Forces Between Molecules

Figure 1-3 The three states of matter: (a) In a gas the individual molecules move freely through space, colliding and rebounding. A gas adapts to the shape of its container and can easily be expanded or compressed. (b) Molecules in a liquid are in contact, but free to slide past one another. A liquid also adapts to the shape of its container, but it has a relatively fixed volume. (c) In a crystalline solid, molecules are packed into a regular array, giving the solid both a fixed volume and a definite shape. Work must be done to break or deform a crystal. Adapted from R. E. Dickerson and J. Geis. *Chemistry, Matter, and the Universe*, W. A. Benjamin, Menlo Park, Calif. 1976.

Although the strongest attractions of an atom are for other atoms to which it is bonded in a molecule, two molecules themselves exert small but appreciable attractions on one another. Molecules are slightly "sticky." These forces, caused by momentary fluctuations in electron distributions around the atoms, are known as van der Waals attractions (after Dutch physicist Johannes van der Waals). They are responsible for the existence of three states (or phases) of matter at different temperatures: solids, liquids, and gases. Temperature is just a measure of the heat energy or energy of motion that a collection of molecules possesses. At low temperatures, the molecules have little energy of motion. The
van der Waals attractions hold them together in an orderly, close-packed crystalline array or lattice (Figure 1-3c). This is the **solid** state. If more energy is fed into the crystal so the temperature rises, the molecules will vibrate about their average or equilibrium positions in the crystal. Enough energy will cause the ordered structure of the molecular crystal to break up, and the molecules will be free to slide past one another, although they are still touching (Figure 1-3b). This is the **liquid** state, and the transition temperature between solid and liquid is called the **melting point**, \( T_m \). The liquid is still held together by van der Waals attractions, although the molecules have too much energy of motion to be locked into a rigid array. If still more energy is given to the liquid, the molecules will begin to move fast enough to overcome the van der Waals attractions, separate entirely from one another, and travel in independent molecular trajectories through space (Figure 1-3a). This is the **gas** phase, and the transition temperature between liquid and gas is called the **boiling point**, \( T_b \). Changes in phase are treated in more detail in Chapter 18. The melting and boiling points of some simple molecules are compared in Table 1-3. In general, larger molecules have higher melting and boiling points, since they have larger surface areas for van der Waals attractions. Thus at 1 atm, pressure \( H_2 \) boils at -252.5°C, \( CH_4 \) boils at -164.0 °C, but \( C_8H_{18} \) must be heated to +125.7°C before the molecules will separate from one another and go into the gas phase.

**Table 1-3. Melting and Boiling Points of Some Simple Molecular Substances**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Molecular Formula</th>
<th>( T_m ) (°C)</th>
<th>( T_b ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gases</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H(_2)</td>
<td>-259.1</td>
<td>-252.5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O(_2)</td>
<td>-218.4</td>
<td>-183.0</td>
</tr>
<tr>
<td>Methane</td>
<td>CH(_4)</td>
<td>-182.5</td>
<td>-164.0</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>H(_2)S</td>
<td>-85.5</td>
<td>-60.7</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl(_2)</td>
<td>-101.0</td>
<td>-34.6</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH(_3)</td>
<td>-77.7</td>
<td>-33.4</td>
</tr>
<tr>
<td><strong>Liquids</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bromine</td>
<td>Br(_2)</td>
<td>-7.2</td>
<td>+58.8</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH(_3)OH</td>
<td>-93.9</td>
<td>+65.0</td>
</tr>
<tr>
<td>Water</td>
<td>H(_2)O</td>
<td>0</td>
<td>+100</td>
</tr>
</tbody>
</table>
Figure 1-4 The $\text{O-H}$ bonds in water and methanol (methyl alcohol) are polar because the oxygen atom has the stronger attraction for the electron pair and pulls negative charge toward itself, leaving the hydrogen with a fractional positive charge. This polarity is of great importance in interactions between molecules.

A second kind of force between molecules also influences melting and boiling points: the **polarity** of the molecules. If two atoms that are connected by an electron-pair covalent bond do not have the same attraction for electrons, then the electron pair will shift toward the atom with the greater electron-pulling power. This will give that atom a slight excess of negative charge (represented by $\delta -$ rather than by just a minus sign, which would imply a full electron charge), and will confer a slight positive charge ($\delta +$) on the atom that lost out in the tug-of-war for the electron pair. Because the electron-attracting power (**electronegativity**) of oxygen is greater than that of hydrogen, the oxygen atom in a molecule of water or methyl alcohol is slightly negative, and the hydrogen atoms are slightly positive (Figure 1-4). Such a molecule is termed polar because it behaves like a tiny electric dipole; that is, the negative charge on the oxygen attracts other nearby positive charges, and the positive charge on each hydrogen attracts other negative charges. This is another attractive force between molecules, in addition to van der Waals attractions. Because of the forces binding its molecules, methanol melts and boils at much higher temperatures than methane, which is similar to it in molecular size. Methanol is a liquid at room temperature, whereas methane is a gas. In water, the attractions between hydrogen and oxygen from different molecules are so strong that they are given the name of **hydrogen bonds**. Hydrogen bonds are especially important in proteins and other giant molecules in living organisms. If it were not for polarity and hydrogen bonding, water would melt and boil at lower temperatures even than $\text{H}_2\text{S}$ (Table 1-3). It would be a gas at room temperature, rather than the Earth’s most common liquid.

**Contributors**

- R. E. Dickerson, H. B. Gray, and G. P. Haight, Jr. Content was used from "Chemical Principles", an introductory college-level text for General Chemistry with permission of the Caltech library and Harry B. Gray, on behalf of the authors.