Intermolecular Forces

Some of the largest trees in the world are giant sequoias (**Figure 1**). Individuals of this species can grow as tall as a 30-storey building. Imagine how difficult it would be to carry a bucket of water to the top of a 30-storey building. Yet, these large trees regularly transport water from their roots up through their large trunks to their branches and leaves. The enormous sequoias require large amounts of water to flow up to an extraordinary height. How do they accomplish this task? They take advantage of the bonds between molecules. WEB LINK

Figure 1 This sequoia is officially the largest giant sequoia. It is 82.9 m tall.

You have learned that atoms can form stable units (molecules) by sharing electrons with other atoms. The bonds connecting the atoms in a molecule are called **intramolecular bonds**. The prefix *intra*- means "within." Covalent bonds are intramolecular bonds. In addition, molecules can be attracted to one another by forces of attraction called intermolecular forces. The prefix *inter*- means "between." **Intermolecular forces** are forces between molecules, not within molecules. These forces can cause large numbers of molecules to aggregate or interact.

intramolecular bond the chemical bond within a molecule

intermolecular force a force that causes one molecule to interact with another molecule; occurs between molecules

In 1873, Johannes van der Waals suggested that observed deviations from the ideal gas law arose because molecules of a gas that has a small but definite volume exert forces on each other. We now know that the forces described by van der Waals are a combination of many types of intermolecular forces, including dipole–dipole forces and London dispersion forces. (You will learn about London dispersion forces later in this section.) These types of intermolecular forces are simply referred to as **van der Waals forces**. Later, the concept of hydrogen bonding was created to explain anomalous (unexpected) properties of certain liquids and solids. In general, intermolecular forces are considerably weaker than the covalent bonds between the atoms in a molecule.

van der Waals forces many types of intermolecular forces, including dipole–dipole forces, London dispersion forces, and hydrogen bonding

To understand the effects of intermolecular forces, think about what happens when a volume of water changes from solid to liquid to gas. The water molecules do not change. The intramolecular bonds between the hydrogen atoms and the oxygen atom do not break or rearrange. Regardless of whether a volume of water is in the solid, liquid, or gas state, each of its molecules always has 1 oxygen atom covalently bonded to 2 hydrogen atoms. Changes in state are due to changes in the forces of attraction *between* the molecules, not changes in the forces that hold atoms together within the molecules.

In ice, water molecules do not have much ability to move, although they can vibrate. If you supply energy to ice through heating, the motions of the molecules increase. The water molecules eventually absorb enough energy to break away from the adjacent molecules and the ice melts. As you supply more thermal energy to the liquid water, the molecules eventually pass into the gaseous state. The added energy allows some water molecules to overcome their attraction to other water molecules, so these water molecules escape into the gas phase. The water has boiled.

This section focuses primarily on the structural and bonding characteristics of substances in the liquid phase. Section 4.8 will focus on the characteristics of substances in the solid phase.

Dipole–Dipole Forces and Hydrogen Bonding

As you learned in Section 4.3, in an electric field molecules with polar bonds often behave as if they have a centre of positive charge and a centre of negative charge, or dipole. Polar molecules attract each other electrostatically by lining up so that the positive and negative ends are close to each other, causing intermolecular forces called **dipole–dipole forces**. In a liquid, where many molecules are close to each other, dipoles attract each other when opposite charges are aligned and repel one another when similar charges face each other. At any point in time, the dipoles find the best compromise between the attractive and repulsive forces.

dipole–dipole force the intermolecular force that is caused when the dipoles of polar molecules position their positive and negative ends near each other

Figure 2(a) illustrates the alignment of polar molecules due to dipole–dipole forces, and **Figure 2(b)** illustrates the attractive and repulsive action of dipole–dipole forces in a liquid. Dipole–dipole forces are only about 1 % as strong as covalent or ionic bonds. They weaken rapidly as the distance between the dipoles increases. In substances at low pressures in the gas phase, where molecules are far apart from each other, these forces are relatively unimportant.

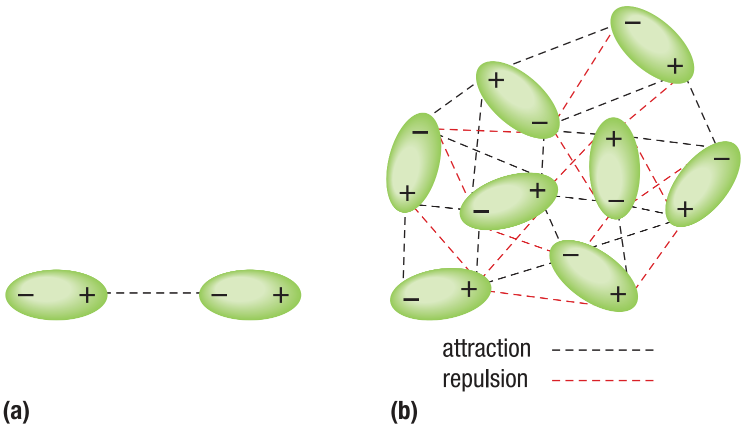


Figure 2 (a) The electrostatic interaction of two polar molecules (b) The interaction of many dipoles in a liquid

There are unusually strong dipole–dipole forces among molecules in which a hydrogen atom is bonded to form a covalent bond with a highly electronegative atom—nitrogen, oxygen, or fluorine. Two factors account for the strengths of these dipole–dipole forces: the great polarity of the covalent bond and the unusual closeness with which the dipoles on these molecules can approach each other. Since dipole–dipole attractions of this type are so strong, they have a special name: **hydrogen bonds**. **Figure 3** shows hydrogen bonding among water molecules. The hydrogen bonding occurs between the partially positive hydrogen atoms and the partially negative oxygen atoms.

hydrogen bond the strong dipole–dipole force that occurs when a hydrogen atom bonded to a highly electronegative atom (oxygen, nitrogen, or fluorine) is attracted to a partially negative atom on a nearby molecule

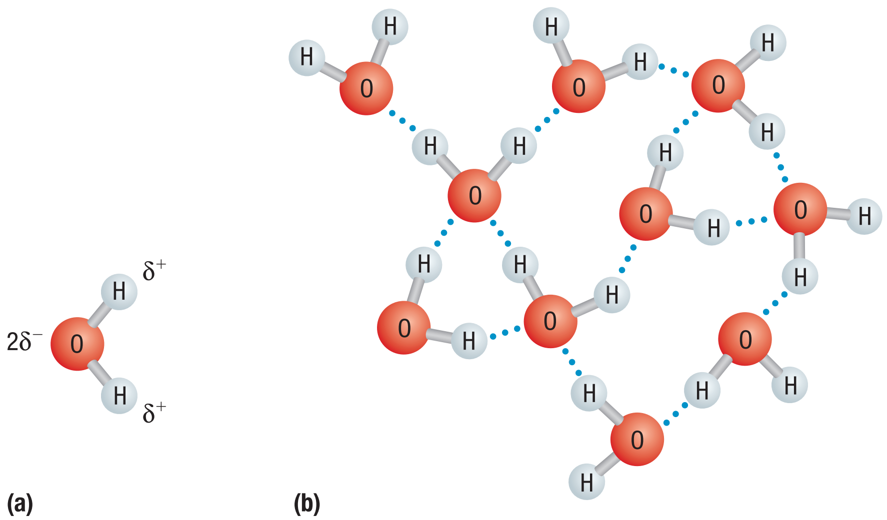


Figure 3 (a) The partial positive and negative dipoles in a water molecule (b) Hydrogen bonding (shown as blue dotted lines) among water molecules. The hydrogen atoms in the water molecules have lost most of their electrons to the more electronegative oxygen atom, so they can be approached more closely by the electron-rich oxygen atoms of adjacent water molecules. Even small changes in distances at the atomic level can result in dramatically larger electrostatic forces.

Investigation 4.7.1

Hydrogen Bonding (page 257)
Now that you have learned how hydrogen bonds form, perform Investigation 4.7.1 to determine the effect of hydrogen bonds on chemical reactions.

Hydrogen bonding has a very important effect on a substance's physical properties. For example, **Figure 4** shows the boiling points of covalent hydrides of elements in Groups 14, 15, 16, and 17 of the periodic table as a function of the period in which the non-hydrogen atom is found. The tetrahedral hydrides of Group 14 (blue line) show a steady increase in boiling point as the molar mass increases. This result is expected. None of these hydrides have molecular dipoles because each has 4 hydrogen atoms distributed symmetrically about the central atom: they are all non-polar molecules. Every molecule with a central atom from Groups 15, 16, or 17 possesses a molecular dipole, but the lightest members in each group, NH_3, HF, and H_2O, have unexpectedly high boiling points. High boiling points mean that these molecules attract other molecules of the same type with forces that are greater than expected. So, it takes more energy than expected to convert these molecules from a liquid state to a gaseous state. Why do these 3 molecules have such highly attractive forces?

UNIT TASK BOOKMARK

As you work on the Unit Task on page 268, consider how the groups in your new periodic table will change. How will the physical properties of the elements change?

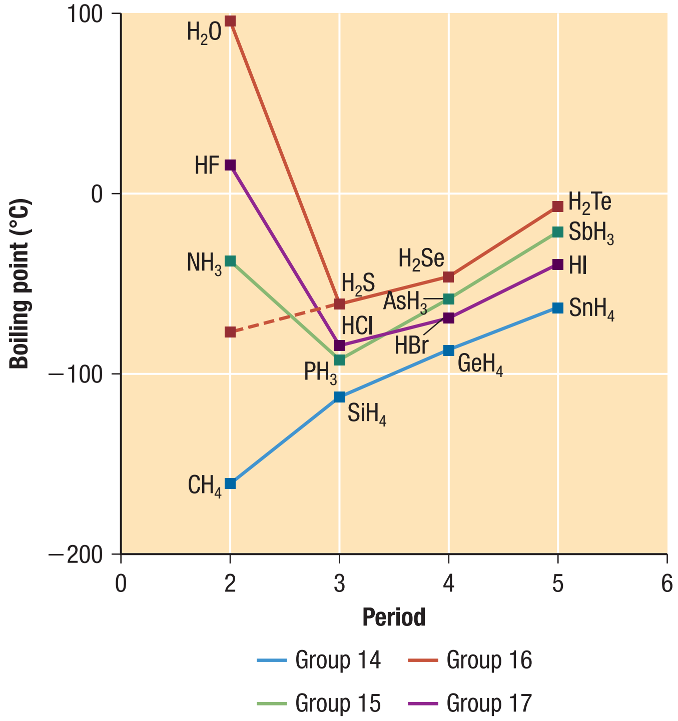


Figure 4 The boiling points of the covalent hydrides of the elements in Groups 14, 15, 16, and 17. The point connected by the dashed line shows the expected boiling point of water if it had no hydrogen bonds.

The especially large dipole–dipole interactions generated by these 3 molecules can be attributed to the large electronegativities of the nitrogen, oxygen, and fluorine atoms they contain. The electronegativities are so large that the hydrogen atom practically loses its electron altogether. Consequently, the negative ends of neighbouring molecules can get very close to the positive hydrogen nucleus (a proton). This results in an unusually large dipole–dipole force of attraction, a hydrogen bond.

Nitrogen, oxygen, and fluorine are the only 3 elements in the periodic table whose atoms have this effect. Atoms of other elements either have a smaller electronegativity or are too large to move inside hydrogen's atomic radius. For example, a chlorine atom has the same electronegativity as a nitrogen atom, but it is too large to get close enough to a hydrogen nucleus on a neighbouring molecule. The unusually strong dipole–dipole forces associated with hydrogen atoms bonded to atoms of nitrogen, oxygen, or fluorine are therefore given the special name of hydrogen bonds. Molecules capable of hydrogen bonding remain in the liquid state even at high temperatures—hence their very high boiling points.

Hydrogen bonds must not be confused with covalent or other intramolecular bonds. As strong and important as hydrogen bonds are, they are still 10 to 20 times weaker than typical covalent bonds. They are, however, central to many important biological systems, such as organic molecules (molecules with a carbon chain backbone). For example, the alcohols methanol, CH_3OH, and ethanol, CH_3CH_2OH, have much higher boiling points than you would expect from their molar masses. The polar O−H bonds in these molecules form hydrogen bonds that result in high boiling points.

Life as we know it would be impossible without hydrogen bonds. Hydrogen bonding is necessary for the proper structure and function of many biological molecules. Proteins are made of chains of different amino acids joined through a covalent amide bond. An amide bond joins the nitrogen atom of an N−H group of one amino acid to the carbon atom of a C=O group of an adjacent amino acid. Both of these functional groups can participate in hydrogen bonding with neighbouring amino acids in other parts of the chain and are partially responsible for the three-dimensional shapes of protein molecules, such as the insulin molecule represented in **Figure 5**. Hydrogen bonds are important to the function of DNA, deoxyribonucleic acid. The three-dimensional structure of DNA is a double helix made of 2 complementary strands held together by hydrogen bonds (**Figure 6**).

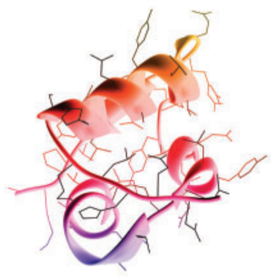


Figure 5 The three-dimensional structure of the insulin protein molecule is in part due to hydrogen bonding between parts of the molecule.

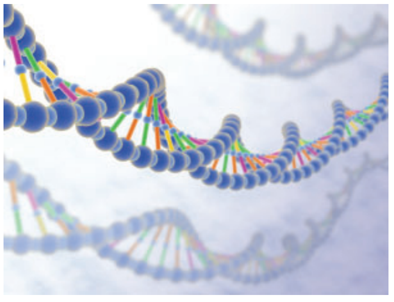


Figure 6 The 2 strands of DNA resemble a twisted ladder. The rungs of the ladder contain hydrogen bonds that form between the bases in each DNA strand.

London dispersion forces the intermolecular forces that exist in non-polar molecules; they increase as the molecular mass increases

London Dispersion Forces

Even molecules without dipoles can exert forces on each other. All substances—even the noble gases—exist in liquid and solid states under certain conditions because of intermolecular forces called **London dispersion forces**. These forces are named after Fritz London, the chemist who first suggested the idea of these forces in non-polar molecules. While studying the boiling points of polar substances, London was not able to identify a specific pattern based on molecular mass and dipole–dipole forces. He hypothesized that there must be an additional force of attraction. He proposed that forces of attraction and/or repulsion exist between any 2 molecules.

To understand the origin of these forces, consider a pair of noble gas atoms. Although you usually assume that the electrons of an atom are uniformly distributed around the nucleus, this is not true at every instant. As the electrons move around the nucleus, a momentary non-symmetrical electron distribution can develop. This effect produces a temporary dipole-like arrangement of charge. The formation of this temporary dipole can affect the electron distribution of a neighbouring atom. An instantaneous dipole that occurs spontaneously in one atom can induce a similar, and opposite, dipole in a neighbouring atom (**Figure 7**).

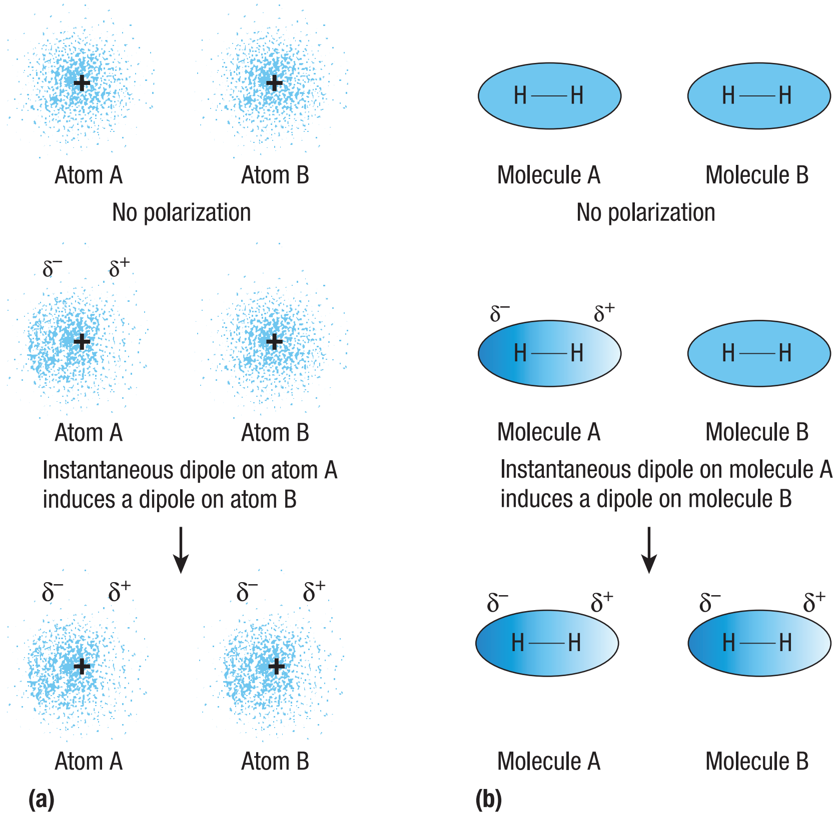


Figure 7 (a) An instantaneous dipole can occur in atom A. This dipole creates an induced dipole on neighbouring atom B. (b) Non-polar molecules such as elemental hydrogen can also develop instantaneous and induced dipoles.

The induced dipole results in an attractive force that is relatively weak and does not last long, but can be very significant for large atoms, for molecules with many atoms, or at low temperatures. For example, when atomic motion slows down sufficiently (in cold temperatures), the attractions due to London dispersion forces can become strong enough to form a solid. These attractions explain why the noble gas elements freeze (**Table 1**).

Note from Table 1 that the freezing point rises as you go down the group. This is because the number of electrons increases as the atomic number increases. Since outer electrons are less tightly held by the nucleus, atoms with more electrons are more easily deformed. This phenomenon is called **polarizability**. The greater an atom's polarizability, the easier it is to deform its charge distribution. Thus, large atoms with many electrons exhibit a higher polarizability than small atoms. The significance of London dispersion forces also increases greatly as the size of the atom increases or as the number of atoms in a molecule increases.

Non-polar molecules such as hydrogen, carbon dioxide, methane, carbon tetrachloride, and alkanes also follow this trend (see Figure 7(b)). Even though none of these molecules has a permanent dipole, they can still attract other molecules through London dispersion forces. All substances experience London dispersion forces. However, these forces are not always apparent because dipole–dipole interactions and hydrogen bonds are much stronger.

Table 1 The Freezing Points of the Group 8A Elements

Element	Freezing point (°C)
helium	−269.7
neon	−248.6
argon	−189.4
krypton	−157.3
xenon	−111.9

polarizability the ability of a substance to form a dipolar charge distribution

Connecting Intermolecular Forces and Physical Properties

Consider some of the physical properties of the hydrogen compounds that form from the Group 14 atoms (C, Si, Ge, and Sn). Based on what you have learned about three-dimensional structure and molecular polarity, you know that these molecules are non-polar tetrahedral molecules. Thus, London dispersion forces are the dominant intermolecular forces present in these molecules. As you go down a group in the periodic table, you would expect the London dispersion forces to increase, so larger molecules should have a greater tendency to stay together. Larger molecules should also have higher melting points and boiling points. The boiling point data in **Table 2** shows that this is exactly what happens.

Numerous physical and chemical properties depend on the nature of intermolecular forces. Hydrogen bonds are the strongest intermolecular forces, and dipole–dipole forces are stronger than London dispersion forces. Therefore, molecules with hydrogen bonds have a greater tendency to stick together than molecules with weaker dipole–dipole forces. Similarly, molecules with dipole–dipole forces have a greater attraction to each other than molecules attracted by London dispersion forces only. So, molecules with dipole–dipole forces and/or hydrogen bonds have higher melting points, boiling points, surface tension, and viscosity than similar-sized molecules with only London dispersion forces.

Regardless of the strength of the dipole, a positive dipole always attracts a negative dipole. Thus, 2 different but polar molecules will tend to attract each other. For example, many ionic compounds interact favourably with water and readily dissolve in it. Since water forms hydrogen bonds, other substances that can also form hydrogen bonds are even more soluble in water than molecules with just dipoles. Some important physical properties that strongly depend on intermolecular forces include melting point, boiling point, viscosity, solubility, binding affinity, miscibility, surface tension, adhesion, hydrophobicity, heat of vaporization, heat of fusion, elasticity, tensile strength, and capacitance.

Table 2 Boiling Points of Group 4A Hydrogen Compounds

Compound	Boiling point (°C)
CH_4	−164
SiH_4	−112
GeH_4	−89
SnH_4	−52

Investigation 4.7.2

Boiling Points and Intermolecular Forces (page 258)
Now that you have learned how to predict the properties of a substance based on its intermolecular forces, perform Investigation 4.7.2 to compare your predictions to known properties of substances.

Tutorial 1 Intermolecular Forces and Physical Properties

In this Tutorial, you will predict physical properties of different substances from the types of intermolecular forces among the molecules.

Sample Problem 1: Predicting Boiling Points

Predict which of the following molecules has the highest boiling point: H_2, I_2, F_2, Br_2, or Cl_2.

Solution

Step 1. Determine the intermolecular force(s) for the set of molecules.

Since these molecules are all molecular elements, each molecule is non-polar. The dominant intermolecular force is therefore the London dispersion force.

Step 2. Determine the molecular mass of each molecule.

See **Table 3.**

Table 3 Molecules and Their Molecular Masses

Molecule	Molecular mass (u)
H_2	2.0
F_2	38.0
Cl_2	70.9
Br_2	159.8
I_2	253.8

Step 3. Identify the molecule with the largest molecular mass.

From Table 3, this molecule is I_2. Since larger molecules have greater London dispersion forces, you can predict that the I_2 molecule has the highest boiling point.

Statement: The I_2 molecule is predicted to have the highest boiling point.

Table 4 lists the boiling points for the molecules in this Sample Problem. I_2 has the highest boiling point; therefore, the Statement is correct.

Table 4 Boiling Points of Several Molecules

Molecule	Boiling point (°C)
H_2	−253
F_2	−188
Cl_2	−34
Br_2	59
I_2	184

Practice

1. Predict which of the following molecules has the highest boiling point: CH_3OH, CH_3CH_2OH, or $CH_3CH_2CH_2OH$. Explain your reasoning. T/I C [ans: $CH_3CH_2CH_2OH$]
2. Of the 2 molecules $CH_3CH_2CH_2CH_2NH_2$ and Cl_2, which should have a lower boiling point? Why? T/I C [ans: Cl_2]

Physical Properties of Liquids

Liquids and liquid solutions are vital to our lives. Water is our most important liquid. Besides being essential to life, water provides a medium for food preparation, transportation, cooling machines, recreation, cleaning, and countless other uses.

Liquids demonstrate many characteristics that help us understand their nature. A liquid is not as compressible as a gas, but liquids have higher densities than gases. Many of the properties of liquids give us direct information about the forces that exist between their entities (molecules, atoms, or ions). For example, when you pour a liquid onto a solid surface, it tends to bead as droplets. This effect is due to the intermolecular forces in the liquid. Although entities in the centre of a drop of liquid are completely surrounded by other entities, those at the surface experience attractions only from the side and below (**Figure 8**). This uneven pull on the surface entities draws them into the body of the liquid. The energy of the system is lowest only if the number of entities at the surface is as low as it can be; that is, if the surface area is minimized. The result is a droplet of liquid with a shape that has the minimum surface area—a sphere.

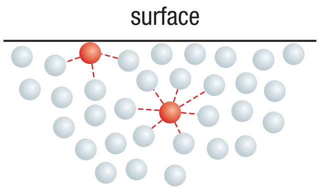


Figure 8 The outer entities of liquid attract entities in the interior. The entities at the surface only interact with entities below and beside them. Remember that the entities in a liquid are in constant motion.

To increase a liquid's surface area, entities must move from the interior of the liquid, where there are many attractions, to the surface, where there are fewer attractions. This movement raises the energy, and the liquid resists. The resistance of a liquid to increase its surface area is the **surface tension** of the liquid. As you would expect, liquids with relatively large intermolecular forces, such as those with polar molecules, have relatively high surface tensions.

surface tension the resistance of a liquid to increase its surface area

Polar liquids also exhibit **capillary action**—the rising of a liquid in a narrow tube. Two types of forces are responsible for capillary action: cohesive forces and adhesive forces. Cohesive forces are intermolecular forces among the entities of the liquid; adhesive forces are the forces between the liquid entities and their container. You have seen examples of cohesion in polar molecules. Adhesive forces come into play when a polar liquid is placed in a container also made from a polar substance. For example, glass contains many oxygen atoms with partial negative charges that attract the positive end of a polar molecule such as water. This force makes the water creep up the walls of a glass tube. Adhesive forces tend to increase the surface area of the water, while cohesive forces try to minimize the surface area. Water has strong cohesive (intermolecular) forces as well as strong adhesive forces toward the glass. The result is that water "pulls itself" up a glass capillary tube (a tube with a small diameter). The height to which the water travels is where the force of gravity on the mass of the water balances the water's attraction to the glass surface. CAREER LINK

capillary action the spontaneous rising of a liquid in a narrow tube

The meniscus that water forms in a narrow tube has a concave shape (**Figure 9(a)**). This shape arises because the adhesive forces among water molecules and glass molecules are stronger than the cohesive forces among the water molecules. On the other hand, a non-polar liquid such as mercury shows a convex meniscus (**Figure 9(b)**). This behaviour is characteristic of a liquid in which the cohesive forces among entities of the liquid are stronger than the adhesive forces among the liquid and glass molecules.

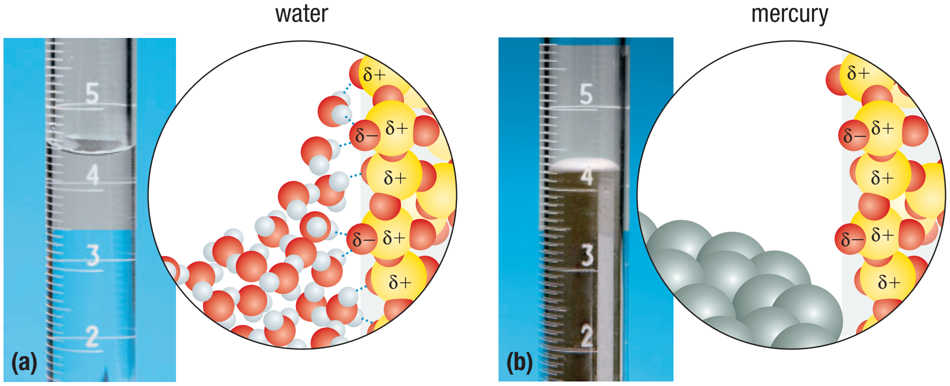
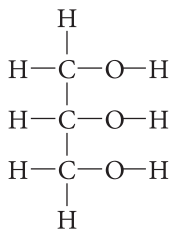


Figure 9 (a) Water molecules have strong adhesive forces toward glass molecules, and form a concave meniscus. (b) Mercury atoms have stronger cohesive than adhesive forces, resulting in a convex meniscus.

viscosity the measure of a liquid's resistance to flow

Another property of liquids that is strongly dependent on intermolecular forces is **viscosity**, the measure of a liquid's resistance to flow. Liquids with large intermolecular forces are highly viscous. For example, glycerol, $C_3H_8O_3$, has the structure



Glycerol has an unexpectedly high viscosity—over 1000 times that of water—due to its ability to form multiple hydrogen bonds with its O–H groups (**Figure 10**).

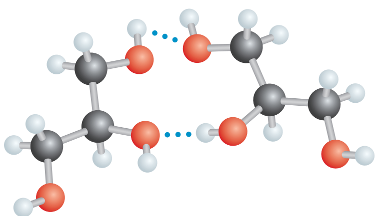


Figure 10 The hydrogen bonding in glycerol gives it a high viscosity.

Longer molecules are usually more viscous than smaller, shorter molecules because long molecules can become tangled with each other. For example, gasoline, with an average length of 8 carbons, is a non-viscous liquid. Yet the hydrocarbon chains in grease, a viscous group of substances, are 20 to 25 carbons long.

How do intermolecular forces explain the transport of water in giant sequoia trees? All plants use very thin tubes called xylem tubes to transport water from the ground to their leaves. In this process, the plant exploits both the surface tension and the capillary action of water. As water evaporates in the leaves, millions of menisci are formed in the tiny vascular bundles of the xylem tubes. As the surface tension of water works to reduce the surface area of these menisci, water molecules interconnected by hydrogen bonds pull each other up the full length of the plant by capillary action, even as high as the upper branches of a giant sequoia.

4.7 Review

Summary

- Intermolecular forces occur between, not within, molecules.
- The attraction between polar molecules is from electrostatic dipole–dipole forces. These forces attract oppositely charged and repel like charged ends of nearby molecules.
- Molecules in which a hydrogen atom is covalently bonded to nitrogen, oxygen, or fluorine form hydrogen bonds, which are unusually strong dipole–dipole interactions.
- Intermolecular forces caused by inducing temporary dipoles in atoms and molecules are called London dispersion forces. All molecules can produce London dispersion forces, but these forces are weak and tend to be important in interactions between non-polar molecules. London dispersion forces typically increase as a molecule's mass and size increase.
- Molecules that have stronger intermolecular forces have higher melting points, boiling points, viscosity, and surface tension than molecules with weaker intermolecular forces.

Questions

1. From the following groups, identify the substance that has the listed property. Explain your answer. K/U
   (a) highest boiling point: HBr, Kr, Cl_2
   (b) highest freezing point: H_2O, NaCl, HBr
   (c) lowest vapour pressure at 25 °C: Cl_2, Br_2, I_2
   (d) lowest freezing point: N_2, CO, CO_2
   (e) lowest boiling point: CH_4, CH_3CH_3, $CH_3CH_2CH_3$
   (f) highest boiling point: HF, HCl, HBr
2. From the following groups, identify the substance that has the listed property. Explain your answer. K/U
   (a) highest boiling point: CCl_4, CF_4, CBr_4
   (b) lowest freezing point: LiF, F_2, HCl
   (c) lowest vapour pressure at 25 °C: CH_3OCH_3, CH_3CH_2OH, $CH_3CH_2CH_3$
   (d) greatest viscosity: HF, H_2O_2
   (e) greatest heat of vaporization: H_2CO, CH_3CH_3, CH_4
3. (a) Why does ammonia have a very high solubility in water?
   (b) Draw a diagram of water interacting with ammonia molecules using Lewis structures. K/U C
4. Predict which substance in each of the following pairs has stronger intermolecular forces, and explain your reasoning: K/U T/I C
   (a) CO_2 or OCS
   (b) SeO_2 or SO_2
   (c) $CH_3CH_2CH_2NH_2$ or $H_2NCH_2CH_2NH_2$
   (d) CH_3CH_3 or H_2CO
   (e) CH_3OH or H_2CO
5. Consider the compounds Cl_2, HCl, F_2, NaF, and HF. Which compound has a boiling point closest to that of argon? Explain your reasoning. K/U T/I
6. The following compounds have boiling points (in no particular order) of −42.1 °C, −23 °C, and 78.5 °C. Match the boiling points to the correct compounds, and give reasons for your answer. K/U T/I
   (a) ethanol, CH_3CH_2OH
   (b) dimethyl ether, CH_3OCH_3
   (c) propane, $CH_3CH_2CH_3$
7. Molecular compounds can have London dispersion forces, dipole–dipole forces, and hydrogen bonding. Identify all the intermolecular forces present in each of the following compounds: K/U T/I
   (a) alcohols (for example, CH_3OH)
   (b) amines (for example, CH_3NH_2)
   (c) hydrocarbons (for example, CH_3CH_3)
   (d) carboxylic acids (for example, CH_3COOH)
   (e) ethers (for example, CH_3OCH_3)
8. For the compounds listed in Question 4, if the molecular masses of the substances were equal, which substance would you expect to have the highest boiling point? Why? K/U T/I