3.4 Covalent Bonds and Lewis Structures
• In 1916 G. N. Lewis proposed that atoms combine in order to achieve a more stable electron configuration.

• Maximum stability results when an atom is isoelectronic with a noble gas.

• An electron pair that is shared between two atoms constitutes a covalent bond.
Covalent Bonding in $\text{H}_2$

Two hydrogen atoms, each with 1 electron, can share those electrons in a covalent bond.

\[
\begin{align*}
\text{H} & \cdot \quad \cdot \text{H} \\
\text{H} : \text{H}
\end{align*}
\]

- Sharing the electron pair gives each hydrogen an electron configuration analogous to helium.
Covalent Bonding in F₂

Two fluorine atoms, each with 7 valence electrons, can share those electrons in a covalent bond.

\[ \text{F} - \text{F} \]

• Sharing the electron pair gives each fluorine an electron configuration analogous to neon.
The Octet Rule

In forming compounds, atoms gain, lose, or share electrons to give a stable electron configuration characterized by 8 valence electrons.

\[ \cdot F: \cdot F: \cdot \]

- The octet rule is the most useful in cases involving covalent bonds to C, N, O, and F.
Example

Combine carbon (4 valence electrons) and four fluorines (7 valence electrons each)

\[ \cdot \text{C} \cdot \quad : \text{F} : \]

to write a Lewis structure for \( \text{CF}_4 \).

\[ \cdot \text{F} \cdot \quad \cdot \text{F} \cdot \quad \cdot \text{C} \cdot \quad \cdot \text{F} \cdot \]

The octet rule is satisfied for carbon and each fluorine.
It is common practice to represent a covalent bond by a line. We can rewrite:

```
:F:
: F: C: F:
: F:
```

as

```
:F--C--F:
```
3.4 Double Bonds and Triple Bonds
Inorganic examples

:O::C::O:  :O=C=O:
Carbon dioxide

H:C::N:  H=C≡N:
Hydrogen cyanide
Organic examples

Ethylene

H : C :: C : H

Acetylene

H : C :: : C : H

H ─ C ≡ C ─ H
3.4 Formal Charges

• Formal charge is the charge calculated for an atom in a Lewis structure on the basis of an equal sharing of bonded electron pairs.
Nitric acid

Formal charge of H

- We will calculate the formal charge for each atom in this Lewis structure.
Nitric acid

Formal charge of H

- Hydrogen shares 2 electrons with oxygen.
- Assign 1 electron to H and 1 to O.
- A neutral hydrogen atom has 1 electron.
- Therefore, the formal charge of H in nitric acid is 0.
Oxygen has 4 electrons in covalent bonds.
Assign 2 of these 4 electrons to O.
Oxygen has 2 unshared pairs. Assign all 4 of these electrons to O.
Therefore, the total number of electrons assigned to O is $2 + 4 = 6$. 
Electron count of O is 6.
A neutral oxygen has 6 electrons.
Therefore, the formal charge of O is 0.
Electron count of O is 6 (4 electrons from unshared pairs + half of 4 bonded electrons).

A neutral oxygen has 6 electrons.

Therefore, the formal charge of O is 0.
Electron count of O is 7 (6 electrons from unshared pairs + half of 2 bonded electrons).

A neutral oxygen has 6 electrons.

Therefore, the formal charge of O is -1.
Electron count of N is 4 (half of 8 electrons in covalent bonds).

A neutral nitrogen has 5 electrons.

Therefore, the formal charge of N is +1.
• A Lewis structure is not complete unless formal charges (if any) are shown.
An arithmetic formula for calculating formal charge.

Formal charge =

group number in periodic table − number of bonds − number of unshared electrons
"Electron counts" and formal charges in NH$_4^+$ and BF$_4^-$
3.5
Drawing Lewis Structures
The order in which the atoms of a molecule are connected is called its constitution or connectivity.

The constitution of a molecule must be determined in order to write a Lewis structure.
Table 1.4 How to Write Lewis Structures

- Step 1: The molecular formula and the connectivity are determined by experiment.
Table 1.4 How to Write Lewis Structures

- Step 1: The molecular formula and the connectivity are determined by experiment.
- Example: Methyl nitrite has the molecular formula $\text{CH}_3\text{NO}_2$. All hydrogens are bonded to carbon, and the order of atomic connections is CONO.
Table 1.4 How to Write Lewis Structures

- Step 2: Count the number of valence electrons. For a neutral molecule this is equal to the number of valence electrons of the constituent atoms.
<table>
<thead>
<tr>
<th>Table 1.4 How to Write Lewis Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>• <strong>Step 2:</strong> Count the number of valence electrons. For a neutral molecule this is equal to the number of valence electrons of the constituent atoms.</td>
</tr>
<tr>
<td>• <strong>Example (CH\textsubscript{3}NO\textsubscript{2}):</strong> Each hydrogen contributes 1 valence electron. Each carbon contributes 4, nitrogen 5, and each oxygen 6 for a total of 24.</td>
</tr>
</tbody>
</table>
**Table 1.4 How to Write Lewis Structures**

- **Step 3:**
  Connect the atoms by a covalent bond represented by a dash.
Step 3: Connect the atoms by a covalent bond represented by a dash.

Example: Methyl nitrite has the partial structure:
Step 4:
Subtract the number of electrons in bonds from the total number of valence electrons.
### Step 4:
Subtract the number of electrons in bonds from the total number of valence electrons.

#### Example:
24 valence electrons – 12 electrons in bonds. Therefore, 12 more electrons to assign.
| Step 5: | Add electrons in pairs so that as many atoms as possible have 8 electrons. Start with the most electronegative atom. |

**Table 1.4 How to Write Lewis Structures**
Step 5:
Add electrons in pairs so that as many atoms as possible have 8 electrons. Start with the most electronegative atom.

Example:
The remaining 12 electrons in methyl nitrite are added as 6 pairs.
**Step 6:**
If an atom lacks an octet, use electron pairs on an adjacent atom to form a double or triple bond.

**Example:**
Nitrogen has only 6 electrons in the structure shown.

![Lewis structure](image-url)
Step 6: If an atom lacks an octet, use electron pairs on an adjacent atom to form a double or triple bond.

Example: All the atoms have octets in this Lewis structure.
Table 1.4  How to Write Lewis Structures

- Step 7:
  Calculate formal charges.

- Example:
  None of the atoms possess a formal charge in this Lewis structure.
Step 7: Calculate formal charges.

Example: This structure has formal charges; is less stable Lewis structure.
Condensed structural formulas

- Lewis structures in which many (or all) covalent bonds and electron pairs are omitted.

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} - \text{C} - \text{C} - \text{C} - \text{H} & \quad \text{can be condensed to:} \\
\text{H} : \text{O} : \text{H} & \\
\text{H} & \\
\end{align*}
\]

\[
\text{CH}_3\text{CHCH}_3 \quad \text{or} \quad (\text{CH}_3)_2\text{CHOH}
\]
3.5

Constitutional Isomers
Constitutional isomers

- Isomers are different compounds that have the same molecular formula.
- Constitutional isomers are isomers that differ in the order in which the atoms are connected.
- An older term for constitutional isomers is “structural isomers.”
A Historical Note

In 1823 Friedrich Wöhler discovered that when ammonium cyanate was dissolved in hot water, it was converted to urea.

- Ammonium cyanate and urea are constitutional isomers of CH$_4$N$_2$O.
- Ammonium cyanate is “inorganic.” Urea is “organic.” Wöhler is credited with an important early contribution that helped overturn the theory of “vitalism.”
Examples of constitutional isomers

Nitromethane

\[
\begin{align*}
\text{H} & \quad \text{O} : \\
\text{H} - \text{C} - \text{N}^+ & \\
\text{H} & \quad \text{O} : \\
\end{align*}
\]

Methyl nitrite

\[
\begin{align*}
\text{H} & \quad \text{O} - \text{N} = \text{O} : \\
\text{H} - \text{C} - \text{O} & \\
\text{H} & \quad \\
\end{align*}
\]

- Both have the molecular formula \( \text{CH}_3\text{NO}_2 \) but the atoms are connected in a different order.
3.5 Resonance
two or more acceptable octet Lewis structures may be written for certain compounds (or ions)
Step 6:
If an atom lacks an octet, use electron pairs on an adjacent atom to form a double or triple bond.

Example:
Nitrogen has only 6 electrons in the structure shown.
Step 6:
If an atom lacks an octet, use electron pairs on an adjacent atom to form a double or triple bond.

Example:
All the atoms have octets in this Lewis structure.
### Step 7:
Calculate formal charges.

### Example:
None of the atoms possess a formal charge in this Lewis structure.

![Lewis structure](image-url)

**Table 1.4 How to Write Lewis Structures**
Step 7: Calculate formal charges.

Example: This structure has formal charges; it is less stable Lewis structure.
Resonance Structures of Methyl Nitrite

- same atomic positions
- differ in electron positions

More stable Lewis structure

Less stable Lewis structure
Resonance Structures of Methyl Nitrite

- same atomic positions
- differ in electron positions

More stable Lewis structure

Less stable Lewis structure
Electrons in molecules are often delocalized between two or more atoms.

Electrons in a single Lewis structure are assigned to specific atoms—a single Lewis structure is insufficient to show electron delocalization.

Composite of resonance forms more accurately depicts electron distribution.
Example

- Ozone ($O_3$)
  - Lewis structure of ozone shows one double bond and one single bond

Expect: one short bond and one long bond

Reality: bonds are of equal length (128 pm)
Ozone (O₃)

- Lewis structure of ozone shows one double bond and one single bond

Resonance:
3.7

The Shapes of Some Simple Molecules
Methane

• **tetrahedral geometry**
• $\text{H}—\text{C}—\text{H}$ angle = 109.5°
Methane

• tetrahedral geometry
• each $\text{H—C—H}$ angle $= 109.5^\circ$
• The most stable arrangement of groups attached to a central atom is the one that has the maximum separation of electron pairs (bonded or nonbonded).
Water

• bent geometry
• H—O—H angle = 105°

but notice the tetrahedral arrangement of electron pairs
Ammonia

- trigonal pyramidal geometry
- H—N—H angle = 107°

but notice the tetrahedral arrangement of electron pairs
Boron Trifluoride

• F—B—F angle = 120°
• trigonal planar geometry allows for maximum separation of three electron pairs
Multiple Bonds

- Four-electron double bonds and six-electron triple bonds are considered to be similar to a two-electron single bond in terms of their spatial requirements.
Formaldehyde: CH$_2$=O

- H—C—H and H—C—O angles are close to 120°
- trigonal planar geometry
Figure 1.12: Carbon Dioxide

- O—C—O angle = 180°
- linear geometry
27 Carbon dioxide, $\text{CO}_2$
28 Water, H₂O
3.7: Polar Covalent Bonds and Electronegativity
Electronegativity is a measure of an element to attract electrons toward itself when bonded to another element.

- An electronegative element attracts electrons.
- An electropositive element releases electrons.
### Pauling Electronegativity Scale

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.5</td>
<td>2.0</td>
<td>2.5</td>
<td>3.0</td>
<td>3.5</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>

- Electronegativity increases from left to right in the periodic table.
- Electronegativity decreases going down a group.
The greater the difference in electronegativity between two bonded atoms, the more polar the bond.

Nonpolar bonds connect atoms of the same electronegativity.
The greater the difference in electronegativity between two bonded atoms; the more polar the bond.

Generalization

\[ \text{polar bonds connect atoms of different electronegativity} \]
3.7  
Molecular Dipole Moments
Dipole Moment

- A substance possesses a dipole moment if its centers of positive and negative charge do not coincide.
  \[ m = e \times d \]
- (expressed in Debye units)

not polar
Relative pulling power of atom
Atom B has greater share
Dipole Moment

- A substance possesses a dipole moment if its centers of positive and negative charge do not coincide.
  \[ m = e \times d \]
- (expressed in Debye units)
Molecular Dipole Moments

- molecule must have polar bonds
  - necessary, but not sufficient
- need to know molecular shape
  - because individual bond dipoles can cancel
Molecular Dipole Moments

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

Carbon dioxide has no dipole moment; \( m = 0 \text{ D} \)
Comparison of Dipole Moments

Carbon tetrachloride

$\mu = 0 \text{ D}$

Dichloromethane

$\mu = 1.62 \text{ D}$
Resultant of these two bond dipoles is 

$m = 0 \text{ D}$

Carbon tetrachloride has no dipole moment because all of the individual bond dipoles cancel.
The individual bond dipoles do not cancel in dichloromethane; it has a dipole moment.

\[ m = 1.62 \text{ D} \]