Chapter 12

Chemical Bonding
by Christopher Hamaker
• Recall that an atom has core and valence electrons.

• Core electrons are found close to the nucleus.

• Valence electrons are found in the most distant $s$ and $p$ energy subshells.

• It is valence electrons that are responsible for holding two or more atoms together in a chemical bond.
Octet Rule

- The **octet rule** states that atoms bond in such a way that each atom acquires eight electrons in its outer shell.

- There are two ways in which an atom may achieve an octet:
  1. Transfer of electrons from one atom to another
  2. Sharing one or more pairs of electrons
Types of Bonds

- **Ionic bonds** are formed when a complete transfer of electrons between atoms occurs, forming ionic compounds.

- **Covalent bonds** are formed when two atoms share electrons to form molecular compounds.
Ionic Bonds

• An **ionic bond** is formed by the attraction between positively charged anions and negatively charged anions.

• This electrostatic attraction is similar to the attraction between opposite poles on two magnets.
Ionic Bonds, Continued

• The ionic bonds formed from the combination of anions and cations are very strong and result in the formation of a rigid, crystalline structure. The structure for NaCl, ordinary table salt, is shown here.
Formation of Cations

- **Cations** are formed when an atom loses valence electrons to become positively charged.
- Most main group metals achieve a noble gas electron configuration by losing their valence electrons, and are *isoelectronic* with a noble gas.
- Magnesium (Group IIA/2) loses its two valence electrons to become Mg$^{2+}$.
- A magnesium ion has 10 electrons ($12 - 2 = 10$ e$^-$) and is isoelectronic with neon.
Formation of Cations, Continued

- We can use electron dot formulas to look at the formation of cations.

- Each of the metals in Period 3 forms cations by losing one, two, or three electrons, respectively. Each metal atom becomes isoelectronic with the preceding noble gas, neon.
Formation of Anions

• **Anions** are formed when an atom gains electrons and becomes negatively charged.

• Most nonmetals achieve a noble gas electron configuration by gaining electrons to become *isoelectronic* with a noble gas.

• Chlorine (Group VIIA/17) gains one valence electron and becomes $\text{Cl}^-$.

• A chloride ion has 18 electrons ($17 + 1 = 18 \text{ e}^-$) and is *isoelectronic* with argon.
Formation of Anions, Continued

- We can also use electron dot formulas to look at the formation of anions.

- The nonmetals in Period 3 gain one, two, or three electrons, respectively, to form anions. Each nonmetal ion is isoelectronic with the following noble gas, argon.

\[
\begin{align*}
\text{Cl}^- & : \text{Cl}^- \\
\text{[Ne]}3s^23p^5 + 1e^- & \rightarrow \text{[Ne]}3s^23p^6 = \text{Ar} \\
\text{S}^{2-} & : \text{S}^{2-} \\
\text{[Ne]}3s^23p^4 + 2e^- & \rightarrow \text{[Ne]}3s^23p^6 = \text{Ar} \\
\text{P}^{3-} & : \text{P}^{3-} \\
\text{[Ne]}3s^23p^3 + 3e^- & \rightarrow \text{[Ne]}3s^23p^6 = \text{Ar}
\end{align*}
\]
Ionic Radii

- The radius of a cation is smaller than the radius of its starting atom.
- The radius of an anion is larger than the radius of its starting atom.

![Ionic Radius Diagram]

- Na atom: $r = 0.186$ nm
- Cl atom: $r = 0.099$ nm
- Na$^+$: $r = 0.095$ nm
- Cl$^-$: $r = 0.181$ nm
Covalent Bonds

- **Covalent bonds** are formed when two nonmetal atoms share electrons, and the shared electrons in the covalent bond belong to both atoms.

- When hydrogen chloride (HCl) is formed, the hydrogen atom shares its one valence electron with the chlorine. This gives the chlorine atom eight electrons in its valence shell, making it isoelectronic with argon.

- The chlorine atom shares one of its valence electrons with the hydrogen, giving it two electrons in its valence shell, and making it isoelectronic with helium.
Bond Length

• When a covalent bond is formed, the valence shells of the two atoms overlap with each other.

• In HCl, the 1s energy sublevel of the hydrogen atom overlaps with the 3p energy sublevel of the chlorine atom. The mixing of sublevels draws the atoms closer together.

• The distance between the two atoms is smaller than the sum of their atomic radii and is the **bond length**.

![Diagram showing atomic radii and bond length](image)
Bond Energy

• Energy is released when two atoms form a covalent bond.

\[ \text{H}(g) + \text{Cl}(g) \rightarrow \text{HCl}(g) + \text{heat} \]

• Conversely, energy is needed to break a covalent bond.

• The energy required to break a covalent bond is referred to as the **bond energy**. The amount of energy required to break a covalent bond is the same as the amount of energy released when the bond is formed.

\[ \text{HCl}(g) + \text{heat} \rightarrow \text{H}(g) + \text{Cl}(g) \]
Electron Dot Formulas of Molecules

• In Section 6.8, we drew electron dot formulas for atoms.

• The number of dots around each atom is equal to the number of valence electrons the atom has.

• We will now draw electron dot formulas for molecules (also called Lewis structures).

• A *Lewis structure* shows the bonds between atoms and helps us visualize the arrangement of atoms in a molecule.
Guidelines for Electron Dot Formulas

1. Calculate the total number of valence electrons by adding all of the valence electrons for each atom in the molecule.

2. Divide the total valence electrons by 2 to find the number of electron pairs in the molecule.

3. Surround the central atom with four electron pairs. Use the remaining electron pairs to complete the octet around the other atoms. The only exception is hydrogen, which only needs two electrons.
4. Electron pairs that are shared by atoms are called *bonding electrons*. The other electrons complete octets and are called *nonbonding electrons*, or lone pairs.

5. If there are not enough electron pairs to provide each atom with an octet, move a nonbonding electron pair between two atoms that already share an electron pair.
1. Count the total number of valence electrons: oxygen has six and each hydrogen has one for a total of eight electrons \([6 + 2(1) = 8 \text{ e}^-]\). The number of electron pairs is 4 \((8/2 = 4)\).

2. Place eight electrons around the central oxygen atom.

3. We can then place the two hydrogen atoms in any of the four electron pair positions. Notice there are two bonding and two nonbonding electron pairs.
4. To simplify, we represent bonding electron pairs with a single dash line called a *single bond*.

5. The resulting structure is referred to as the *structural formula* of the molecule.
1. Count the total number of valence electrons: each oxygen has six and sulfur has six for a total of 24 electrons \([3(6) + 6 = 24 \text{ e}^{-}]\). This gives us 12 electron pairs.

2. Place four electron pairs around the central sulfur atom and attach the three oxygens. We started with 12 electron pairs and have eight left.

3. Place the remaining electron pairs around the oxygen atoms to complete each octet.

4. One of the oxygens does not have an octet, so move a nonbonding pair from the sulfur to provide two pairs between the sulfur and the oxygen.
Resonance

- The two shared electron pairs constitute a **double bond**.
- The double bond can be placed between the sulfur and any of the three oxygen atoms. The structural formula can be shown as any of the structures below. This phenomenon is called **resonance**.

\[ \text{O} \equiv \text{S} \equiv \text{O} \quad \text{O} \equiv \text{S} \equiv \text{O} \quad \text{O} \equiv \text{S} \equiv \text{O} \]

\[ \text{O} \quad \text{O} \quad \text{O} \]
Electron Dot Formula for NH$_4^+$

1. The total number of valence electrons is $5 - 4(1) - 1 = 8$ e$^-$. We must subtract one electron for the positive charge. We have four pairs of electrons.

2. Place four electron pairs around the central nitrogen atom and attach the four hydrogens.

3. Enclose the polyatomic ion in brackets and indicate the charge outside the brackets.
1. The total number of valence electrons is $4 + 3(6) + 2 = 24$ e\textsuperscript{-}. We must add one electron for the negative charge. We have 12 pairs of electrons.

2. Place four electron pairs around the central carbon atom and attach the three oxygens. Use the remaining electron pairs to give the oxygen atoms their octets.

3. One oxygen does not have an octet. Make a double bond and enclose the ion in brackets.
Polar Covalent Bonds

- *Covalent bonds* result from the sharing of valence electrons.

- Often, the two atoms do not share the electrons equally. That is, one of the atoms holds onto the electrons more tightly than the other.

- When one of the atoms holds the shared electrons more tightly, the bond is *polarized*.

- A *polar covalent bond* is one in which the electrons are not shared equally.
Electronegativity

• Each element has an innate ability to attract valence electrons.

• **Electronegativity** is the ability of an atom to attract electrons in a chemical bond.

• Linus Pauling devised a method for measuring the electronegativity of each of the elements.

• Fluorine is the most electronegative element.
Electronegativity, Continued

• Electronegativity increases as you go left to right across a period.

• Electronegativity increases as you go from bottom to top in a family.
Electronegativity Differences

- The electronegativity of H is 2.1; Cl is 3.0.
- Since there is a difference in electronegativity between the two elements (3.0 – 2.1 = 0.9), the bond in H–Cl is polar.
- Since Cl is more electronegative, the bonding electrons are attracted toward the Cl atom and away from the H atom. This will give the Cl atom a slightly negative charge and the H atom a slightly positive charge.
Delta (δ) Notation for Polar Bonds

- We use the Greek letter delta, δ, to indicate a polar bond.

- The negatively charged atom is indicated by the symbol δ−, and the positively charged atom is indicated by the symbol δ+. This is referred to as delta notation for polar bonds.

\[ \delta^+ \text{H}–\text{Cl} \delta^- \]
Delta (\(\delta\)) Notation for Polar Bonds, Continued

- The hydrogen halides HF, HCl, HBr, and HI all have polar covalent bonds.

- The halides are all more electronegative than hydrogen and are designated with a \(\delta^-\).
Nonpolar Covalent Bonds

• What if the two atoms in a covalent bond have the same or similar electronegativities?

• The bond is not polarized and it is a nonpolar covalent bond. If the electronegativity difference is less than 0.5, it is usually considered a nonpolar bond.

• The diatomic halogen molecules have nonpolar covalent bonds.
Coordinate Covalent Bonds

• A covalent bond resulting from one atom donating a lone pair of electrons to another atom is called a \textit{coordinate covalent bond}.

• A good example of a molecule with a coordinate covalent bond is ozone, O$_3$.

\begin{align*}
\text{:O::O: + O:} & \rightarrow \text{:O::O:O:} \\
\text{nonbonding electron pair} & \quad \text{coordinate covalent bond}
\end{align*}
Hydrogen Bonds

- The bond between H and O in water is very polar.
- Therefore, the oxygen is partially negative, and the hydrogens are partially positive.
- As a result, the hydrogen atom on one molecule is attracted to the oxygen atom on another.
- This intermolecular attraction is referred to as a hydrogen bond.
Shapes of Molecules

• Electron pairs surrounding an atom repel each other. This is referred to as \textit{Valence Shell Electron Pair Repulsion (VSEPR) theory}.

• The \textit{electron pair geometry} indicates the arrangement of bonding and nonbonding electron pairs around the central atom.

• The \textit{molecular shape} indicates the arrangement of atoms around the central atom as a result of electron repulsion.
Tetrahedral Molecules

• Methane, CH$_4$, has four pairs of bonding electrons around the central carbon atom.

• The four bonding pairs (and, therefore, atoms) are repelled to the four corners of a tetrahedron. Thus, the electron pair geometry is tetrahedral.

• The molecular shape is also tetrahedral.
In ammonia, NH$_3$, the central nitrogen atom is surrounded by three bonding pairs and one nonbonding pair.

Thus, the electron pair geometry is tetrahedral and the molecular shape is *trigonal pyramidal*.
Bent Molecules

• In water, H₂O, the central O atom is surrounded by two nonbonding pairs and two bonding pairs.

• Thus, the electron pair geometry is tetrahedral and the molecular shape is bent.
• In carbon dioxide, CO$_2$, the central C atom is bonded to each oxygen by two electron pairs (a double bond).

• According to VSEPR theory, the electron pairs will repel each other and they will be at opposite sides of the C atom.

• Thus, the electron pair geometry and the molecular shape are both *linear*. 

O :: C :: O
### TABLE 12.1  SUMMARY OF VSEPR THEORY

<table>
<thead>
<tr>
<th>BONDING/NONBONDING ELECTRON PAIRS</th>
<th>ELECTRON PAIR GEOMETRY</th>
<th>MOLECULAR SHAPE</th>
<th>BOND ANGLE</th>
<th>EXAMPLE MOLECULE</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 / 0</td>
<td>tetrahedral</td>
<td>tetrahedral</td>
<td>109.5°</td>
<td>CH₄</td>
</tr>
<tr>
<td>3 / 1</td>
<td>tetrahedral</td>
<td>trigonal</td>
<td>107°</td>
<td>NH₃</td>
</tr>
<tr>
<td>2 / 2</td>
<td>tetrahedral</td>
<td>pyramidal</td>
<td>104.5°</td>
<td>H₂O</td>
</tr>
<tr>
<td>4 / 0</td>
<td>linear</td>
<td>linear</td>
<td>180°</td>
<td>CO₂</td>
</tr>
<tr>
<td>4 / 0</td>
<td>trigonal planar</td>
<td>trigonal</td>
<td>120°</td>
<td>CH₂O</td>
</tr>
</tbody>
</table>
Nonpolar Molecules with Polar Bonds

- $\text{CCl}_4$ has polar bonds, but the overall molecule is nonpolar.
- Using VSEPR theory, the four chlorine atoms are at the four corners of a tetrahedron.
- The chlorines are each $\delta^-$, while the carbon is $\delta^+$. 
- The net effect of the polar bonds is zero, so the molecule is nonpolar.
Diamond Versus Graphite

• Why is diamond colorless and hard, while graphite is black and soft when both are pure carbon?
• Diamond has a three-dimensional structure, whereas graphite has a two-dimensional structure.
• The layers in graphite are able to slide past each other easily.
Chemical bonds hold atoms together in molecules.

Atoms bond in such a way as to have eight electrons in their valence shell. This is called the octet rule.

There are two types of bonds: ionic and covalent.

Ionic bonds are formed between a cation and an anion.

Covalent bonds are formed from the sharing of electrons.
• *Electron dot formulas* help us visualize the arrangements of atoms in a molecule.

• Electrons are shared unequally in *polar covalent bonds*.

• *Electronegativity* is a measure of the ability of an atom to attract electrons in a chemical bond.

• Electronegativity increases from left to right and from bottom to top on the periodic table.
• VSEPR theory can be used to predict the shapes of molecules.

• The *electron pair geometry* indicates the arrangement of bonding and nonbonding pairs around a central atom.

• The *molecular shape* indicates the arrangement of atoms in a molecule.