1.12 Covalent Bonding

covalent bond a bond that arises when two atoms share one or more pairs of electrons between them. The shared electron pairs are attracted to the nuclei of both atoms.

molecule two or more atoms that are joined by covalent bonds

chemical entity a chemical unit, such as an atom, an ion, or a molecule

Figure 1

The pair of shared electrons between the nuclei of two chlorine atoms results in a single covalent bond.

Lewis structure a representation of covalent bonding based on Lewis symbols, with shared electron pairs shown as lines and lone pairs shown as dots

lone pair a pair of valence electrons that is not involved in bonding In the previous section, you learned about ionic compounds. When a metal and a nonmetal come in contact, the result is a *transfer of electrons*, the production of positive and negative ions, and the formation of an *ionic compound*. When two nonmetals, such as two chlorine atoms, come in contact, a transfer of electrons would result in less stable atoms. If an electron were transferred from one chlorine atom to another, one chlorine atom would attain eight electrons in its outermost shell, but the other atom would be left with six electrons—a less stable situation. Instead of transferring electrons, the chlorine atoms *share* electrons in order to become more stable. The bond that is formed as a result of sharing electrons is called a **covalent bond**. Atoms that are covalently bonded form chemical entities called **molecules** (**Figure 1**). A **chemical entity** is a single chemical unit, such as an atom, an ion, or a molecule. When two atoms form a covalent bond, the sharing of valence electrons allows both atoms to satisfy the octet rule.

In a hydrogen molecule, two hydrogen atoms share a pair of electrons (one from each atom) and, therefore, form a single covalent bond. Some molecules contain double and triple covalent bonds. For example, oxygen molecules, $O_{2(g)}$, are composed of two oxygen atoms held together by a double covalent bond (two shared electron pairs). Nitrogen molecules, $N_{2(g)}$, are composed of two nitrogen atoms held together by a triple covalent bond (three shared electron pairs).

Molecules can be represented by **Lewis structures**. A Lewis structure shows the electrons that are shared between the atoms as a dash, and the remaining surrounding valence electrons as dots. The pairs of valence electrons that surround each atom are referred to as **lone pairs**. The Lewis structure of a chlorine molecule is shown below.

$$: \overset{\cdots}{\operatorname{Cl}} \cdot + \cdot \overset{\cdots}{\operatorname{Cl}} : \to : \overset{\cdots}{\operatorname{Cl}} - \overset{\cdots}{\operatorname{Cl}} :$$

SAMPLE problem

Drawing Lewis Structures

(a) Draw Lewis symbols for the reaction between two iodine atoms, and draw a Lewis structure for the resulting iodine molecule.

Step 1: Draw Lewis Symbols for Atoms

Draw Lewis symbols for the two iodine atoms. Arrange the iodine atoms as you would expect them to be arranged in an iodine molecule. Since there are only two atoms, they are side by side.



Step 2: Arrange Shared Electron Pairs According to Octet Rule

Arrange the electrons so that at least one pair of electrons is shared by the two atoms and each atom is surrounded by a total of eight electrons, thus obeying the octet rule. Since iodine is found in Group VII, it has seven valence electrons. Each iodine atom contributes one electron to form a shared electron pair.

Step 3: Represent Bonds as Lines

The shared electron pair (covalent bond) is represented by a line.

:<u>I</u> — <u>I</u>:

Step 4: Rewrite Chemical Equation Using Lewis Symbols and Lewis Structures

 $: \underbrace{\vec{I}} \cdot + \cdot \underbrace{\vec{I}} : \longrightarrow : \underbrace{\vec{I}} - \underbrace{\vec{I}} :$

(b) Draw Lewis symbols for the reaction between two oxygen atoms, and draw a Lewis structure for the resulting oxygen molecule.

Step 1: Draw Lewis Symbols for Atoms

Draw Lewis symbols for the two oxygen atoms. Arrange the oxygen atoms as you would expect them to be arranged in an oxygen molecule. Since there are only two atoms, they are side by side.

Step 2: Arrange Shared Electron Pairs According to Octet Rule

Arrange the electrons so that at least one pair of electrons is shared by the two atoms and each atom is surrounded by a total of eight electrons, thus obeying the octet rule. Since oxygen is found in Group VI, it has six valence electrons. Each oxygen atom contributes two electrons to form two shared electron pairs. Lone pairs repel each other and move as far apart as possible.

Step 3: Represent Bonds as Lines

A shared electron pair is represented by a line. Since an oxygen molecule has two shared electron pairs, there are two lines, representing a double bond.

 $\dot{0} = 0$

Step 4: Rewrite Chemical Equation Using Lewis Symbols and Lewis Structures

$$0:+:0 \longrightarrow 0=0$$

(c) Draw Lewis symbols for the reaction between two nitrogen atoms, and draw a Lewis structure for the resulting nitrogen molecule.

Step 1: Draw Lewis Symbols for Atoms

Draw Lewis symbols for the two nitrogen atoms. Arrange the nitrogen atoms as you would expect them to be arranged in a nitrogen molecule. Since there are only two atoms, they are side by side.



Step 2: Arrange Shared Electron Pairs According to Octet Rule

Arrange the electrons so that at least one pair of electrons is shared by the two atoms and each atom is surrounded by a total of eight electrons, thus obeying the octet rule. Since nitrogen is found in Group V, it has five valence electrons. Each nitrogen atom contributes three electrons to form three shared electron pairs. Lone pairs repel each other and move as far apart as possible.

N:N:

Step 3: Represent Bonds as Lines

A shared electron pair is represented by a line. Since a nitrogen molecule has three shared electron pairs, there are three lines, representing a triple bond.

 $:N \equiv N$:

Step 4: Rewrite Chemical Equation Using Lewis Symbols and Lewis Structures

$$: N \cdot + \cdot N : \rightarrow : N \equiv N$$

(d) Draw Lewis symbols for the reaction between two hydrogen atoms and one oxygen atom. Draw a Lewis structure for the resulting water molecule.

Step 1: Draw Lewis Symbols for Atoms

Draw Lewis symbols for the two hydrogen atoms and one oxygen atom. Arrange the atoms as you would expect them to be arranged in a water molecule. In general, molecules are symmetrical. Here the oxygen atom is placed in the middle, with the hydrogen atoms on each side.

Step 2: Arrange Shared Electron Pairs According to Octet Rule

Arrange the electrons so that at least one pair of electrons is shared by the two atoms and each atom is surrounded by a total of eight electrons, thus obeying the octet rule. Since oxygen is found in Group VI, it has six electrons in its outer shell. Therefore, it requires two more electrons in order to satisfy the octet rule. Hydrogen can donate one electron to a shared pair and needs one electron in order to become stable. (It is an exception to the octet rule.) Therefore, each hydrogen atom donates one electron to oxygen, forming a

shared pair. The result is a single bond between each hydrogen atom and the central oxygen atom. Hydrogen is stable since it now has two electrons in its outermost shell, achieving the noble gas configuration of helium.

Step 3: Represent Bonds as Lines

A shared electron pair is represented by a line. Since an oxygen molecule has two shared pairs of electrons, there are two lines, one going to each hydrogen atom.



Step 4: Rewrite Chemical Equation Using Lewis Symbols and Lewis Structures



Example

Draw Lewis symbols for the reaction between two oxygen atoms and a carbon atom. Draw the Lewis structure for the resulting carbon dioxide molecule.

Solution

$$[o: \cdot c \cdot :o]$$

$$[o::c::o]$$

$$[o::c::o]$$

$$0:+\cdot C \cdot +:0 \rightarrow 0=C=0$$

Practice

Understanding Concepts

- 1. Draw Lewis symbols for the reaction between two bromine atoms.
- **2.** Draw Lewis symbols for the reaction between one nitrogen atom and three hydrogen atoms. Draw the Lewis structure for the resulting ammonia molecule.
- **3.** Draw Lewis symbols for the reaction between one carbon atom and four hydrogen atoms. Draw the Lewis structure for the resulting methane molecule.
- **4.** Draw Lewis symbols for the reaction between one silicon atom and two oxygen atoms. Draw the Lewis structure for the resulting silicon dioxide molecule.

Electronegativity

electronegativity a measure of an atom's ability to attract a shared pair of electrons within a covalent bond

Electronegativity is a measure of an atom's ability to attract the pair of electrons it shares with another atom within a covalent bond. **Table 1** lists the electronegativities of some elements. In general, metals have lower electronegativities than nonmetals. Fluorine has the highest electronegativity: 4.0. Therefore, it has the greatest ability to attract shared electrons.

	-	
	Element	Electronegativity
	Н	2.1
Metals	Li	1.0
	Ве	1.5
	Na	0.9
	Mg	1.2
	К	0.8
	Са	1.0
Nonmetals	С	2.5
	N	3.0
	0	3.5
	F	4.0
	Р	2.1
	S	2.5
	CI	3.0

 Table 1
 The Electronegativities of Some Elements

One factor that plays a role in determining an atom's electronegativity is the atom's atomic radius. The larger an atom is, the weaker its attraction for shared electron pairs. The many layers of electron shells that separate the shared electrons from the positively charged nucleus act as a shield between the positive charge of the nucleus and the negative charge of the shared electrons. An atom with a small atomic radius has a stronger attraction for a shared pair of electrons than a larger atom. Electronegativity *decreases* as you descend a family in the periodic table because atomic radii *increase*. Electronegativity *increases* as you move from left to right across the periodic table because atomic radii decrease—there are more protons in the nucleus, causing a stronger attraction for electrons (**Figure 2**). Metals generally have lower electronegativities than nonmetals.



Polar and Nonpolar Covalent Bonds

If an electron pair is shared equally, then the bond is a **nonpolar covalent bond**. The two hydrogen atoms in a hydrogen molecule, $H_{2(g)}$, are held together by a nonpolar covalent bond because the two identical hydrogen nuclei (one proton each) attract electrons with equal force (**Figure 3**). Think of a nonpolar covalent bond as a tug of war in which both people who are tugging have exactly the same strength of pull.

Even though a covalent bond involves the sharing of electrons, the sharing is not always equal. The shared electron pair may spend more time around one atom than around the other atom. When an electron pair is not shared equally, there is a localized negative charge around one atom, represented by the symbol δ^- . The other atom is more positively charged. It has a localized positive charge, represented by δ^+ . The bond between the two atoms is called a **polar covalent bond**. A polar covalent bond has a slightly negative end and a slightly positive end.

Whether or not a bond is polar covalent depends on the difference between the electronegativities of the bonded atoms. Hydrogen chloride, $HCl_{(g)}$, is an example of a molecule that has a polar covalent bond (**Figure 4**). In a hydrogen chloride molecule, the electron pair is unequally shared because chlorine has a higher electronegativity than hydrogen. The electron pair of the covalent bond therefore spends a greater amount of time in the space surrounding the chlorine nucleus than in the space surrounding the hydrogen end of the molecule has a slightly positive charge, δ^+ , and the chlorine end has a slightly negative charge, δ^- .

Figure 2

In general, electronegativity decreases as you descend a family and increases as you travel across a period from left to right. This trend is related to atomic radius, which increases as you move down the periodic table and decreases as you move from left to right across the periodic table.

nonpolar covalent bond a bond in which an electron pair is shared equally between a pair of atoms having the same electronegativity



Figure 3

Two identical atoms are bonded together by a nonpolar covalent bond.

polar covalent bond a bond in which an electron pair is shared unequally between a pair of atoms that have different electronegativities



Figure 4

In hydrogen chloride, $\text{HCl}_{(g)}$, the shared electron pair spends more time near the chlorine atom. Therefore, the chlorine end of hydrogen chloride possesses a slightly negative charge, represented by δ^- . Since the hydrogen atom's electron spends more time around the chlorine atom, the hydrogen end has a slightly positive charge, represented by δ^+ . **polar molecule** a molecule that has a slightly positive charge on one end and a slightly negative charge on the other end

nonpolar molecule a molecule that has no charged ends

Polar and Nonpolar Molecules

Polar molecules are molecules that have a positively charged end and a negatively charged end. **Nonpolar molecules** do not have charged ends. The polarity of a molecule depends on two characteristics of the molecule:

- 1. the presence of polar covalent bonds;
- 2. the three-dimensional shape (geometry) of the molecule.

Ammonia, $NH_{3(g)}$, is a polar molecule because it contains polar covalent bonds and a pyramidal shape (**Figure 5(a)**). Nitrogen forms covalent bonds with three hydrogen atoms. Because nitrogen has a higher electronegativity than hydrogen, it has a stronger attraction for each of the three shared electron pairs. Therefore, ammonia has a positively charged end and a negatively charged end.

Methane, $CH_{4(g)}$, contains slightly polar covalent bonds between the carbon atom and each of the four hydrogen atoms. Because carbon is slightly more electronegative than hydrogen, it has a stronger attraction for each of the shared electron pairs. Methane is a nonpolar molecule, however, because its polar covalent bonds are all arranged symmetrically about the central carbon atom (**Figure 5(b**)). Molecules made up of identical atoms, such as nitrogen, $N_{2(g)}$, contain only nonpolar covalent bonds. They are always linear in shape and nonpolar (**Figure 5(c**)).



Figure 5

- (a) Ammonia, NH_{3(g)}, has polar covalent bonds and a pyramidal shape. The lone pair of electrons in the nitrogen atom repels the electrons in the hydrogen atoms, causing them to move closer to each other. The result is a polar molecule.
- **(b)** Methane, $CH_{4(g)}$, has slightly polar covalent bonds and a symmetrical tetrahedral shape, resulting in a nonpolar molecule.
- (c) Nitrogen, N_{2(g)}, has nonpolar bonds. Both nitrogen nuclei have equal pull on the shared electron pairs.

Intermolecular Bonds

Covalent bonds are strong forces of attraction that hold the atoms of a molecule together. Molecules are attracted to other molecules by a group of much weaker forces of attraction, known as **intermolecular bonds** (bonds between molecules). The strength of intermolecular bonds determines the physical state (solid, liquid, or gas) of a molecular compound at a particular temperature and pressure, and also determines the melting point and boiling point of the compound. Intermolecular bonds are broken when a molecular compound melts and boils.

intermolecular bonds bonds between molecules; forces of attraction that form between a molecule and its neighbouring molecules

There are two different types of intermolecular bonds that we will consider. One type, called the **dipole-dipole force (DDF)**, occurs between polar molecules, such as hydrogen chloride, HCl. The slightly positive end of one hydrogen chloride molecule is attracted to the slightly negative end of a neighbouring hydrogen chloride molecule (Figure 6). Another type of intermolecular bond, called the London dispersion force, occurs between all molecules, polar and nonpolar. It is the most important intermolecular bond that occurs between nonpolar molecules. London dispersion forces (LDF) are formed when the electrons in the atoms of a molecule happen to be located on one side of the atoms, leaving a deficiency of electrons on the other side. The side of the atoms with more electrons develops a temporary negative charge, and the side with fewer electrons develops a temporary positive charge. If the same thing happens to the atoms of a neighbouring molecule at the same time, the atoms of the two molecules, and thus the molecules themselves, experience a force of attraction: the positive side of one molecule attracts the negative side of the other molecule. Since electrons move quickly, the dipole lasts for only a fraction of a second.

If the molecules are large and have lots of atoms in them, then the chance of creating London dispersion forces between atoms of adjacent molecules is much higher. London dispersion forces, therefore, arise more often (and are more effective) between molecules composed of large numbers of atoms, where the chance of electron imbalances is high. Dipole–dipole forces and London dispersion forces are referred to as **van der Waals forces**, after the nineteenth-century chemist who first suggested the existence of intermolecular bonds.

dipole-dipole force (DDF) an intermolecular force of attraction that forms between the slightly positive end of one polar molecule and the slightly negative end of an adjacent polar molecule

London dispersion force (LDF)

an intermolecular force of attraction that forms between atoms of neighbouring molecules as a result of a temporary imbalance in the position of the atoms' electrons; forms between all molecules, polar and nonpolar

van der Waals forces forces of attraction between molecules, such as the dipole–dipole force and the London dispersion force



Figure 6

The slightly positive end of one hydrogen chloride molecule is attracted to the slightly negative end of the other hydrogen chloride molecule, creating a dipole–dipole force between them.

TRYTHIS activity

Building Molecular Models

In section 1.2, you learned about the importance of models for understanding how matter behaves. Lewis structures are models that are used to represent molecules. You can also represent molecules using three-dimensional molecular models. In this activity, you will build molecular models of different compounds using a molecular model kit.

Materials: molecular model kit

- **1.** In your molecular model kit, identify the pieces that represent the following elements: chlorine, oxygen, hydrogen, nitrogen, and carbon.
- (a) Copy and complete **Table 2** by drawing the Lewis structures for the following molecules: O₂, CO₂, H₂O, CH₄, H₂, HCl, C₂H₂, and CCl₄.
- 2. Build models of the molecules in Table 2.
- (b) Describe the shape of each molecule you built. Is it linear, bent, pyramidal, or tetrahedral?
- (c) What do the holes in the round pieces represent? What do the pegs or springs represent?
- (d) Which molecules contain single bonds? Which molecules contain double bonds, and which contain triple bonds?
- (e) Identify the polar and nonpolar molecules.

 Table 2
 Lewis Structures

Molecule	02	CO ₂	H ₂ O	CH ₄	H ₂	HCI	C_2H_2	CCI ₄
Lewis structure								



Figure 7

Water is a polar molecule due to the difference in the electronegativities of oxygen and hydrogen, and its bent shape.

Water

Water is an excellent example of a polar molecule. The difference between the electronegativities of the oxygen and hydrogen atoms is 1.4. Since oxygen has the higher electronegativity, the electrons spend more time around oxygen than they do around hydrogen. Therefore, the oxygen end of a water molecule has a slightly negative charge. (Since hydrogen has the lower electronegativity and therefore less attraction for the electron pair, the hydrogen end of the molecule is slightly positive.) The arrangement of atoms and covalent bonds forms a bent molecule that is highly polar (**Figure 7**).

Section 1.12 Questions

Understanding Concepts

- Which of the following pairs of atoms form covalent bonds, and which form ionic bonds? How do you know?
 - (a) sulfur and oxygen
 - (b) sodium and iodine
 - (c) bromine and bromine
- **2.** Draw a Lewis structure for each of the following molecules:

(a)	F ₂	(c)	02	(e)	CO_2
(b)	H ₂	(d)	H_2S		

- **3.** Which of the molecules in question 2 are polar molecules? Which are nonpolar?
- **4.** How are a covalent bond and an ionic bond different? How are they similar?
- Using the periodic table and your knowledge of electronegativity, predict which of the atoms in the following pairs has a higher electronegativity. Justify your prediction.
 - · beryllium and strontium
 - · sodium and chlorine
- **6.** Identify the more polar bond in each of the following pairs.
 - (a) H–F and H–Cl (e) C–H and N–H
 - (b) N–O and C–O (f) S–O and P–O
 - (c) S–H and O–H (g) C–N and N–N
 - (d) P–Cl and S–Cl
- **7.** Explain how some molecules that contain polar covalent bonds can be nonpolar.
- 8. (a) What is an intermolecular bond?
 - (b) What type(s) of intermolecular forces of attraction may form between nonpolar molecules? What type(s) may form between polar molecules? Give reasons in both cases.
- 9. Copy and complete Table 3.

Table 3 Intermolecular Forces

Molecule	Intermolecular force(s) (LDF, DDF, or both)
hydrogen, H ₂	
carbon tetrachloride, CCl_4	
hydrogen sulfide, H ₂ S	

10. How do intermolecular bonds help to explain why the boiling point of methane, CH₄, is much lower than the boiling point of hydrogen bromide, HBr?

Applying Inquiry Skills

11. A student was given four sample liquids and asked to determine whether the liquids were affected by a positively charged object or a negatively charged object. The student tested a thin stream of each liquid by holding a positively charged object near the liquid stream. The student then repeated the procedure using a negatively charged object. Complete the Prediction, Observations, Analysis, and Synthesis in the following lab report:

Question

How does a charged object affect a thin stream of each of the following liquids: NCI_3 , H_2O , Br_2 , and CCI_4 ?

Prediction

(a) Using what you know about polar and nonpolar molecules, predict an answer to the Question.

Observations

Table 4	Effects of Charged Objects on Fo	our Liquids
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Sample	Positive charge	Negative charge
1	There was no effect.	There was no effect.
2	There was no effect.	There was no effect.
3	The stream moved toward the charged object.	The stream moved toward the charged object.
4	The stream moved toward the charged object.	The stream moved toward the charged object.

(b) Which of the four substances could be samples 1 and 2? Which could be samples 3 and 4?

Analysis

(c) Use your Observations to answer the Question.

Synthesis

- (d) Provide a theoretical explanation to justify your answer for (b).
- (e) Speculate as to why the liquids were affected by both positive and negative charges.