

## 11.3: Intermolecular Forces: The Forces That Hold Condensed States Together

### Key Concept Video Intermolecular Forces

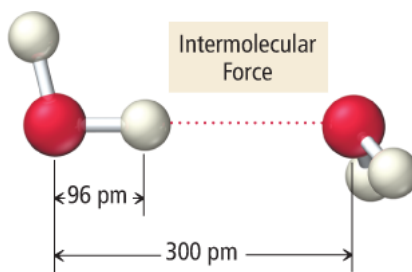
The structure of the particles that compose a substance determines the strength of the intermolecular forces that hold the substance together, which in turn determine whether the substance is a solid, liquid, or gas at a given temperature. At room temperature, moderate to strong intermolecular forces tend to result in liquids and solids (high melting and boiling points), and weak intermolecular forces tend to result in gases (low melting and boiling points).

Intermolecular forces originate from the interactions between charges, partial charges, and temporary charges on molecules (or atoms and ions), much as bonding forces originate from interactions between charged particles in atoms. Recall from [Section 4.3](#) that according to Coulomb's law, the potential energy ( $E$ ) of two oppositely charged particles (with charges  $q_1$  and  $q_2$ ) decreases (becomes more negative) with increasing magnitude of charge and with decreasing separation ( $r$ ).

$$E = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r} \quad (\text{When } q_1 \text{ and } q_2 \text{ are opposite in sign, } E \text{ is negative.})$$

Therefore, as we have seen, protons and electrons are attracted to each other because their potential energy decreases as they get closer together. Similarly, molecules with partial or temporary charges are attracted to each other because *their* potential energy decreases as they get closer together. However, intermolecular forces, even the strongest ones, are generally *much weaker* than bonding forces.

The reason intermolecular forces are relatively weak compared to bonding forces is also related to Coulomb's law. Bonding forces are the result of large charges (the charges on protons and electrons) interacting at very close distances. Intermolecular forces are the result of smaller charges (as we shall see in the following discussion) interacting at greater distances. For example, consider the interaction between two water molecules in liquid water:



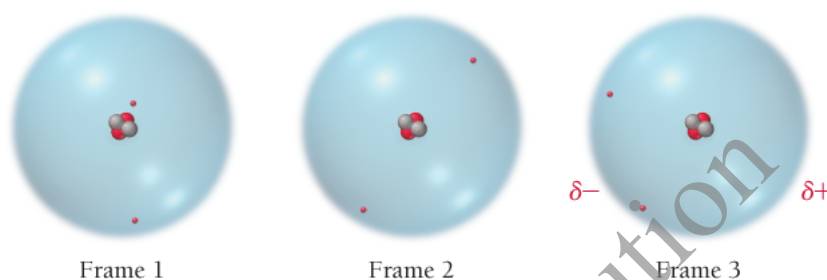
The length of an O-H bond in liquid water is 96 pm; however, the average distance between water molecules in liquid water is about 300 pm. The larger distances between molecules, as well as the smaller charges involved (the partial charges on the hydrogen and oxygen atoms), result in weaker forces. To break the O-H bonds in water, we have to heat the water to thousands of degrees Celsius. However, to

break the O—H bonds in water, we have to heat the water to thousands of degrees Celsius. However, to completely overcome the intermolecular forces *between* water molecules, we have to heat water only to its boiling point, 100 °C (at sea level).

In this section, we examine several different types of intermolecular forces, including dispersion forces, dipole–dipole forces, hydrogen bonding, and ion–dipole forces. The first three of these can potentially occur in all substances; the last one occurs only in mixtures.

## Dispersion Force

The intermolecular force present in all molecules and atoms is the **dispersion force**<sup>Ⓢ</sup> (also called the London force). Dispersion forces are the result of fluctuations in the electron distribution within molecules or atoms. Because all atoms and molecules have electrons, they all exhibit dispersion forces. The electrons in an atom or molecule may, *at any one instant*, be unevenly distributed. Imagine a frame-by-frame movie of a helium atom in which each “frame” captures the position of the helium atom’s two electrons.



The nature of dispersion forces was first recognized by Fritz W. London (1900–1954), a German American physicist.

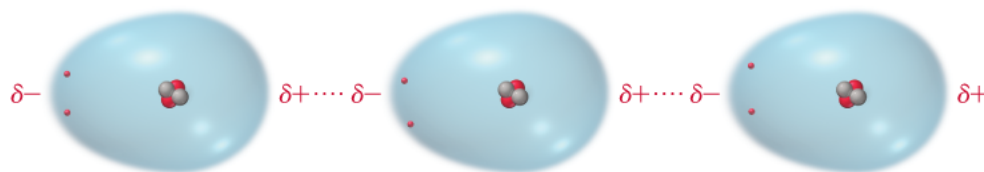
In any one frame, the electrons may not be symmetrically arranged around the nucleus. In frame 3, for example, helium’s two electrons are on the left side of the helium atom. At that instant, the left side of the atom will have a slightly negative charge ( $\delta^-$ ). The right side of the atom, which temporarily has no electrons, will have a slightly positive charge ( $\delta^+$ ) because of the charge of the nucleus. This fleeting charge separation is called an *instantaneous dipole* or a *temporary dipole*. As shown in Figure 11.4<sup>Ⓢ</sup>, an instantaneous dipole on one helium atom induces an instantaneous dipole on its neighboring atoms because the positive end of the instantaneous dipole attracts electrons in the neighboring atoms. The neighboring atoms then attract one another—the positive end of one instantaneous dipole attracting the negative end of another. This attraction is the dispersion force.

**Figure 11.4 Dispersion Interactions**

The temporary dipole in one helium atom induces a temporary dipole in its neighbor. The resulting attraction between the positive and negative charges creates the dispersion force.

### Dispersion Force

An instantaneous dipole on any one helium atom induces instantaneous dipoles on neighboring atoms, which then attract one another.



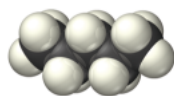
The *magnitude* of the dispersion force depends on how easily the electrons in the atom or molecule move or *polarize* in response to an instantaneous dipole, which in turn depends on the size (or volume) of the electron cloud. A larger electron cloud results in a greater dispersion force because the electrons are held less tightly by the nucleus and therefore polarize more easily. If all other variables are constant, the dispersion force increases with increasing molar mass because molecules or atoms of higher molar mass generally have more electrons dispersed over a greater volume. We can see evidence for the increase in dispersion force with increasing molar mass by examining the boiling points of the noble gases in [Table 11.3](#). Boiling points generally increase with increasing strength of intermolecular forces because more thermal energy is required to separate the particles from the liquid state into the gas state when those particles are more strongly attracted to one another. Notice in [Table 11.3](#) that as the molar masses and electron cloud volumes of the noble gases increase, greater dispersion forces result in higher boiling points.

To polarize means to form a dipole moment (see [Section 5.2](#)).

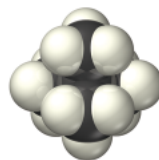
**Table 11.3 Boiling Points of the Noble Gases**

Noble Gas	Molar Mass (g/mol)	Boiling Point (K)
He	4.00	4.2
Ne	20.18	27
Ar	39.95	87
Kr	83.80	120
Xe	131.30	165

Molar mass alone, however, does not determine the magnitude of the dispersion force. Compare the molar masses and boiling points of *n*-pentane and neopentane:



***n*-Pentane**  
molar mass = 72.15 g/mol  
boiling point = 36.1 °C

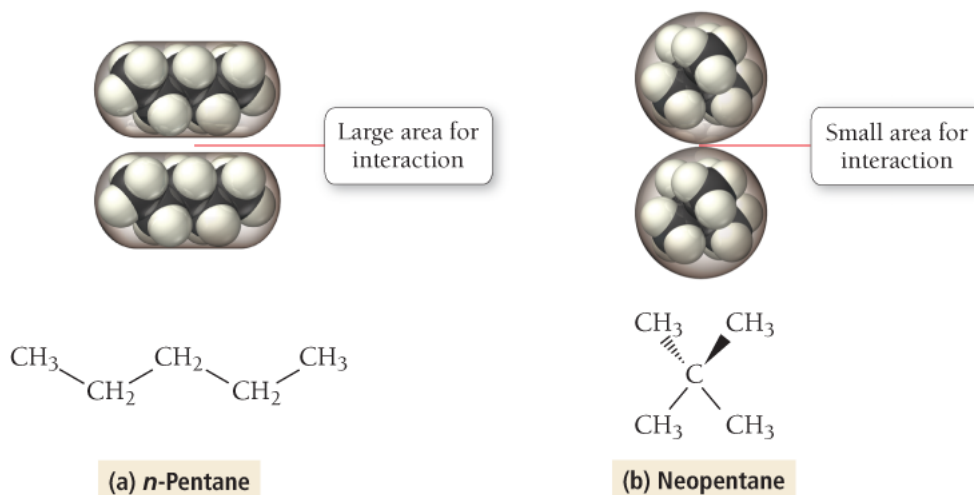


**Neopentane**  
molar mass = 72.15 g/mol  
boiling point = 9.5 °C

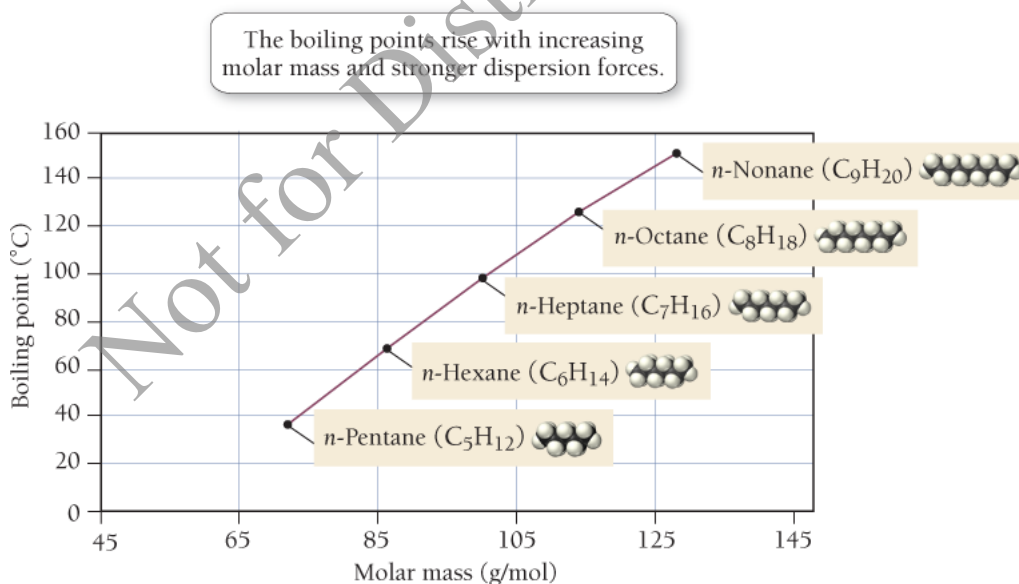
These molecules have identical molar masses (they are isomers), but *n*-pentane has a higher boiling point than neopentane. Why? Because the two molecules have different structures. The *n*-pentane molecules are long and can interact with one another along their entire length, as shown in [Figure 11.5\(a\)](#). In contrast, the bulky, round shape of neopentane molecules results in a smaller area of interaction between neighboring molecules, as shown in [Figure 11.5\(b\)](#). The result is a lower boiling point for neopentane.

**Figure 11.5 Dispersion Force and Molecular Shape**

(a) The straight shape of *n*-pentane molecules allows them to interact with one another along the entire length of the molecules. (b) The nearly spherical shape of neopentane molecules allows for only a small area of interaction. Thus, dispersion forces are weaker in neopentane than in *n*-pentane, resulting in a lower boiling point.



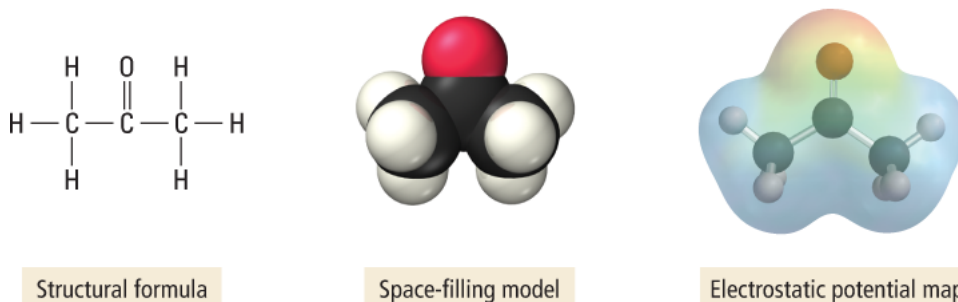
Although molecular shape and other factors must always be considered in determining the magnitude of dispersion forces, molar mass can act as a guide when we are comparing dispersion forces within a family of similar elements or compounds, as shown in Figure 11.6.

**Figure 11.6 Boiling Points of the *n*-Alkanes****Conceptual Connection 11.2 Dispersion Forces**

## Dipole–Dipole Force

The **dipole–dipole force** exists in all molecules that are polar. Polar molecules have electron-rich regions (which have a partial negative charge) and electron-deficient regions (which have a partial

positive charge). For example, consider acetone:

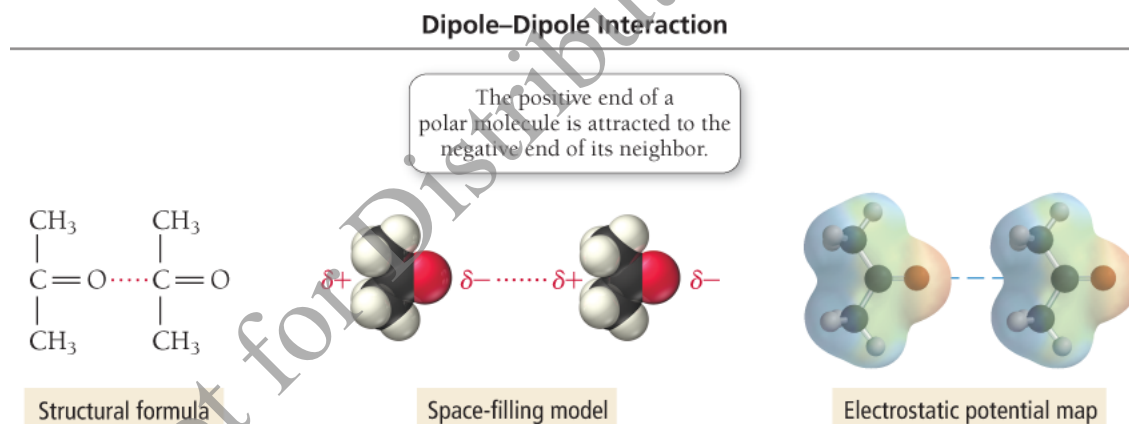


See [Section 5.10](#) to review how to determine if a molecule is polar.

The image on the right is an electrostatic potential map of acetone; these kinds of maps were first introduced in [Chapter 5](#) (see [Section 5.10](#)). Recall that the red areas indicate electron-rich regions in the molecule and that the blue areas indicate electron-poor regions. Acetone has an electron-rich region surrounding the oxygen atom (because oxygen is more electronegative than the rest of the molecule) and electron-poorer regions surrounding the carbon and hydrogen atoms. The result is that acetone has a **permanent dipole** that can interact with other acetone molecules, as shown in [Figure 11.7](#).



**Figure 11.7 Dipole–Dipole Interaction**

Molecules with permanent dipoles, such as acetone, are attracted to one another via dipole–dipole interactions.



The positive end of one permanent dipole attracts the negative end of another; this attraction is the dipole–dipole force. Polar molecules, therefore, have higher melting and boiling points than nonpolar molecules of similar molar mass. Remember that all molecules (including polar ones) have dispersion forces. *In addition*, polar molecules have dipole–dipole forces. This additional attractive force raises their melting and boiling points relative to nonpolar molecules of similar molar mass.

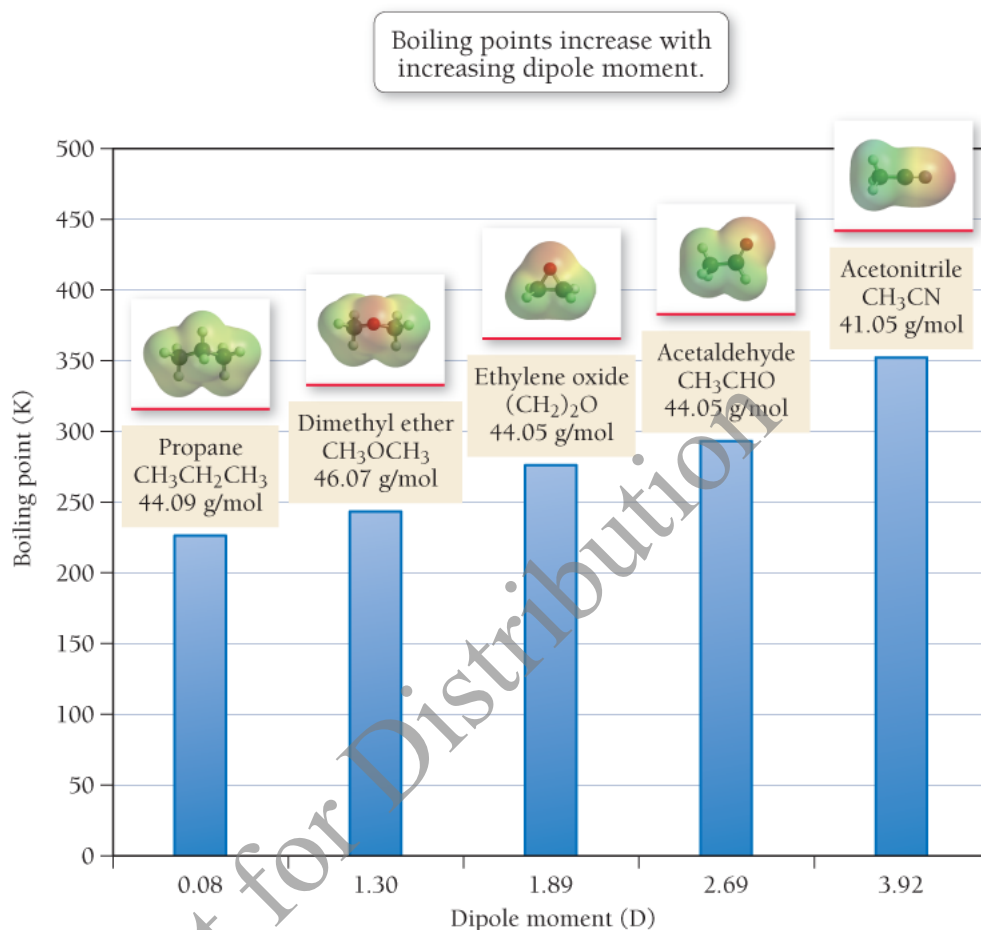
For example, consider formaldehyde and ethane.

Name	Formula	Molar Mass (amu)	Structure	bp (°C)	mp (°C)
Formaldehyde	CH <sub>2</sub> O	30.03	<div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: center;"> <math>\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{H} \end{array}</math> </div> <div style="margin: 0 10px;">  </div> </div>	−19.5	−92
			<div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: center;"> <math>\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \end{array}</math> </div> <div style="margin: 0 10px;">  </div> </div>		

Ethane	$C_2H_6$	30.07	$\begin{array}{c} H-C-C-H \\   \quad   \\ H \quad H \end{array}$		-88	-172
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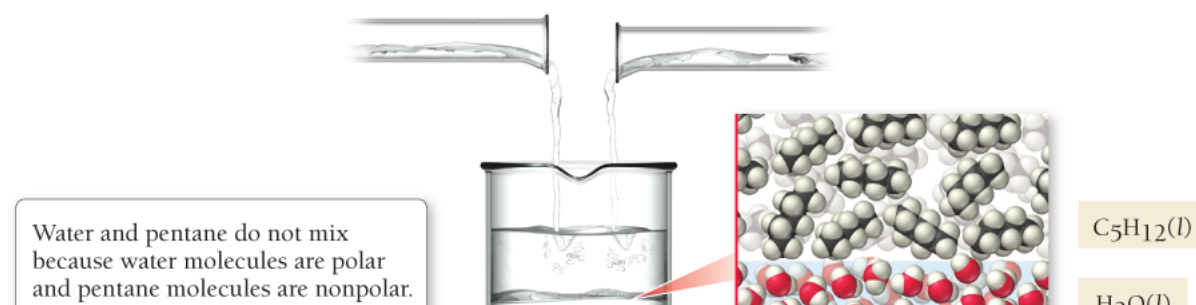
Formaldehyde is polar and has a higher melting point and boiling point than nonpolar ethane, even though the two compounds have the same molar mass. [Figure 11.8](#) shows the boiling points of a series of molecules with similar molar mass but progressively greater dipole moments. Notice that the boiling points increase with increasing dipole moment.

**Figure 11.8 Dipole Moment and Boiling Point**



The polarity of molecules is also important in determining the **miscibility**—the ability to mix without separating into two states—of liquids. In general, polar liquids are miscible with other polar liquids but are not miscible with nonpolar liquids. For example, water, a polar liquid, is not miscible with pentane ( $C_5H_{12}$ ), a nonpolar liquid ([Figure 11.9](#)). Similarly, water and oil (also nonpolar) do not mix. Consequently, oily hands or oily stains on clothes cannot be cleaned with plain water.

**Figure 11.9 Polar and Nonpolar Compounds**



### Example 11.1 Dipole–Dipole Forces

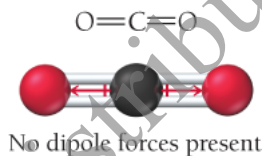
Which of these molecules have dipole–dipole forces?

- a.  $\text{CO}_2$
- b.  $\text{CH}_2\text{Cl}_2$
- c.  $\text{CH}_4$

**SOLUTION** A molecule has dipole–dipole forces if it is polar. To determine if a molecule is polar, (1) *determine if the molecule contains polar bonds* and (2) *determine if the polar bonds add together to form a net dipole moment*.

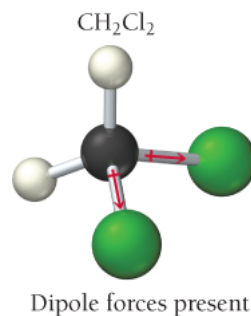
a.  $\text{CO}_2$

1. Because the electronegativity of carbon is 2.5 and that of oxygen is 3.5 (Figure 5.3),  $\text{CO}_2$  has polar bonds.
2. The geometry of  $\text{CO}_2$  is linear. Consequently, the dipoles of the polar bonds cancel, so the molecule is *nonpolar* and does not have dipole–dipole forces.



b.  $\text{CH}_2\text{Cl}_2$

1. The electronegativity of C is 2.5, that of H is 2.1, and that of Cl is 3.0. Consequently,  $\text{CH}_2\text{Cl}_2$  has two polar bonds (C–Cl) and two bonds that are nearly nonpolar (C–H).
2. The geometry of  $\text{CH}_2\text{Cl}_2$  is tetrahedral. Because the C–Cl bonds and the C–H bonds are different, their dipoles do not cancel but sum to a net dipole moment. The molecule is polar and has dipole–dipole forces.

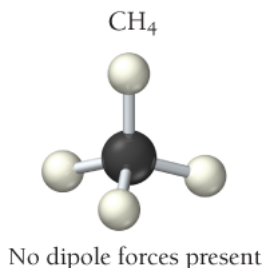


c.  $\text{CH}_4$

1. Because the electronegativity of C is 2.5 and that of hydrogen is 2.1, the C–H

bonds are nearly nonpolar.

2. In addition, because the geometry of the molecule is tetrahedral, any slight polarities that the bonds might have will cancel.  $\text{CH}_4$  is therefore nonpolar and does not have dipole–dipole forces.



**FOR PRACTICE 11.1** Which molecules have dipole–dipole forces?

- a.  $\text{Cl}_4$
- b.  $\text{CH}_3\text{Cl}$
- c.  $\text{HCl}$

#### Interactive Worked Example 11.1 Dipole–Dipole Forces

#### Conceptual Connection 11.3 Dipole–Dipole Interaction

## Hydrogen Bonding

Polar molecules that contain hydrogen atoms bonded directly to small electronegative atoms—most importantly fluorine, oxygen, or nitrogen—exhibit an intermolecular force called **hydrogen bonding**.  $\text{HF}$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$ , for example, all undergo hydrogen bonding. The hydrogen bond is a sort of *super* dipole–dipole force. The large electronegativity difference between hydrogen and these electronegative elements causes the hydrogen atom to have a fairly large partial positive charge ( $\delta^+$ ) within the bond, while the F, O, or N atom has a fairly large partial negative charge ( $\delta^-$ ). In addition, since these atoms are all quite small, the H atom on one molecule can approach the F, O, or N atom on an adjacent molecule very closely. The result is a strong attraction between the H atom on one molecule and the F, O, or N on its neighbor—an attraction called a **hydrogen bond**.

For example, in  $\text{HF}$ , the hydrogen atom in one molecule is strongly attracted to the fluorine atom on a neighboring molecule (Figure 11.10). The electrostatic potential maps in Figure 11.10 show the large differences in electron density that result in unusually large partial charges.

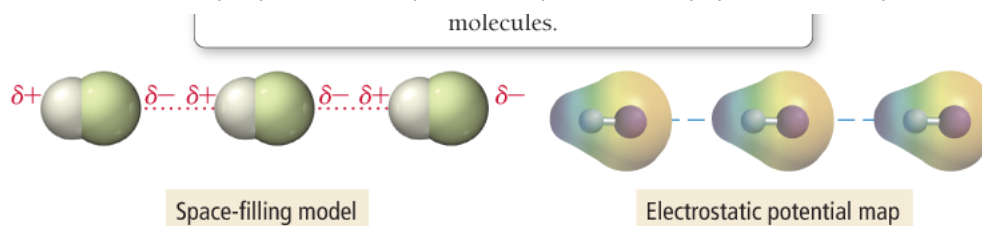
**Figure 11.10 Hydrogen Bonding in HF**

The hydrogen of one  $\text{HF}$  molecule, with its partial positive charge, is attracted to the fluorine of its neighbor, with its partial negative charge. This dipole–dipole interaction is an example of a hydrogen bond.

### Hydrogen Bonding

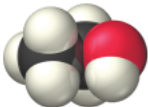
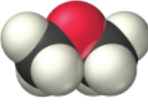
When H bonds directly to F, O, or N, the bonding atoms acquire relatively large partial charges, giving rise to strong dipole–dipole attractions between neighboring





Hydrogen bonds should not be confused with chemical bonds. Chemical bonds occur *within a molecule*, whereas hydrogen bonds—like dispersion forces and dipole–dipole forces—are intermolecular forces that occur *between molecules*. A typical hydrogen bond is only 2–5% as strong as a typical covalent chemical bond. Hydrogen bonds are, however, the strongest of the three *intermolecular* forces we have discussed so far. Substances composed of molecules that form hydrogen bonds often have higher melting and boiling points than substances composed of molecules that do not form hydrogen bonds.

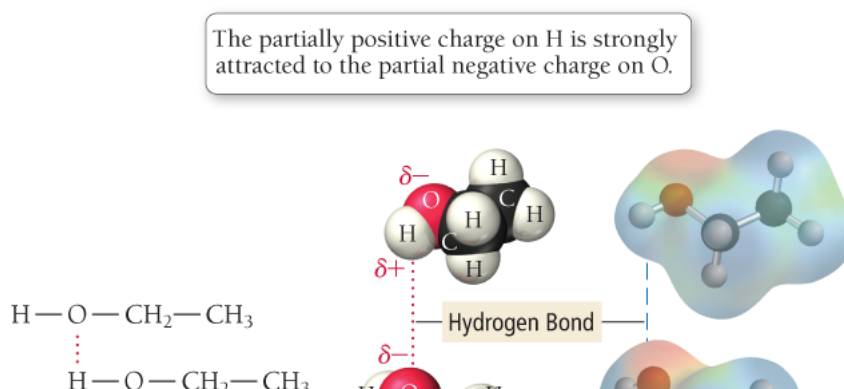
For example, consider the differences in boiling points and melting points between ethanol and diethyl ether (the two molecules on the cover of this book):

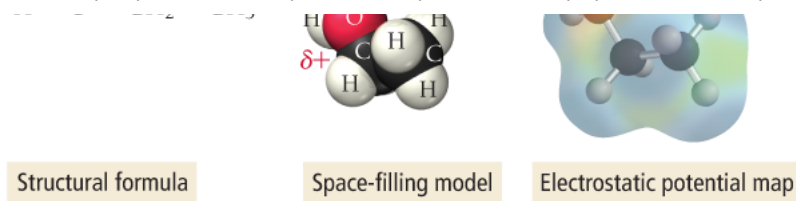
Name	Formula	Molar Mass (amu)	Structure	bp (°C)	mp (°C)
Ethanol	<chem>C2H6O</chem> 	46.07	<chem>CH3CH2OH</chem>	78.3	–114.1
Dimethyl Ether	<chem>C2H6O</chem> 	46.07	<chem>CH3OCH3</chem>	–22.0	–141

The two compounds have identical molar masses (in fact, the two compounds are isomers), yet their boiling and melting points are different. Ethanol is a liquid at room temperature while dimethyl ether is a gas. Why? Because the structure of ethanol allows it to undergo hydrogen bonding. Ethanol contains hydrogen bonded directly to oxygen, so ethanol molecules form hydrogen bonds with each other as shown in [Figure 11.11](#). The hydrogen that is directly bonded to oxygen in an individual ethanol molecule is also strongly attracted to the oxygen on neighboring molecules. This strong attraction makes the boiling point of ethanol 78.3 °C. In contrast, dimethyl ether does not exhibit hydrogen bonding because, in the dimethyl ether molecule, the oxygen atom is not bonded directly to hydrogen. This results in lower boiling and melting points.

**Figure 11.11 Hydrogen Bonding in Ethanol**

The left side shows the structural formula, the center shows the space-filling models, and the right side shows the electrostatic potential maps.





Water is another molecule with hydrogen bonding (Figure 11.12). Figure 11.13 shows the boiling points of the simple hydrogen compounds of the Group 4A and Group 6A elements. In general, boiling points increase with increasing molar mass, as expected, based on increasing dispersion forces. However, because of hydrogen bonding, the boiling point of water (100 °C) is much higher than expected based on its molar mass (18.0 g/mol). Without hydrogen bonding, all the water on our planet would be gaseous.

Figure 11.12 Hydrogen Bonding in Water

### Hydrogen Bonding in Water

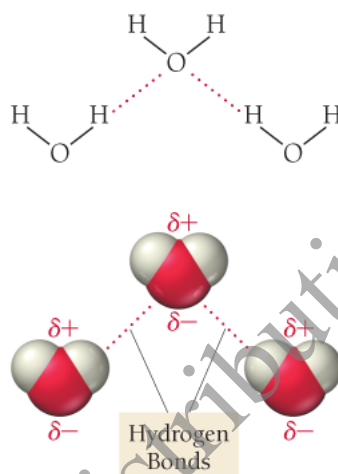
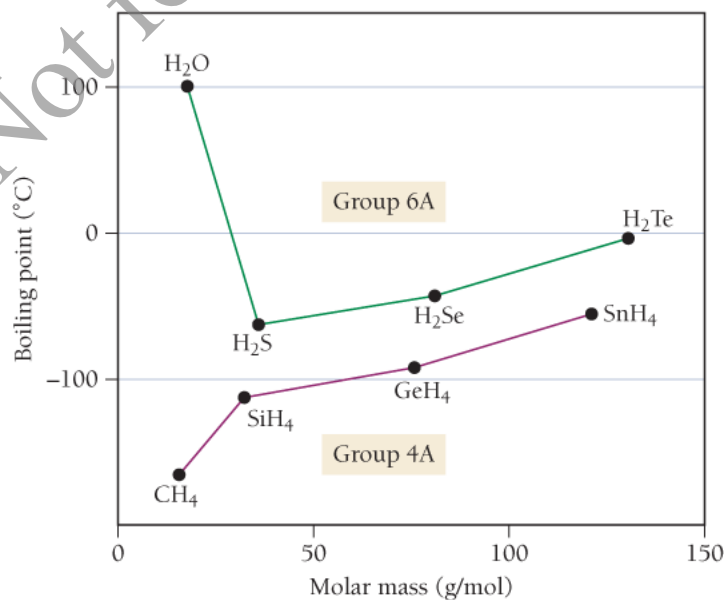


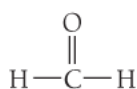
Figure 11.13 Boiling Points of Group 4A and 6A Compounds

Because of hydrogen bonding, the boiling point of water is anomalous compared to the boiling points of other hydrogen-containing compounds.

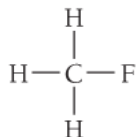


**Example 11.2 Hydrogen Bonding**

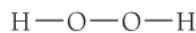
One of these compounds is a liquid at room temperature. Which one and why?



formaldehyde



fluoromethane



hydrogen peroxide

**SOLUTION** The three compounds have similar molar masses.

formaldehyde	30.03 g/mol
fluoromethane	34.03 g/mol
hydrogen peroxide	34.02 g/mol

Therefore, the strengths of their dispersion forces are similar. All three compounds are also polar, so they have dipole–dipole forces. Hydrogen peroxide, however, is the only one of these compounds that also contains H bonded directly to F, O, or N. Therefore, it also has hydrogen bonding and is likely to have the highest boiling point of the three. Because the example states that only one of the compounds is a liquid, you can safely assume that hydrogen peroxide is the liquid. Note that, although fluoromethane *contains* both H and F, H is not *directly bonded* to F, so fluoromethane does not have hydrogen bonding as an intermolecular force. Similarly, formaldehyde *contains* both H and O, but H is not *directly bonded* to O, so formaldehyde does not have hydrogen bonding either.

**FOR PRACTICE 11.2** Which compound has the higher boiling point, HF or HCl? Why?

**Interactive Worked Example 11.2 Hydrogen Bonding**

## Ion–Dipole Force

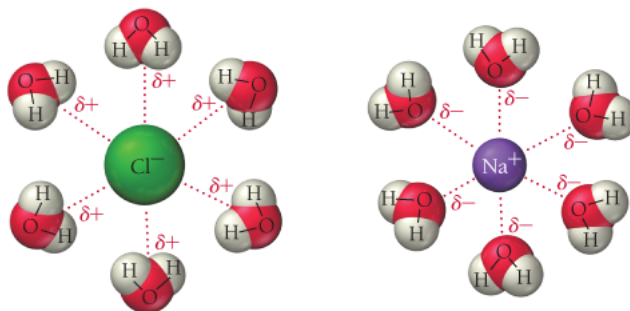
The **ion–dipole force** occurs when an ionic compound is mixed with a polar compound; it is especially important in aqueous solutions of ionic compounds. For example, when sodium chloride is mixed with water, the sodium and chloride ions interact with water molecules via ion–dipole forces, as shown in [Figure 11.14](#). The positive sodium ions interact with the negative poles of water molecules, while the negative chloride ions interact with the positive poles. Ion–dipole forces are the strongest types of intermolecular forces discussed in this section and are responsible for the ability of ionic substances to form solutions with water. We will discuss aqueous solutions more thoroughly in [Chapter 13](#).

**Figure 11.14 Ion–Dipole Forces**

Ion–dipole forces exist between  $\text{Na}^+$  and the negative ends of  $\text{H}_2\text{O}$  molecules and between  $\text{Cl}^-$  and the positive ends of  $\text{H}_2\text{O}$  molecules.

## Ion-Dipole Forces

The positively charged end of a polar molecule such as  $\text{H}_2\text{O}$  is attracted to negative ions, and the negatively charged end of the molecule is attracted to positive ions.



Summarizing Intermolecular Forces (as shown in **Table 11.4**):

- Dispersion forces are present in all molecules and atoms and increase with increasing molar mass. These forces are always weak in small molecules but can be significant in molecules with high molar masses.
- Dipole-dipole forces are present in polar molecules.
- Hydrogen bonds, the strongest of the intermolecular forces that can occur in pure substances (second only to ion-dipole forces in general), are present in molecules containing hydrogen bonded directly to fluorine, oxygen, or nitrogen.
- Ion-dipole forces are present in mixtures of ionic compounds and polar compounds. These forces are very strong and are especially important in aqueous solutions of ionic compounds.

**Table 11.4 Types of Intermolecular Forces**

Type	Present In	Molecular Perspective	Strength
Dispersion	All molecules and atoms		0.05–20+ kJ/mol
Dipole-dipole	Polar molecules		3–20+ kJ/mol
Hydrogen bonding	Molecules containing H bonded to F, O, or N		10–40 kJ/mol
Ion-dipole	Mixtures of ionic compounds and polar compounds		30–100+ kJ/mol

**Conceptual Connection 11.4 Intermolecular Forces and Boiling Point**

Interactive

Not for Distribution

*Not for Distribution*

*Not for Distribution*

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