}} \text{cation} + \text{anion} \quad \text{(IE and EA)}
   \]

   \[
   \text{Lattice Energy} \quad \text{Ionic Compound} \quad \text{(Lattice Energy)}
   \]

   \[\text{Lattice Energy: energy released when gaseous ions combine to form crystalline solid (an ionic compound)}\]

   e.g., LE of NaCl is 787 kJ/mole:

   \[
   \text{Na}^+ (g) + \text{Cl}^- (g) \rightarrow \text{NaCl} (s) + 787 \text{ kJ}
   \]

2. Octet Rule

   \text{In forming ionic compounds, atoms tend to gain or lose electrons in order to achieve a stable valence shell electron configuration of 8 electrons.}

   Group I metals \rightarrow +1 cations (Li^+, Na^+, etc.)
   Group II metals \rightarrow +2 cations (Mg^{2+}, \text{Ca}^{2+}, \text{etc.})
   \text{Al (group III)} \rightarrow Al^{3+}
   Group VII (17) \rightarrow -1 anions (F^-, Cl^-, Br^-, etc.)
   Group VI (16) \rightarrow -2 anions (O^{2-}, S^{2-}, etc.)
   Group V (15) \rightarrow -3 anions (N^{3-}, P^{3-})

   e.g., \[\text{Na} \quad 2s^2 \ 2p^6 \ 3s^1 \rightarrow \text{Na}^+ \quad 2s^2 \ 2p^6 \ \{\sim \text{Ne}\}\]
   \[\text{Cl} \quad 3s^2 \ 3p^5 \rightarrow \text{Cl}^- \quad 3s^2 \ 3p^6 \ \{\sim \text{Ar}\}\]
3. **Lewis Symbols**

simple notation for showing number of valence electrons

<table>
<thead>
<tr>
<th>Cl</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>group VII</td>
<td>group VI</td>
</tr>
<tr>
<td>7 valence e⁻</td>
<td>6 valence e⁻</td>
</tr>
<tr>
<td>3s² 3p⁵</td>
<td>2s² 2p⁴</td>
</tr>
</tbody>
</table>

\[ \text{Cl} \cdot : \cdot \text{Cl} \]

\[ \text{O} \cdot : \cdot \text{O} \]

e.g., Use Lewis Symbols to illustrate the formation of a compound of sodium and sulfur

\[ \text{Na}_2\text{S} \quad \text{Na}^+ \text{ combined with } \text{S}^{2-} \]

\[ \text{Na} \cdot + \cdot \text{S} \cdot + \cdot \text{Na} \rightarrow 2 \text{Na}^+ [\cdot \cdot \cdot : \cdot \cdot]^{2-} \]

**Covalent Bonding**

1. **Covalent Bond Formation**

   *results from sharing of one or more pairs of electrons between 2 atoms*

Examples:

\[ \text{H} \cdot + \text{H} \cdot \rightarrow \text{H} : \text{H} \quad \text{or} \quad \text{H} - \text{H} \]

\[ \text{H} \cdot + : \text{F} \cdot \rightarrow \text{H} : \cdot \cdot \text{F} : \quad \text{or} \quad \text{H} - \cdot \cdot \text{F} : \]

2. **Octet Rule -- for covalent bonding**

   *In forming covalent bonds, atoms tend to share sufficient electrons so as to achieve a stable outer shell of 8 electrons around both atoms in the bond.*
3. Multiple Bonds -- "double" and "triple" bonds

**double bond:** sharing of 2 pairs of electrons between two atoms
**triple bond:** sharing of 3 pairs of electrons between two atoms

<table>
<thead>
<tr>
<th>Type of Bond:</th>
<th>single</th>
<th>double</th>
<th>triple</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond Order:</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

Examples:
- O\textsubscript{2} \{ O=O double bond \}
- N\textsubscript{2} \{ N≡N triple bond \}
- CO\textsubscript{2} \{ two C=O double bonds \}
4. Coordinate Covalent Bond

*Both electrons in the bond formally come from the same atom.*
(Once formed, however, the bond is just like any other covalent bond!)

\[
\begin{array}{c}
\text{H} \quad \text{H} \\
\text{H} \quad \text{H}
\end{array}
\quad \text{+} \quad \\
\begin{array}{c}
\text{NH} \quad \text{BH} \\
\text{H} \quad \text{H}
\end{array}
\quad \text{→} \quad \\
\begin{array}{c}
\text{H} \quad \text{H} \\
\text{H} \quad \text{H}
\end{array}
\quad \text{or} \quad \\
\begin{array}{c}
\text{H} \quad \text{H} \\
\text{H} \quad \text{H}
\end{array}
\]

5. Electronegativity and Bond Polarity

*Electronegativity* tendency of an atom *in a molecule* to attract electrons to itself

Electronegativity Increases

\[
\begin{array}{c}
\text{Periodic Table}
\end{array}
\]

e.g., Cl is more electronegative than H, so there is partial charge separation in the H-Cl bond:

\[
\begin{array}{c}
\delta^+ \\
\text{H} \quad \text{Cl}
\end{array}
\quad \text{or} \quad \\
\begin{array}{c}
\delta^- \\
\text{H} \quad \text{Cl}
\end{array}
\]

the H-Cl bond is described as "polar" and is said to have a "dipole"

the entire HCl molecule is also polar as a result

more complex molecules can be polar or nonpolar, depending on their 3-D shape (Later)
Lewis Electron Dot Formulas

1. **General Procedure**  --  stepwise process
   
   - Write the skeletal structure  (which atoms are bonded?)
   - Count *all valence electrons* (in pairs)
   - Place 2 electrons in each bond
   - Complete the octets of the terminal atoms
   - Put any remaining electron pairs on the central atom, or
   - Use multiple bonds if needed to complete the octet of the central atom
   - Show formal charges and resonance forms as needed

Apply the **OCTET RULE** as follows:

   - H never has more than 2 electrons  (i.e., one bond)
   - 2nd row elements (e.g.,  C, N, O) *almost always* have an octet and
     **never have more than 8 electrons** (sometimes Boron has only 6)
   - 3rd row and higher elements can have more than 8 electrons but **only after the octets of any 2nd row elements are completed**

2. **Formal Charge**  --  the "apparent" charge on an atom in a covalent bond

   \[
   \text{formal charge} = (\text{# of valence } e^- \text{ in the isolated atom}) - (\text{# of bonds to the atom}) - (\text{# of unshared electrons on the atom})
   \]

   { minimize formal charges whenever possible }

Write Lewis Dot Formulas:  \( \text{NH}_3 \),  \( \text{NH}_4^+ \),  \( \text{SF}_2 \),  \( \text{SF}_4 \)
3. Resonance

When multiple bonds are present, a single Lewis structure may not adequately describe the compound or ion -- occurs whenever there is a "choice" of where to put a multiple bond.

e.g., the HCO$_2^-$ ion is a "resonance hybrid" of two "contributing resonance structures"

![Resonance Structures](image.png)

the C-O bond order is about 1.5 (average of single and double bonds)

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**Examples**

Write Lewis Electron Dot Structures (including formal charges and/or resonance as needed) for the following compounds and ions.

<table>
<thead>
<tr>
<th>PF$_3$</th>
<th>HCN</th>
<th>SF$_5^-$</th>
<th>NO$_2^-$</th>
<th>SOCl$_2$</th>
<th>O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO$_3$</td>
<td>H$_2$CO</td>
<td>N$_3^-$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Bond Energies and Heats of Reaction (\(\Delta H\))

*Bond Energy* is the energy required to break a chemical bond.

Tabulated values (Table 9.3) are *average* bond energies in units of kJ / mole.

*Bond-breaking is endothermic, bond-making is exothermic.*

\(\Delta H\) for a reaction can be estimated from bond energies as follows. (Counting ALL bond energies as positive values!)

\[
\Delta H^{\circ} \approx \sum \text{BE (bonds broken)} - \sum \text{BE (bonds formed)}
\]

**Problem**

Use data in Table 9.3 to estimate \(\Delta H^{\circ}\) for the reaction.

\[
\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3-\text{CH}_2-\text{OH}
\]

<table>
<thead>
<tr>
<th>Bonds Broken</th>
<th>Bonds Formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C 612</td>
<td>C-C 348</td>
</tr>
<tr>
<td>H-O 463</td>
<td>C-H 412</td>
</tr>
<tr>
<td>(\Sigma) = 1,075</td>
<td>C-O 360</td>
</tr>
<tr>
<td>(\Sigma) = 1,120</td>
<td></td>
</tr>
</tbody>
</table>

\[
\therefore \Delta H^{\circ} = 1,075 - 1,120 = -45 \text{ kJ/mole}
\]

This estimate compares well with the value calculated from Standard Heats of Formation (Chapter 6).

Use tabulated \(\Delta H^{\circ}_f\) values from textbook:

\[
\Delta H^{\circ} = \sum \Delta H^{\circ}_f \text{ (products)} - \sum \Delta H^{\circ}_f \text{ (reactants)}
\]

\[
\Delta H^{\circ} = (-278) - [ (+51.9) + (-285.9) ] = -43 \text{ kJ/mole}
\]