Chapter 3

Bonding: General Concepts
Electrostatic Attractions and Repulsions

$H_2^+$

$H_2$
Energy of Interaction
Electronegativity

- **Electronegativity (EN, expressed as $\chi$)**, is a measure of the ability of an atom to attract bonding electrons to itself when the atom is in a molecule.

- **Mulliken’s EN**
  
  Absolute EN, $\chi = (\text{IE} + \text{EA})/2$

- **Pauling’s EN**

  define $\chi_H = 2.2$

  $\Delta \chi = \chi_A - \chi_B = [\Delta_{AB}(\text{kJ})/96.49]^{1/2} = [\Delta_{AB}(\text{kcal})/23.06]^{1/2}$

  $\Delta_{AB} = D(\text{A-B}) - [D(\text{A-A}) \times D(\text{B-B})]^{1/2}$

  Bond dissociation energy of A-B
Pauling’s Electronegativities

![Electronegativity Chart](chart.png)
Electronegativity Difference and Bond Type

- Two identical atoms have the same electronegativity and share a bonding electron pair equally. This is called a **non-polar covalent bond**. (For $\chi_A \sim \chi_B$, or $|\chi_A - \chi_B| < 0.3$)

- In covalent bonds between atoms with somewhat larger electronegativity differences ($0.3 < |\chi_A - \chi_B| < 1.8$), electron pairs are shared unequally. The electrons are drawn closer to the atom of higher electronegativity, and the bond is called a **polar covalent bond**.

- With still larger differences in electronegativity ($|\chi_A - \chi_B| > 1.8$), electrons may be completely transferred from metal to nonmetal atoms to form **ionic bonds**.
Interionic Forces of Attraction - Coulombic Force

\[ E = \frac{(Z^+Z^-)}{4\pi\varepsilon r} \]
Formation of a Crystal of Sodium Chloride
The Lewis Theory of Chemical Bonding

- Electrons, particularly valence electrons, play a fundamental role in chemical bonding.
- When metals and non-metals combine, valence electrons usually are transferred from the metal to the non-metal atoms giving rise to **ionic bonds**.
- In combinations involving only non-metals, one or more *pairs* of valence electrons are *shared* between the bonded atoms producing **covalent bonds**.
- In losing, gaining, or sharing electrons to form chemical bonds, atoms tend to acquire the electron configurations of noble gases.
Lewis Symbols

- In a **Lewis symbol**, the chemical symbol for the element represents the nucleus and core electrons of the atom, and dots around the symbol represent the *valence* electrons.
Lewis Structures Of Simple Molecules

- A **Lewis structure** is a combination of Lewis symbols that represents the formation of covalent bonds between atoms.

- In most cases, a Lewis structure shows the bonded atoms with the electron configuration of a noble gas; that is, the atoms obey the **octet rule**. (H obeys the **duet rule**.)
Lewis Structures (continued)

- The shared pairs of electrons in a molecule are called **bonding pairs**.
- In common practice, the bonding pair is represented by a dash (-).
  \[ \text{H} : \text{H} \quad \text{or} \quad \text{H} \equiv \text{H} \]
- The other electron pairs, which are not shared, are called **non-bonding pairs**, or **lone pairs**.
  \[ : \text{C} \equiv \bigcirc \cdot \bigcirc \]
The non-metals of the second period (except boron?) tend to form a number of covalent bonds equal to \textit{eight minus the group number}.
Coordinate Covalent Bonds

In some cases, one atom provides both electrons of the shared pair to form a bond called a **coordinate covalent bond (or dative bond)**.

For example:
- *hydronium ions* \( \text{H}_3\text{O}^+ \)
- \( \text{F}_3\text{B}-\text{NH}_3 \)
Multiple Covalent Bonds

- The covalent bond in which one pair of electrons is shared is called a **single bond**.
- Multiple bonds can also form:
  - **Double bonds** have two shared pairs of electrons.
  - **Triple bonds** have three shared pairs of electrons.
- A double bond is represented by two dashes (\(=\)).
- A triple bond is represented by three dashes (\(\equiv\)).
Polar and Non-polar Covalent Bonds

Nonpolar covalent bond

\[ \text{H} - \text{H} \]

Polar covalent bond

\[ \text{H} - \text{Cl} \]
Formal Charge

Formal charge = # of valence electrons
  - [# of lone pair electrons + ½ (bonding electrons)]

- Usually, the most plausible Lewis structure is one with no formal charges.
- When formal charges are required, they should be as small as possible.
- Negative formal charges should appear on the most electronegative atoms.
- Adjacent atoms in a structure should not carry formal charges of the same sign.
Lewis Structures & Formal Charge

**CO**

\[ \text{:C} \equiv \text{O:} \]

\[ \text{FC}(C) = 4 - 2 - 3 = -1 \]

\[ \text{FC}(O) = 6 - 2 - 3 = +1 \]

**CO}_2\]

\[ \overset{\text{(0)}}{\text{O}} = \overset{\text{(0)}}{\text{C}} = \overset{\text{(0)}}{\text{O}} \]

\[ \text{FC}(C) = 4 - 0 - 4 = 0 \]

\[ \text{FC}(O) = 6 - 4 - 2 = 0 \]

**N}_2\text{O}\]

\[ \overset{\text{(1)}}{\text{N}} = \overset{\text{(-1)}}{\text{N}} = \overset{\text{(0)}}{\text{O}} \]

\[ \leftrightarrow \overset{\text{(0)}}{\text{N}} \equiv \overset{\text{(1)}}{\text{N}} - \overset{\text{(-1)}}{\text{O}} \leftrightarrow \overset{\text{(-2)}}{\text{N}} \equiv \overset{\text{(-1)}}{\text{N}} - \overset{\text{(1)}}{\text{O}} \]

\[ \overset{\text{(-2)}}{\text{N}} = \overset{\text{(+1)}}{\text{O}} = \overset{\text{(-1)}}{\text{N}} \]

\[ \overset{\text{(-1)}}{\text{N}} = \overset{\text{(+2)}}{\text{O}} = \overset{\text{(-1)}}{\text{N}} \]

Resonance structures
Resonance: Delocalized Bonding

- **Resonance theory** states that whenever a molecule or ion can be represented by two or more plausible Lewis structures that differ only in the distribution of electrons, the true structure is a composite, or hybrid, of them.
- The different plausible structures are called **resonance structures**.

\[ \text{ benzene structure } \leftrightarrow \text{ resonance structures} \]

- The actual molecule or ion that is a hybrid of the resonance structures is called a **resonance hybrid**.
- Electrons that are part of the resonance hybrid are spread out over several atoms and are referred to as being **delocalized**.
Oxoacids: HNO₃, H₂SO₄, HClO₄

\[ \text{ClO}_4^- \]

\[ \begin{array}{c}
\text{(0)} \\
\text{O} \\
\text{O} \\
\text{C} \\
\text{O} \\
\text{(4-1)} \end{array} \quad \leftrightarrow \quad \begin{array}{c}
\text{(0)} \\
\text{O} \\
\text{O} \\
\text{C} \\
\text{O} \\
\text{(4-1)} \end{array} \quad \leftrightarrow \quad \begin{array}{c}
\text{(1-1)} \\
\text{O} \\
\text{O} \\
\text{C} \\
\text{O} \\
\text{(4-1)} \end{array} \quad \leftrightarrow \quad \begin{array}{c}
\text{(1-1)} \\
\text{O} \\
\text{O} \\
\text{C} \\
\text{O} \\
\text{(1-1)} \end{array} \]

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\text{O} \\
\text{O} \\
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\text{O} \\
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\text{(0)} \\
\text{O} \\
\text{O} \\
\text{C} \\
\text{O} \\
\text{(4-1)} \end{array} \]
Molecules that Don’t Follow the Octet Rule

- Molecules with an odd number of valence electrons have at least one of them unpaired and are called **free radicals**.

  ![N=O](image1)

  ![N=O](image2)

- Some molecules have incomplete octets. These are usually compounds of Be, B, and Al, generally have some unusual bonding characteristics, and are often quite reactive.

  ![BF3](image3)
Molecules that Don’t Follow the Octet Rule (continued)

- Some compounds have expanded valence shells, which means that the central atom has more than eight electrons around it.
  e.g. SF$_6$, PCl$_5$  hypervalent compounds

\[
\begin{align*}
\text{SF}_6 & : \quad F & F & F & S & F & F \\
\text{PCl}_5 & : \quad F & P & F & F & F & F
\end{align*}
\]
<table>
<thead>
<tr>
<th></th>
<th>Oxidation number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>The sum of the oxidation numbers of all the atoms in the species is equal to its total charge</td>
</tr>
<tr>
<td>2.</td>
<td>For atoms in their elemental form</td>
</tr>
<tr>
<td>3.</td>
<td>For atoms of Group 1</td>
</tr>
<tr>
<td></td>
<td>For atoms of Group 2</td>
</tr>
<tr>
<td></td>
<td>For atoms of Group 13/11 (except B)</td>
</tr>
<tr>
<td></td>
<td>For atoms of Group 14/16 (except C, Si)</td>
</tr>
<tr>
<td>4.</td>
<td>For hydrogen</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>For fluorine</td>
</tr>
<tr>
<td>6.</td>
<td>For oxygen</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Halogens</td>
</tr>
</tbody>
</table>

*To determine an oxidation number, work through the following rules in the order given. Stop as soon as the oxidation number has been assigned. These rules are not exhaustive, but they are applicable to a wide range of common compounds.*
The term **bond order** indicates whether a covalent bond is single (b.o. = 1), double (b.o. = 2), or triple (b.o. = 3).

**Bond length** is the distance between the nuclei of two atoms joined by a covalent bond.

Bond length depends on the particular atoms in the bond and on the bond order.

The length of the covalent bond joining unlike atoms is the sum of the covalent radii of the two atoms.

Bond lengths are usually measured in picometers ($10^{-12}$ meter).
A Visualization of Bond Dissociation Energy
Bond Enthalpies

- **Bond-dissociation enthalpy** ($D$) is the quantity of energy required to break one mole of covalent bonds between atoms in a molecule in the *gas* phase.
  
  - **BE of H-H**
    
    \[ \text{BE of H-H} = 436 \text{ kJ/mol} \]

- An **average bond enthalpy** is the average of the bond-dissociation enthalpies for a number of different molecules containing the particular bond.

  - **Average BE of O-H**
    
    \[ \text{average BE of O-H} = \frac{(499 + 428)}{2} = 464 \text{ J/mol} \]
Process

\[
\begin{align*}
\text{CH}_4(g) & \rightarrow \text{CH}_3(g) + \text{H}(g) \quad & 435 \\
\text{CH}_3(g) & \rightarrow \text{CH}_2(g) + \text{H}(g) \quad & 453 \\
\text{CH}_2(g) & \rightarrow \text{CH}(g) + \text{H}(g) \quad & 425 \\
\text{CH}(g) & \rightarrow \text{C}(g) + \text{H}(g) \quad & 339 \\
\hline
\text{Total} & & 1652 \\
\text{Average} & = \frac{1652}{4} & = 413
\end{align*}
\]

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Measured C—H Bond Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCBr\textsubscript{3}</td>
<td>380</td>
</tr>
<tr>
<td>HCCl\textsubscript{3}</td>
<td>380</td>
</tr>
<tr>
<td>HCF\textsubscript{3}</td>
<td>430</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{6}</td>
<td>410</td>
</tr>
</tbody>
</table>
3.25 The correlation of bond strength and bond order.

3.26 The correlation of bond length and bond order. The key for the points is the same as in Fig. 3.25.
3.27 The correlation of bond length and bond strength. The key for the points is the same as in Fig. 3.25.
# Representative Bond Lengths & Average Bond Enthalpies

**TABLE 9.1 Some Representative Bond Lengths and Bond Energies**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length, pm</th>
<th>Bond Energy, kJ/mol</th>
<th>Bond</th>
<th>Bond Length, pm</th>
<th>Bond Energy, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—H</td>
<td>74</td>
<td>436</td>
<td>C—O</td>
<td>143</td>
<td>360</td>
</tr>
<tr>
<td>H—C</td>
<td>110</td>
<td>414</td>
<td>C=O</td>
<td>120</td>
<td>736&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>H—N</td>
<td>100</td>
<td>389</td>
<td>C—Cl</td>
<td>178</td>
<td>339</td>
</tr>
<tr>
<td>H—O</td>
<td>97</td>
<td>464</td>
<td>N—N</td>
<td>145</td>
<td>163</td>
</tr>
<tr>
<td>H—S</td>
<td>132</td>
<td>368</td>
<td>N=O</td>
<td>145</td>
<td>163</td>
</tr>
<tr>
<td>H—F</td>
<td>92</td>
<td>565</td>
<td>O—O</td>
<td>145</td>
<td>163</td>
</tr>
<tr>
<td>H—Cl</td>
<td>127</td>
<td>431</td>
<td>O=O</td>
<td>121</td>
<td>498</td>
</tr>
<tr>
<td>H—Br</td>
<td>141</td>
<td>364</td>
<td>F—F</td>
<td>143</td>
<td>159</td>
</tr>
<tr>
<td>H—I</td>
<td>161</td>
<td>297</td>
<td>Cl—Cl</td>
<td>199</td>
<td>243</td>
</tr>
<tr>
<td>C—C</td>
<td>154</td>
<td>347</td>
<td>Br—Br</td>
<td>228</td>
<td>193</td>
</tr>
<tr>
<td>C≡C</td>
<td>134</td>
<td>611</td>
<td>I—I</td>
<td>266</td>
<td>151</td>
</tr>
<tr>
<td>C—N</td>
<td>147</td>
<td>305</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C≡N</td>
<td>128</td>
<td>615</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C≡N</td>
<td>116</td>
<td>891</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>The value for the C—O bond in CO<sub>2</sub> is considerably different: 799 kJ/mol.
<table>
<thead>
<tr>
<th>2nd row elements without lone pairs</th>
<th>BE increases</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—C</td>
<td>347</td>
</tr>
<tr>
<td>Si—C</td>
<td>301</td>
</tr>
<tr>
<td>Ge—C</td>
<td>242</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2nd row elements with lone pairs</th>
<th>3rd row elements with lone pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>N—O</td>
<td>C—Cl</td>
</tr>
<tr>
<td>163</td>
<td>326</td>
</tr>
<tr>
<td>P—O</td>
<td>Si—Cl</td>
</tr>
<tr>
<td>368</td>
<td>401</td>
</tr>
<tr>
<td>As—O</td>
<td>Ge—Cl</td>
</tr>
<tr>
<td>330</td>
<td>339</td>
</tr>
<tr>
<td></td>
<td>Sn—Cl</td>
</tr>
<tr>
<td></td>
<td>314</td>
</tr>
</tbody>
</table>
Bond Enthalpies & $\Delta H_{\text{reaction}}$

- The sum of the enthalpy changes for breaking the old bonds and forming the new bonds is the enthalpy change for the reaction.

\[
\text{C}_2\text{H}_6 + \text{Cl}_2 \overset{\Delta H}{\rightarrow} \text{C}_2\text{H}_5\text{Cl} + \text{HCl}
\]

\[\Delta H_{\text{reaction}} = \Delta H_{\text{bond broken}} + \Delta H_{\text{bond formed}}\]

\[= \sum D(\text{bonds broken}) - \sum D(\text{bonds formed})\]

\[\Delta H = [D(\text{C-H}) + D(\text{Cl-Cl})] - [D(\text{C-Cl}) + D(\text{H-Cl})]\]

\[= [414 + 243] - [339 + 431] = -113 \text{ kJ/mol}\]
Molecular Geometry

- The **molecular geometry**, or the shape of a molecule is described by the geometric figure formed when the **atomic nuclei** are imagined to be joined by the appropriate straight lines.

- Determination of **molecular geometry**
  1. **Valence-Shell Electron-Pair Repulsion (VSEPR)**
     - Pairs of valence electrons in bonded atoms repel one another.
     - The mutual repulsions push electron pairs as far from one another as possible.

  2. **Ligand Field Stabilization Energy**
     - Mainly for compounds with the central atoms as transition metals
Molecular Geometry of Water

- Bond length: O-H = 95.8 pm
- Bond angle: H-O-H = 104.45°
Electron-Group Geometries

- An **electron group** is any collection of valence electrons, localized in a region around a central atom, that repels other groups of valence electrons.
- The mutual repulsions among electron groups lead to an orientation of the groups that are called **electron-group geometry**.
# Electron-Group Geometries

<table>
<thead>
<tr>
<th>#. of Electron Pair</th>
<th>Electron-group Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear</td>
</tr>
<tr>
<td>3</td>
<td>trigonal planar</td>
</tr>
<tr>
<td>4</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>5</td>
<td>Trigonal bipyramidal</td>
</tr>
<tr>
<td>6</td>
<td>octahedral</td>
</tr>
</tbody>
</table>
A Balloon Analogy
Geometries of Methane

#. of electron group on C = 1/2 (4 + 4) = 4

Electron group geometry: tetrahedral

VSEPR notation AX$_4$

Molecular geometry: tetrahedral
Molecular Geometry of Water

#. of electron group on O = \frac{1}{2} (6 + 2) = 4

Electron group geometry: tetrahedral

VSEPR notation \( AX_2E_2 \)

Molecular geometry: bent

A: the central atom in a structure
X: terminal atoms
E: the lone pairs of electrons

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Electron Repulsion

- Lone-pair – Lone-pair > Lone-pair – Bonding-pair
  > Bonding-pair – Bonding-pair

- Triple bond > Double bond > Single bond
Molecular Geometry for Iodine Pentafluoride (IF$_5$)

#. of electron group on I = 1/2 (7 + 5) = 6

Electron group geometry: octahedral

VSEPR notation AX$_5$E

Molecular geometry: Square pyramidal
Molecular Geometry for Sulfur Tetrafluoride (SF$_4$)

#. of electron group on S = 1/2 (6 + 4) = 5

Electron group geometry: trigonal bipyramidal

VSEPR notation AX$_4$E

Molecular geometry: trigonal pyramidal or Seesaw
Molecular Geometry for Iodine Trifluoride (IF$_3$)

#. of electron group on I = 1/2 (7 + 3) = 5

Electron group geometry: trigonal bipyramidal

VSEPR notation AX$_3$E$_2$

Molecular geometry: triangular or T-shaped
Molecular Geometry for Iodine Tetrafluoride Ion (IF$_4^-$)

#. of electron group on I = 1/2 (7 + 4 +1) = 6

Electron group geometry: octahedral

VSEPR notation AX$_4$E$_2$

Molecular geometry: Square planar