TYPES OF CHEMICAL BONDING

Ionic Bonding
- two atoms of opposite charge electrically attracted to one another

Covalent Bonding
- two atoms each sharing electrons within a molecular orbital

Metallic Bonding
- positive metal ions held together in a lattice with a “sea of electrons”

An actual chemical bond is a blend of all three types of bonding. Most often, one type is dominant over others. We will concentrate on ionic and covalent bonding.

LEWIS STRUCTURES

Only valence electrons are important in bonding.

Lewis dot structures show valence electrons surrounding atom.

We visualize the four valence orbitals of an atom as the sides of a box. Electrons are put into orbitals according to Hund’s rule.

Examples

Be has 2 valence electrons. 
Therefore Lewis structure is

N has 5 valence electrons. 
Therefore Lewis structure is

Br has 7 valence electrons. 
Therefore Lewis structure is

C has 4 valence electrons. 
Therefore Lewis structure is
**OCTET RULE** – Generally atoms prefer electron configurations with 8 valence electrons.

Atoms bond with each other so that every atom has 8 electrons in its outer shell.
- Atoms may take electrons from each other or they may share electrons.

Octet rule is able to explain a lot of chemistry. I. e., it is able to explain why certain elements combine together in specific proportions.

**Exceptions to the octet rule are plentiful.** We will consider these later.

**IONIC BONDING**
- Oppositely charged ions attract each other.
- Metal atoms lose e⁻ and nonmetal atoms gain e⁻.
- Ions attract each other to form ionic lattice.

Lewis structures can be used to illustrate ionic bonding.

Consider Potassium and Bromine

\[ \text{K}^+ (\text{Br}^-) \]

Consider Calcium and Fluorine

\[ \text{Ca}^{2+} (2 \text{F}^-) \]

Lewis structures will be much more illuminating when we consider the sharing of electrons (covalent bonding).
**Lattice Energy** – energy of released when positive and negative ions form crystal lattice due to their attraction for each other.

Creation of an ionic compound can be decomposed into many small steps; therefore, lattice energy can be decomposed into many smaller energy steps.

These steps are virtual steps. We don’t do them one by one in the lab. But overall, when an ionic compound is formed from the reaction of individual elements, these steps must have happened somehow.

A. **Creation of gaseous metal ions from solid metal.**
   1. Heat metal to melting point.
   2. Melt metal.

   3. Heat molten metal to boiling point.
   4. Boil metal to form metal gas atoms.

   5. Ionize metal gas atoms to form metal gas ions.

B. **Creation of gaseous nonmetal ions from nonmetal.**
   1. If solid, heat solid to melting point.
   2. Melt solid.

   3. If liquid, heat liquid to boiling point.

   5. If molecular element, diassociate molecules into atoms.
      \[ \text{I}_2(g) \rightarrow 2 \text{I}(g) \]
      \[ \text{P}_4(g) \rightarrow 4 \text{P}(g) \]

   6. Allow nonmetal atoms capture electrons to become nonmetal anions.

C. **Gaseous metal cations and gaseous nonmetal anions are attracted to each other to form solid lattice.**

   - Energy released is called **lattice energy**.
     -(Technically, the opposite of lattice energy)
   - Much energy is used to create gaseous ions. Even more energy is released as lattice energy.
   - Stability of ionic compounds is due to large lattice energy.
   - To examine lattice energy, we need to know about Coulomb’s law.
COULOMB’S LAW
- fundamental law of physics (hugely important in chemistry)

\[ E = k \frac{q_1 q_2}{r_{12}} \]

- \( E \) – energy of interaction
- \( q_1 \) – charge of ion 1
- \( q_2 \) – charge of ion 2
- \( k \) – proportionality constant
- \( r_{12} \) – distance between ion 1 and ion 2

Three items of note about Coulomb’s law
1. If the energy is negative, ions must be oppositely charged.
2. The higher the charge, the greater the energy.
3. The higher the distance, the smaller the energy.

Coulomb’s Law and Lattice Energy
- Coulomb’s law can be used to make relative assessments of lattice energy.

Example: Which compound has greater lattice energy: LiBr or CaO?

\[ \text{Li}^+ – \text{Br}^- \]
\[ \text{Ca}^{2+} – \text{O}^{2-} \leftarrow \text{higher charges means greater lattice energy} \]

- Distance between ions is also important but to a much lesser degree.
- Smaller distance means higher lattice energy.
- Note that since ions are oppositely charged, the lattice energy is a negative value.
  - Greater lattice energy means a more negative value.

Example: Which compound has higher lattice energy: NaCl or CsCl?

Charges are identical; however, cesium ion is much larger than sodium ion.

\[ \text{Na}^+ --- \text{Cl}^- \]
\[ \text{Cs}^+ \text{---------Cl}^- \leftarrow \text{greater distance between charges means smaller lattice energy} \]

Therefore, NaCl has higher lattice energy.
**COVALENT BONDING**
- Atoms that are bonded “share” valence electrons.
- Sharing is what creates covalent bond.
- When atoms bond covalently, new entity termed **molecule** is formed.
- Nuclei are bound together by their mutual attraction toward the shared electrons.

**Bonding in Diatomic Molecules**

**Hydrogen**

\[
\begin{align*}
\text{H} + \text{H} & \rightarrow \text{H} = \text{H} \\
\text{H} & \equiv \text{H} \\
\text{H} & \equiv \text{H}
\end{align*}
\]

- each atom contributes e\(^{-}\) to the bond
- e\(^{-}\) in bond belongs to both atoms (e\(^{-}\) are shared)
- now each atom has full shell (like He)
- note hydrogen is first exception to octet rule

**Fluorine**

\[
\begin{align*}
\text{F} + \text{F} & \rightarrow \text{F} = \text{F} \\
\text{F} & \equiv \text{F} \\
\text{F} & \equiv \text{F}
\end{align*}
\]

- Since both atoms share electrons in bond, both atoms have 8 valence electrons, octet rule is satisfied.

**Hydrogen fluoride**

\[
\begin{align*}
\text{H} + \text{F} & \rightarrow \text{H} = \text{F} \\
\text{H} & \equiv \text{F} \\
\text{H} & \equiv \text{F}
\end{align*}
\]

**Oxygen**

\[
\begin{align*}
\text{O} + \text{O} & \rightarrow \text{O} = \text{O} \\
\text{O} & \equiv \text{O} \\
\text{O} & \equiv \text{O}
\end{align*}
\]

- note that a molecule can have more than one covalent bond

**Nitrogen**

\[
\begin{align*}
\text{N} + \text{N} & \rightarrow \text{N} = \text{N} \\
\text{N} & \equiv \text{N} \\
\text{N} & \equiv \text{N}
\end{align*}
\]
Bonding in Polyatomic Molecules

Rules of thumb in polyatomic bonding
1. Carbon will form 4 covalent bonds per atom.
2. Oxygen will form 2 covalent bonds per atom.
3. Nitrogen will form 3 covalent bonds per atom.
4. Hydrogen will form 1 covalent bond per atom.
5. Halogens will form 1 covalent bond per atom.

ELECTRONEGATIVITY
In covalent bonding, sharing of electrons is rarely perfect. One atom will draw electrons closer to itself than the other atom.

Consider Methanol, CH₃OH

Electronegativity – ability of an atom in a molecule to attract electrons to itself.
- symbol is χ (Greek chi)
Periodicity of Electronegativity

POLAR COVALENT BONDS
- bond between two atoms where electrons are imperfectly shared
- bond has poles, region that are have more positive or negative charge
- more electronegative atom is slightly negative relative to less electronegative atom

\[ \delta^+ \quad \delta^- \]

\[
\begin{array}{c}
C \\
\end{array}
\quad
\begin{array}{c}
O \\
\end{array}
\]

\( \delta \) – small change in charge density

Note: Metallic bonds can be polar also.

COORDINATE COVALENT BONDS
- covalent bond formed when one atom “shares” two electrons in an orbital.
- the B – N bond in H₃BNH₃ is a coordinate covalent bond.

\[
\begin{array}{c}
H \quad H \\
H \quad H \\
H \quad H \\
\end{array}
\quad
\begin{array}{c}
H \quad H \\
H \quad H \\
H \quad H \\
\end{array}
\]

\[
\begin{array}{c}
H \\
H \\
\end{array}
\quad
\begin{array}{c}
H \\
H \\
\end{array}
\quad
\begin{array}{c}
H \\
H \\
\end{array}
\]
METALLIC BONDING

Metal atoms are arranged in a lattice. Metallic bonding holds lattice together.
- Metallic bonds are much different from ionic or covalent bonds.
- Metal ions have a fixed position within a “sea of electrons”.

Characteristics of Metallic Bonding
1. The orbitals where the valence electrons exist are spread throughout the metal.
   - The wave nature of electron extends throughout the whole metal crystal.

2. The energy levels of the orbitals where valence electrons exist are very close together.

3. The excited states of the electrons are very close to the ground states.
   - I.e., the gap in energy between the highest ground state electron and the lowest excited state electron is zero.

Consequences of Metallic Bonding
1. Metals are very ductile and malleable because the sea of electrons is flexible.
   - If the arrangement of atoms changes, the sea of electrons can rearrange quickly.

2. Metals have high electrical conductivities because the electrons are easily placed in an excited state when they are pushed by an external voltage.

3. Metals have high heat conductivities because the thermal motion can be easily carried by the electrons within an excited state.
ELECTRONEGATIVITY AND BONDING

When the electronegativities of the two atoms involved in a bond are known, the type of bonding can be predicted. Consider two atoms, A and B.

<table>
<thead>
<tr>
<th>Atom A</th>
<th>Atom B</th>
<th>Bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than 2.2</td>
<td>Less than 2.2</td>
<td>metallic</td>
</tr>
<tr>
<td>Greater or = 2.2</td>
<td>Less than 1.7</td>
<td>ionic</td>
</tr>
<tr>
<td>Greater or = 2.2</td>
<td>Greater or = 1.7</td>
<td>covalent</td>
</tr>
</tbody>
</table>

Is one of the atoms greater or equal to 2.2? No: Bonding is metallic

Is the other atom greater or equal to 1.7? No: Bonding is ionic

Yes: Bonding is covalent

Examples

<table>
<thead>
<tr>
<th>2.1</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
<th>3.0</th>
<th>3.5</th>
<th>4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Be</td>
<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
</tr>
</tbody>
</table>

1. Characterize the bonding of CF₄

\[ \chi_C = 2.5 \quad \chi_F = 4.0 \quad \Rightarrow \quad \text{Bonding is covalent} \]
- Both nonmetal atoms want the electrons, so the compromise is a covalent bond.

CF₄ is used to etch circuit boards.

2. Characterize the bonding of Li₂O₂

\[ \chi_{Li} = 1.5 \quad \chi_{O} = 3.5 \quad \Rightarrow \quad \text{Bonding is ionic} \]
- Metal atom doesn’t want electrons and nonmetal atom wants electron, so ionic bonding results.

Li₂O₂ is used in subs to convert CO₂ to O₂.

BeH₂ forms polymer [long chain] rather than molecule.

3. Characterize the bonding of BeH₂

\[ \chi_{Be} = 1.5 \quad \chi_{H} = 2.1 \quad \Rightarrow \quad \text{Bonding is metallic} \]
- Both metal atoms don’t want the electrons, so the valence electrons become delocalized in a metallic bond.
SYSTEMATIC METHOD FOR DETERMINING LEWIS DOT STRUCTURES

Do the following steps in order.
1. Sum the number of valence electrons from all atoms in the molecule.
2. Add or subtract appropriate number of electrons, if molecule is charged. (Polyatomic ion)
3. Identify the central atom and decide how other atoms are bonded to it.
   - least electronegative atom is usually central atom
   - hydrogen is never central atom
4. Draw bonds between atoms. (Subtract 2 e\textsuperscript{-} for each bond from total number of valence e\textsuperscript{-})
5. Complete octets of peripheral atoms. (Subtract 1 e\textsuperscript{-} for each electron used from total number of valence e\textsuperscript{-})
6. Put remaining electrons in pairs on central atom. (if possible)
7. If central atom has too few electrons to complete octet, change lone pairs on peripheral atoms to bonds between central atom and peripheral atom.
8. Write Lewis structure as to minimize formal charges. (More about formal charges in a bit.)

   - Most correct Lewis structure will have negative formal charge on most electronegative atom. (Also, any positive charge must be on least electronegative atom.)

Examples

Draw the Lewis structure for PCl\textsubscript{3}.

1. \# of e\textsuperscript{-} = 5 + 3(7) = 26 e\textsuperscript{-}
2. Central atom is P.

Used in the manufacture of pesticides and flame retardants.
Draw the Lewis Structure of SO$_3$.

1. # of e$^-$ = 6 + 3(6) = 24 e$^-$
2. Note: one electron is subtracted.
3. Central atom is S.

Also known as sulfuric acid anhydride (just add water!)

7. Central atom has too few electrons, use multiple bond.

Draw the Lewis Structure of NH$_4^+$.

1. # of e$^-$ = 5 + 4(1) – 1 = 8 e$^-$
2. Note: one electron is subtracted.
3. Central atom is N.

Ammonium (as part of ammonium chloride) can be used to clean soldering irons.
Draw the Lewis Structure of SF₄.

1. \# of e⁻ = 6 + 4(7) = 34 e⁻
3. Central atom is S.

6. Put remaining electrons on central atom.

- more about exceptions to octet rule later

Sulfur tetrafluoride is an important reagent used to change hydrocarbons into fluorocarbons (refrigerants).

**Lewis Structures With More Than One Central Atom.**

Recall the reminders given previously concerning polyatomic bonding.

1. Carbon will form 4 covalent bonds per atom.
2. Oxygen will form 2 covalent bonds per atom.
3. Nitrogen will form 3 covalent bonds per atom.
4. Hydrogen will form 1 covalent bond per atom.
5. Halogens will form 1 covalent bond per atom.

Also keep in mind that hydrogen will never be a central atom and the halogens will be a central atom generally in oxyacid anions such BrO₃⁻.

Most difficult detail of constructing Lewis structures is deciding how central atoms are connected.

Often the chemical formula gives hints as how to make structure.
Example: Draw the Lewis dot structure for methanol, CH₃OH.

Note the chemical formula implies that three hydrogens are bonded to carbon and one hydrogen is bonded to oxygen.

⇒ Carbon and oxygen must be bonded to each other.

# of e⁻ = 4 + 6 + 4(1) = 14 e⁻

Methanol is not directly toxic, but the metabolized products of formic acid and formaldehyde are.

Example: Draw the Lewis dot structure for formaldehyde, CH₂O.

Formaldehyde is a carcinogen, but there is no better substance for the preservation of tissues.

Example: Draw the Lewis dot structure for propane, CH₃CH₂CH₃.

Propane can be used in heaters and refrigerators!
Example: Draw the Lewis dot structure for acetamide, CH₃C(O)NH₂.

We look to the chemical formula for help in deciding how to arrange atoms. The O atom is put in parenthesis to clue us that the oxygen atom is above the chain of central atoms.

Thus central atom skeleton looks like

```
    H   O   H
   |     |   
H — C — C — N — H
   |     |   
   H   H
```

Note that one carbon is deficient of electrons. Multiple bond must be used.

So! Which one is correct??

Acetamide is a plasticizer (substance that softens hard plastics)

Formal Charge
Each atom within a Lewis structure can be assigned a charge based on the number of valence electrons it normally has versus the number of valence electrons actually has.

Rules for Determining Formal Charge
1. Start with normal # of valence e⁻ for atom.
2. Subtract number of nonbonding e⁻ surrounding atom.
3. Subtract ½ number of bonding electrons surrounding atom.
Example: Which atom is assigned the 1+ charge in the ammonium ion?

\[
\begin{array}{c}
\text{H} \\
\text{N} \\
\text{H} \\
\end{array}
\quad ^{+}
\]

Formal Charge of H:  \(1 - 0 - \frac{1}{2}(2) = 0\)
Formal Charge of N:  \(5 - 0 - \frac{1}{2}(8) = 1\)

Therefore, the N atom has positive charge in NH\(^+\) ion.

Example: What are the formal charges of the atoms within a water molecule?

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{H} \\
\end{array}
\]

Formal Charge of H:  \(1 - 0 - \frac{1}{2}(2) = 0\)
Formal Charge of O:  \(6 - 4 - \frac{1}{2}(4) = 0\)

Example: What are the formal charges of the atoms in the thiocyanate ion given the Lewis structure below?

\[
\begin{array}{c}
\text{S} \\
\text{C} \\
\text{N} \\
\end{array}
\]

Formal Charge of S:  \(6 - 4 - \frac{1}{2}(4) = 0\)
Formal Charge of C:  \(4 - 0 - \frac{1}{2}(8) = 0\)
Formal Charge of N:  \(5 - 4 - \frac{1}{2}(4) = -1\)

The negative charge of the thiocyanate ion lies on the nitrogen atom.

- Note: This is sensible, since the nitrogen atom is the most electronegative of the three atoms.

Thiocyanate ion used to test for the presence of the Fe\(^{3+}\) in solution. The Fe(SCN)\(^{2+}\) ion is the color of blood.
Using Formal Charge to Determine Lewis Structures

Recall rule 8 of our procedure to construct Lewis structures.
8. Write Lewis structure as to minimize formal charges.
   - Most correct Lewis structure will have negative formal charge on most electronegative atom. (Also, any positive charge on least electronegative atom.)

Example: Which of the following Lewis structures is correct for carbon dioxide?

Note both Lewis structures satisfy octet rule. But the correct one has minimized formal charge.

Using multiple bonds in Lewis structures also minimizes formal charge.

Consider NO$_3^-$

Formal Charge of N: $5 - 0 - \frac{1}{2}(6) = +2$
Formal Charge of O: $6 - 6 - \frac{1}{2}(2) = -1$

Most nitrate compounds are very soluble.
RESONANCE
- Sometimes more than one correct Lewis structure can be drawn.
- In that case, actual structure is a blend of correct structures.

Consider the nitrate ion again

- Double-headed arrows indicate resonance structures.

Resonance structure implies the following:
- Double bond is not confined to a single O – N pair.
- Double bond is distributed over all three O – N pairs.
- Thus we can consider the bonding between each O – N pair to be 1½ bonds.
- Also the formal charge on each O is 3/5.
Consider oxalate ion, $\text{C}_2\text{O}_4^{2-}$

- resonance adds to the stability of a compound or polyatomic ion.

Double bond is distributed over both oxygen atoms.

Oxalate is a mild reducing agent (adds electrons to other substances) and converts to carbon dioxide.
BENZENE
An important application of the idea of resonance is the molecule benzene, C₆H₆.

To illustrate that the double bonds form an uninterrupted circle, often benzene is written as

The resonance in benzene makes it an exceptionally stable molecule. It is extremely important in the chemistry of carbon (organic chemistry).

Benzene is part of polystyrene which is a polymer used to make Styrofoam.

EXCEPTIONS TO OCTET RULE
Three usual exceptions to Octet Rule
1. Molecules with odd number of e⁻ (rare)
   Example: ClO₂

   Others are NO and NO₂

   - note chlorine atom has 7 e⁻, not 8 e⁻
2. Molecules where atom has less than octet
   - common in beryllium and boron compounds
   Example: BF$_3$

   ![BF$_3$ diagram]

   - Hmm! Why don’t we create double bond to satisfy octet rule. Look at formal charge.
   ![BF$_3$ formal charge]

3. Molecules where atom has more than octet
   - relatively common
   - only atom in third row or below can “expand its octet”.
     - valence shell is larger, more electrons can fit around the central atom

   Recall previous example of SF$_4$

   ![SF$_4$ diagram]

   - note sulfur has ten electrons
   - sulfur has “expanded its octet”

   Example: I$_3^-$
   \[ \text{# of } e^- = 3(7) + 1 = 22 e^- \]

   ![I$_3^-$ diagram]

   The triiodine ion makes starch blue-purple.
BOND LENGTHS

The length of the covalent bond depends on two items.
1. The atomic radii of the atoms involved in the bond.
   Example:
   \[
   \begin{align*}
   d(C - H) &= 109 \text{ pm} \quad r(H) = 37 \text{ pm} \\
   d(C - F) &= 133 \text{ pm} \quad r(F) = 72 \text{ pm} \\
   d(C - Cl) &= 177 \text{ pm} \quad r(Cl) = 100 \text{ pm} \\
   d(C - Br) &= 194 \text{ pm} \quad r(Br) = 114 \text{ pm} \\
   d(C - I) &= 213 \text{ pm} \quad r(I) = 133 \text{ pm} \\
   \end{align*}
   \]

   \[r(C) = 77 \text{ pm}\]

2. The number of bonds between the atoms.
   Example:
   \[
   \begin{align*}
   d(N - N) &= 146 \text{ pm} \quad d(C - C) = 154 \text{ pm} \\
   d(N = N) &= 122 \text{ pm} \quad d(C = C) = 134 \text{ pm} \\
   d(N \equiv N) &= 110 \text{ pm} \quad d(C \equiv C) = 121 \text{ pm} \\
   \end{align*}
   \]

   Generally, the shorter the bond length, the higher the bond dissociation energy.

   \[
   \begin{align*}
   d(C - C) &= 154 \text{ pm} \quad E_{\text{dis}} = 348 \text{ kJ/mol} \\
   d(C = C) &= 134 \text{ pm} \quad E_{\text{dis}} = 614 \text{ kJ/mol} \\
   d(C \equiv C) &= 121 \text{ pm} \quad E_{\text{dis}} = 839 \text{ kJ/mol} \\
   \end{align*}
   \]

BOND ENTHALPIES

When two atoms bond together, the chemical energy of the system decreases.

Consider an energy level diagram of before bonding and after bonding.

\[
\begin{align*}
\text{H} \quad \bullet && \quad \bullet \quad \text{H} \\
\uparrow && \quad \downarrow \\
\text{H} - \text{H} && \text{before} \quad \text{after}
\end{align*}
\]

The energy released when two unbonded atoms become bonded is called the bond enthalpy.

Aside: Enthalpy is another word for heat. We learn more about heat and enthalpy in Chapter 6.

The bond enthalpy increases as atoms are more strongly bonded together. As the strength of the bond increases, the distance between the atoms decreases.

Bond enthalpies are an experimentally found quantity; i. e., we can’t predict bond enthalpies from periodic table.
Bond Enthalpies and Chemical Changes

**All chemical changes involve the breaking and creation of bonds.**

If we can understand what bonds are breaking and what bonds are forming, then we can use bond enthalpies to estimate the energy (technically, enthalpy) change of the reaction.

To break a bond, we input (add) the bond enthalpy. When a bond is formed, the bond enthalpy is released (subtracted).

Example: Given the table of bond enthalpies below, calculate the energy change, when two molecules of hydrogen and one molecule of oxygen change into two molecules of water.

![Chemical reaction diagram](image)

**TABLE OF BOND ENTHALPIES**

<table>
<thead>
<tr>
<th>Bond</th>
<th>E (kJ/mol)</th>
<th>Bond</th>
<th>E (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C – H</td>
<td>413</td>
<td>H – H</td>
<td>436</td>
</tr>
<tr>
<td>C – C</td>
<td>348</td>
<td>N – N</td>
<td>163</td>
</tr>
<tr>
<td>C – O</td>
<td>358</td>
<td>N = N</td>
<td>418</td>
</tr>
<tr>
<td>C = C</td>
<td>614</td>
<td>N ≡ N</td>
<td>941</td>
</tr>
<tr>
<td>C ≡ C</td>
<td>839</td>
<td>O – H</td>
<td>463</td>
</tr>
<tr>
<td>C = O</td>
<td>1072</td>
<td>O = O</td>
<td>495</td>
</tr>
</tbody>
</table>


Overall the energy change is