Models of Chemical Bonding
- Bonds are forces holding atoms or ions together
- Bonds form as a result of lowering of the total energy (energy of separated species is higher than that of bonded species)

9.1 Types of Bonding
- Bond formation is accompanied by rearrangement of valence electrons
- Complete transfer of electrons between metals (low I) and nonmetals (high A)
  - Formation of ions \( \rightarrow \) ionic bonding
  - Electrostatic attraction between oppositely charged ions
- Sharing of electrons between nonmetals (high I, high A)
  - Formation of molecules \( \rightarrow \) covalent bonding
  - Attraction between the nuclei and the shared electrons
  - The shared electrons are localized between the bonded atoms
- Sharing of electrons between metals (low I, low A)
  - Formation of metallic solids \( \rightarrow \) metallic bonding
  - Attraction between metal cations and a “sea” of shared electrons
  - The shared electrons are delocalized in the entire volume of the metal

9.2 The Ionic Bonding Model
- The octet rule – when atoms bond, they gain, lose, or share electrons in order to attain an octet (eight) or a duplet (two) configuration of a noble gas
  - Most s- and p-block metals form cations by loosing all valence electrons (loosing all dots)
    - s-block metals achieve the electron configuration of the previous noble gas; p-block metals achieve a pseudo-noble gas electron configuration
  - Nonmetals form anions by gaining electrons until they reach the configuration of the next noble gas

Lewis Symbols for Atoms and Ions
- Lewis symbol \( \rightarrow \) chemical symbol + a dot for each valence electron
  - For metals, the # of dots equals the max. # of e’s lost in cation formation
  - For nonmetals, the # of unpaired dots equals the # of e’s gained in anion formation or the # of covalent bonds the element forms

Example:
Predict the formula of magnesium chloride using Lewis structures.
Mg – group 2 \( \rightarrow \) 2 valence e\(^-\) \( \rightarrow \) loss of 2 e\(^-\)
Cl – group 17 \( \rightarrow \) 7 valence e\(^-\) \( \rightarrow \) gain of 1 e\(^-\)

\[ :\text{Cl}^- + \text{Mg}^2+ + \text{Cl}^- \rightarrow 2[\text{Cl}^-]^+ + \text{Mg}^{2+} \]

Formula: MgCl\(_2\)
Lattice Energy (Lattice Enthalpy)

- Lattice enthalpy ($\Delta H_L$) – the enthalpy change for the separation of 1 mol of an ionic compound into isolated gaseous ions
  
  \[ MX(s) \rightarrow M^+(g) + X^-(g) \quad \Delta H_L > 0 \]

- At constant pressure the lattice enthalpy is numerically equal to the heat of formation of one mol of the ionic compound from gaseous ions
  
  \[ M^+(g) + X^-(g) \rightarrow MX(s) \quad \Delta H_f < 0 \]

- The heat released in the formation comes from the potential energy drop due to the attraction between the oppositely charged ions

\[ \text{Size factor} - \Delta H_L \text{ decreases moderately with increasing the size of the ion} \]

\[ \text{(Li}^+ < \text{Na}^+ < \text{K}^+) \]

\[ \text{Charge factor} - \Delta H_L \text{ increases greatly with increasing the charges of the ions} \]

\[ \text{(Li}^+, \text{F}^- < \text{Mg}^{2+}, \text{O}^{2-}) \]

Examples:

Lattice enthalpies in kJ/mol:

- LiCl $\rightarrow$ 861
- NaCl $\rightarrow$ 787
- KCl $\rightarrow$ 717
- MgO $\rightarrow$ 392

- LiF $\rightarrow$ 1050

\[ \text{Size factor} - \Delta H_L \text{ decreases moderately with increasing the size of the ion} \]

\[ \text{(Li}^+ < \text{Na}^+ < \text{K}^+) \]

\[ \text{Charge factor} - \Delta H_L \text{ increases greatly with increasing the charges of the ions} \]

\[ \text{(Li}^+, \text{F}^- < \text{Mg}^{2+}, \text{O}^{2-}) \]

\[ \text{Example: Calculate the lattice enthalpy of KBr} \]

\[ \Delta H_f = \Delta H_{at} + (I + A) + (-\Delta H_L) \]

\[ \Delta H_L = \Delta H_{at} + I + A - \Delta H_f \]

\[ \Delta H_f = \Delta H_f(K, g) + \Delta H_f(\text{Br}, g) + I(K) + A(\text{Br}) - \Delta H_f(\text{KBr}, s) \]

Data from Appendix B and Figures 8.12 & 8.14:

\[ \Delta H_L = (89) + (112) + (419) + (-325) - (-394) \text{ kJ/mol} \]

\[ \Delta H_L = 689 \text{ kJ/mol} \]

- The Born-Haber cycle shows that the energy required for atoms to lose or gain electrons is supplied by the lattice energy of ionic solids

Lattice enthalpies are measured indirectly through Hess’s law using the Born-Haber cycle

Atomization of elements $\rightarrow \Delta H_{at}$ (formation of gas phase atoms)

Ionization (cations) $\rightarrow I$

Ionization (anions) $\rightarrow A$

Formation of solid (from gaseous ions) $\rightarrow -\Delta H_L$

Formation of solid (from elements) $\rightarrow \Delta H_f$

\[ \Delta H_f = \Delta H_{at} + (I + A) + (-\Delta H_L) \]

The Properties of Ionic Compounds

- Ionic solids are crystalline solids (regular three-dimensional arrays of stacked ions)
  
  - High melting and boiling points – very strong attractions between the ions (hard to separate)
  
  - Hard, rigid and brittle
  
  - Do not conduct electricity in the solid state, but conduct electricity when melted or dissolved (electrolytes)

- Lattice enthalpies are measured indirectly through Hess’s law using the Born-Haber cycle

Atomization of elements $\rightarrow \Delta H_{at}$ (formation of gas phase atoms)

Ionization (cations) $\rightarrow I$

Ionization (anions) $\rightarrow A$

Formation of solid (from gaseous ions) $\rightarrow -\Delta H_L$

Formation of solid (from elements) $\rightarrow \Delta H_f$

\[ \Delta H_f = \Delta H_{at} + (I + A) + (-\Delta H_L) \]
9.3 The Covalent Bonding Model

Formation of covalent bonds

- **Covalent bond** – a result of atoms sharing a pair of electrons
  \[ \text{H}^+ + \text{·H} \rightarrow \text{H}:	ext{H} \]
  - The electron density between the nuclei increases
  - The two positive nuclei are attracted to the negative charge of the shared pair of e⁻

- **Octet rule** – in covalent bonding atoms share pairs of electrons until they reach octet (or duplet) configurations of noble gases
  - The number of shared e⁻ pairs equals the number of electrons an atom needs in order to complete its octet (or duplet) structure

- **Lewis structures** – diagrams showing the distribution of electrons in a molecule
  - **Shared (bonding) e⁻** pairs – between the atoms (can be expressed as lines representing bonds)
  - **Lone e⁻** pairs – not involved in bonding (not shared)

**Example:**

Write the Lewis structures of HCl and Cl₂ and determine the number of shared and lone e⁻ pairs.

\[ \text{H}::\text{Cl}: \rightarrow \text{H}:	ext{Cl} : \text{or} \ H—\text{Cl} : \]

3 lone pairs at Cl and 1 bonding (shared) pair

\[ \text{:Cl}::\text{Cl}: \rightarrow \text{:Cl}:\text{Cl} : \text{or} \ :\text{Cl}—\text{Cl}: \]

6 lone pairs at Cl and 1 bonding (shared) pair

**Types of bonds**

- **Single bond** – a single bonding (shared) pair
- **Multiple bonds** – double or triple bonds (2 or 3 bonding pairs)

**Bond order** – number of bonds linking two atoms

- Single bond → \[ \text{Cl}—\text{Cl} : \text{or} \ :\text{Cl}—\text{Cl}: \]
- Double bond → \[ \text{O}—\text{O} : \text{or} \ :\text{O}—\text{O}: \]
- Triple bond → \[ \text{N}—\text{N} : \text{or} \ :\text{N}≡\text{N}: \]

**Bond Energy (Enthalpy) and Bond Length**

- **Bond enthalpy** \( (\Delta H_B) \) – the enthalpy change for the dissociation of one mole bonds from molecules in the gas phase
  \[ \text{A-B(g)} \rightarrow \text{A(g)} + \text{B(g)} \quad \Delta H_B > 0 \]
- \( \Delta H_B \) is a measure of the strength and stability of chemical bonds
  - Large \( \Delta H_B \) ⇔ stronger bonds
  - The strength of the bond between a given pair of atoms varies slightly in different molecules
  - **Average bond enthalpies** \( (\Delta H_B) \) – averaged over many compounds
• Bond strength (\(\Delta H_B\)) increases with increasing the bond order:
  - \(\text{N} \equiv \text{N}\): 945 kJ/mol
  - \(\text{O} = \text{O}\): 498 kJ/mol
  - \(\text{F} \equiv \text{F}\): 159 kJ/mol

• In general, bond strength (\(\Delta H_B\)) increases with decreasing the size of the bonded atoms:
  - \(\text{H} \equiv \text{F}\): 565 kJ/mol
  - \(\text{H} \equiv \text{Cl}\): 427 kJ/mol
  - \(\text{H} \equiv \text{Br}\): 363 kJ/mol
  - \(\text{H} \equiv \text{I}\): 295 kJ/mol

• Bond length – the distance between the nuclei of two bonded atoms:
  - Bond lengths increase with decreasing the bond order:
    - \(\text{N} \equiv \text{N}\): 110 pm
    - \(\text{O} = \text{O}\): 121 pm
    - \(\text{F} \equiv \text{F}\): 143 pm
  - Bond lengths increase with increasing the size of the bonded atoms:
    - \(\text{Cl} \equiv \text{Cl}\): 199 pm
    - \(\text{Br} \equiv \text{Br}\): 228 pm
    - \(\text{I} \equiv \text{I}\): 266 pm

  – Average bond lengths – averaged over many compounds:

• In general, a shorter bond is a stronger bond:

Table 9.4 The Relation of Bond Order, Bond Length, and Bond Energy

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Order</th>
<th>Average Bond Length (pm)</th>
<th>Average Bond Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O</td>
<td>1</td>
<td>143</td>
<td>358</td>
</tr>
<tr>
<td>C=O</td>
<td>2</td>
<td>123</td>
<td>745</td>
</tr>
<tr>
<td>C≡O</td>
<td>3</td>
<td>113</td>
<td>1070</td>
</tr>
<tr>
<td>C≡C</td>
<td>1</td>
<td>154</td>
<td>347</td>
</tr>
<tr>
<td>C≡C</td>
<td>2</td>
<td>134</td>
<td>614</td>
</tr>
<tr>
<td>N≡N</td>
<td>3</td>
<td>121</td>
<td>839</td>
</tr>
<tr>
<td>N≡N</td>
<td>1</td>
<td>146</td>
<td>160</td>
</tr>
<tr>
<td>N≡N</td>
<td>2</td>
<td>122</td>
<td>418</td>
</tr>
<tr>
<td>N≡N</td>
<td>3</td>
<td>110</td>
<td>945</td>
</tr>
</tbody>
</table>

• Covalent radii of atoms – contributions of individual atoms to the lengths of covalent bonds (average values are tabulated and depend on the bond order):

The Properties of Covalent Compounds

• Molecular compounds – most covalent compounds consist of molecules (water, sugar, …)
  - Low melting and boiling points – the forces holding the molecules together are much weaker than the covalent bonds inside the molecules
  - Soft solids (often gases or liquids)
  - Poor electrical conductors in the solid state as well as when melted or dissolved (non-electrolytes)

• Covalent network solids – three-dimensional arrays of covalently bonded atoms (diamond, quartz, …)
  - Very high melting and boiling points – very strong covalent bonds hold the atoms together
  - Extremely hard
  - Poor electrical conductors

9.5 Electronegativity and Bond Polarity

• Electronegativity (EN) – the ability of an atom to attract the shared electrons in a bond (electron-pulling power)
  - In general, EN increases with increasing the ionization energy and electron affinity of atoms
  - EN increases up and to the right in the periodic table (opposite to the atomic size trend)
EN can be used to determine the oxidation numbers of elements in compounds
- The more electronegative atom in a bond is assigned all shared (bonding) electrons
- Each atom in a bond is assigned all unshared (lone pair) electrons
\[ \text{Ox#} = (\text{#valence e}^-) - (\text{#shared e}^- + \text{#unshared e}^-) \]

Example: HCl (Cl is more EN than H)
\[
\begin{align*}
\text{Cl} & \rightarrow \text{Ox#} = 7 - (2 + 6) = -1 \\
\text{H} & \rightarrow \text{Ox#} = 1 - (0 + 0) = +1
\end{align*}
\]

Polar Covalent Bonds
- The EN difference (ΔEN) between the bonded atoms determines the character of a covalent bond
- **Nonpolar covalent bond** – ΔEN = 0 → equal sharing of the bonding electrons (H–H, F–F, ...)
- **Polar covalent bond** – ΔEN > 0 → unequal sharing of the bonding electrons (H–O, C–F, ...)
  - The more electronegative atoms acquire partial negative charges (have greater share of the bonding electrons)
  - The less electronegative atoms acquire partial positive charges

Formation of a bond dipole expressed by a polar arrow
- Polar arrow points from (δ+) to (δ-)
- Bond polarity increases with increasing ΔEN

Example:
Which of the following bonds is more polar?
O–H (in H₂O) or N–H in (NH₃)
EN order → H < N < O
⇒ ΔEN(O-H) > ΔEN(N-H)
⇒ the O-H bond is more polar

Partial ionic character of polar covalent bonds
- Due to the partial charges
- Ionic character increases with increasing of ΔEN
- No bonds are 100% ionic (partial covalent character)
9.6 Metallic Bonding (see page 382 in textbook)

The Electron-sea Model
- A metallic solid can be viewed as an array of metal cations (nuclei + core electrons) attracted by a sea of their valence electrons
  - The valence electrons are delocalized (shared between all atoms)

Properties of metals
- Good electrical and heat conductors – due to the mobility of the electron-sea
- Moderately high melting points – the attractions between the cations and the electron-sea are not greatly disturbed by melting

- High boiling points – the metal ions and electrons have to be separated
- Malleable and ductile – metal cations can slide past each other without disturbing the interaction with the electron-sea too much