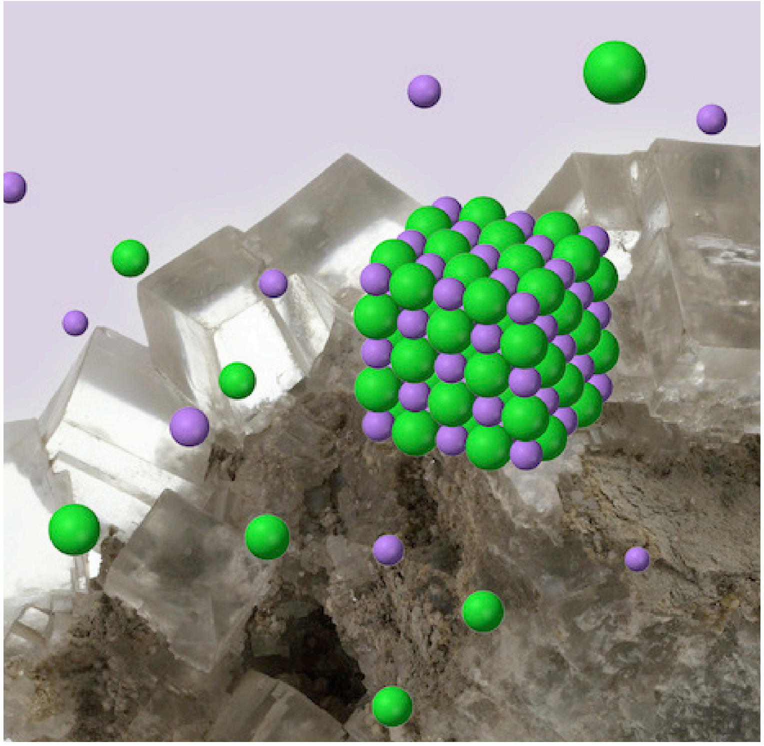


Chapter 6

How Atoms Bond

THE MAIN IDEA

Atoms bond by exchanging or sharing electrons.

6.8 Molecular Polarity

When all the bonds in a molecule are nonpolar, the molecule as a whole is also nonpolar—as is the case with H_2, O_2, and N_2. When a molecule consists of only two atoms and the bond between them is polar, the polarity of the molecule is the same as the polarity of the bond—as with HF and HCl.

Complexities arise when assessing the polarity of a molecule containing more than two atoms. Consider carbon dioxide, CO_2, shown in **Figure 6.31**. The cause of the dipole in either of the carbon–oxygen bonds is oxygen's greater pull on the bonding electrons (because oxygen is more electronegative than carbon). At the same time, however, the oxygen atom on the opposite side of the carbon pulls those electrons back to the carbon. The net result is an even distribution of bonding electrons around the entire molecule. So, dipoles that are of equal strength but pull in opposite directions in a molecule effectively cancel each other, with the result that the molecule as a whole is nonpolar.

Figure 6.32 illustrates a similar situation in boron trifluoride, BF_3, where three fluorine atoms are oriented 120° from one another around a central boron atom. Because the angles are all the same and because each fluorine atom pulls on the electrons of its boron–fluorine bond with the same force, the resulting polarity of this molecule is zero.

As is discussed further in the next chapter, nonpolar molecules have only relatively weak attractions to other nonpolar molecules. This lack of attraction between nonpolar molecules

Figure 6.31 >
There is no net dipole in a carbon dioxide molecule, so the molecule is nonpolar. This is analogous to two people in a tug-of-war. As long as they pull with equal force but in opposite directions, the rope remains stationary.

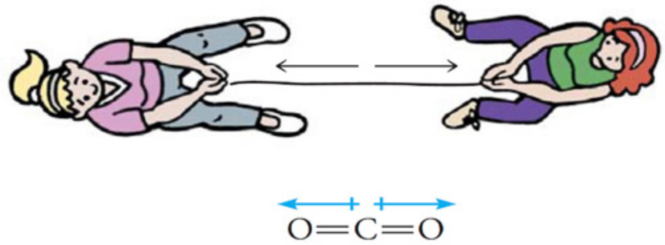
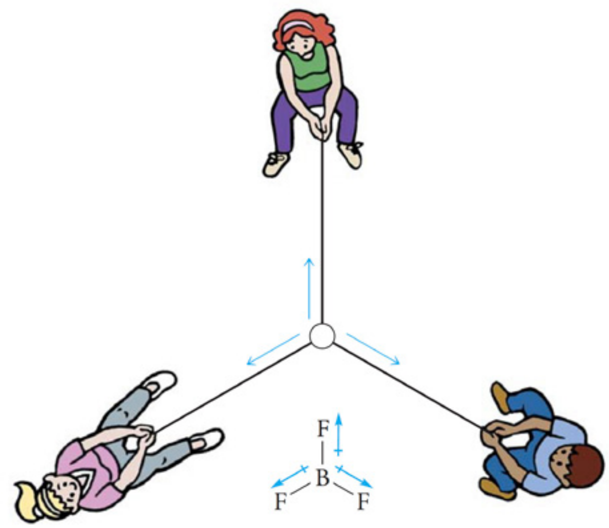


Figure 6.32 >
The three dipoles of a boron trifluoride molecule oppose one another at 120° angles, which makes the overall molecule nonpolar. This is analogous to three people pulling with equal force on ropes attached to a central ring. As long as they all pull with equal force and all maintain the 120° angles, the ring will remain stationary.

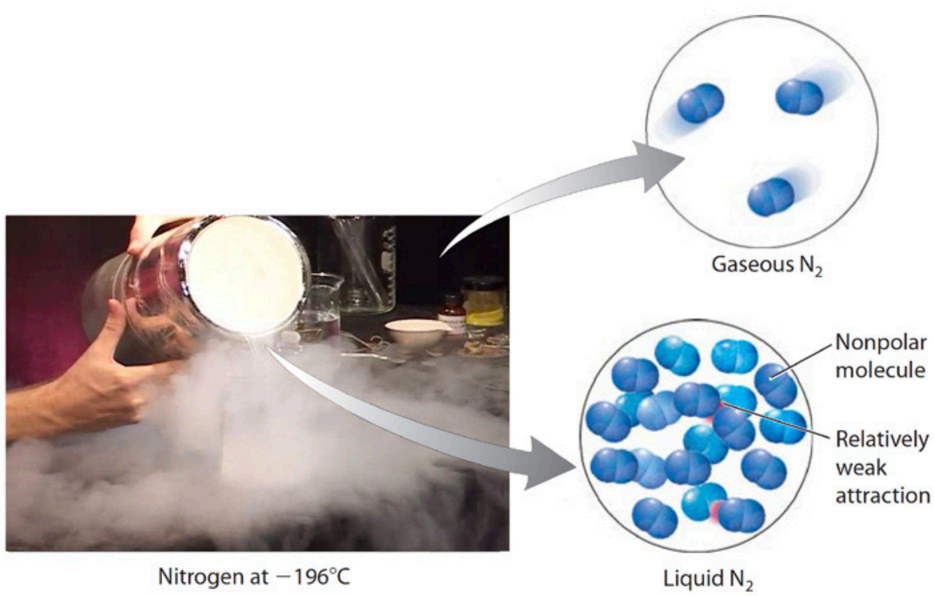


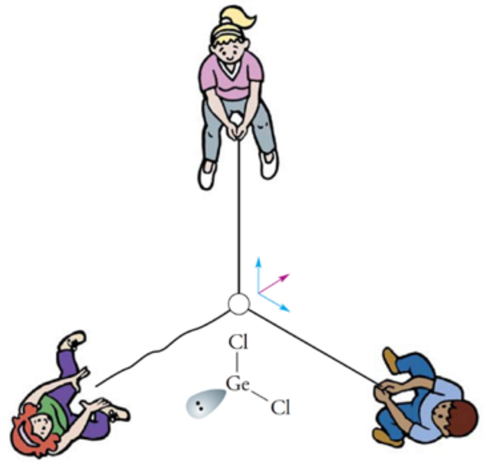
FOR YOUR INFORMATION

Polar interactions between molecules are many times weaker than the attractions between ions within an ionic bond. The polar attractions described here and the ionic bonds described earlier are both electrical attractions. The main difference between them is one of magnitude.

explains the low boiling points of many nonpolar substances. Recall from Section 2.7 that boiling is a process wherein the molecules of a liquid separate from one another as they go into the gaseous phase. When there are only weak attractions between the molecules of a liquid, less heat energy is required to liberate the molecules from one another and allow them to enter the gaseous phase. This translates into a relatively low boiling point for the liquid, as shown for nitrogen, N_2 in **Figure 6.33**. The boiling points of hydrogen, H_2; oxygen, O_2; carbon dioxide, CO_2; and boron trifluoride, BF_3, are also quite low for the same reason.

Figure 6.33 >
Nitrogen is a liquid at temperatures below its chilly boiling point of –196°C. Nitrogen molecules are not very attracted to one another because they are nonpolar. As a result, the small amount of heat energy available at –196°C is enough to separate them and allow them to enter the gaseous phase.



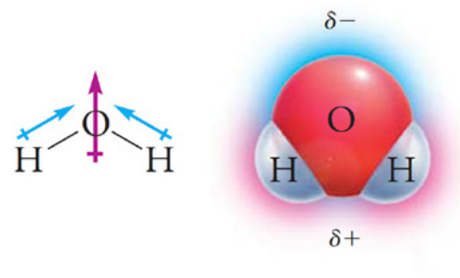


< Figure 6.34

The two strongly electronegative chlorine atoms in $GeCl_2$ pull germanium's lone pair inward. By analogy, if one person eases off in a three-way tug-of-war but the other two continue to pull, the ring moves in the direction of the purple arrow.

There are many instances, however, in which the dipoles of different bonds in a molecule do *not* cancel each other. Reconsider the rope analogy of **Figure 6.32**. As long as everyone pulls equally, the ring stays put. Imagine, however, that one person begins to ease off on the rope. Now the pulls are no longer balanced, and the ring begins to move away from the person who is slacking off, as **Figure 6.34** shows. Likewise, if one person began to pull harder, the ring would move away from the other two people.

A similar situation occurs in molecules in which polar covalent bonds are not equal and opposite. Perhaps the most relevant example is water, H_2O. Each hydrogen–oxygen covalent bond has a relatively large dipole because of the great electronegativity difference. Because of the bent shape of the molecule, however, the two dipoles, shown in blue in **Figure 6.35,** do not cancel each other the way the C–O dipoles in **Figure 6.31** do. Instead, the dipoles in the water molecule work together to give an overall dipole, shown in purple, for the molecule



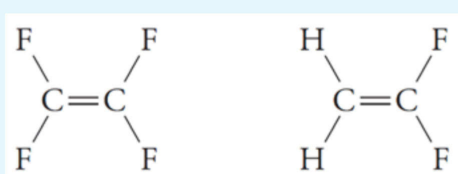
(a) (b)

∧ Figure 6.35

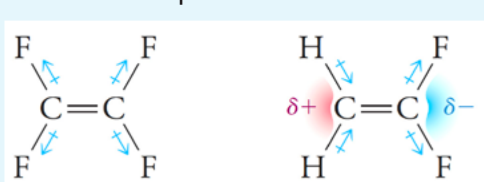
(a) The individual dipoles in a water molecule add together to give a large overall dipole for the whole molecule, shown in purple. (b) The region around the oxygen atom is therefore slightly negative, and the region around the two hydrogen atoms is slightly positive.

CONCEPT **CHECK**

Which of these molecules is polar, and which is nonpolar?



CHECK YOUR ANSWER Symmetry is often the greatest clue for determining polarity. Because the molecule on the left is symmetrical, the dipoles on the two sides cancel each other. This molecule is therefore nonpolar.



Because the molecule on the right is less symmetrical (more "lopsided"), it is a polar molecule.

CHEMICAL CONNECTIONS

How is a glacier connected to a lone pair of electrons?

Figure 6.36 illustrates how polar molecules electrically attract one another and, as a result, are relatively difficult to separate. In other words, polar molecules can be thought of as being "sticky," which is why it takes more energy to separate them—to change the substance's phase. For this reason, substances composed of polar molecules typically have higher boiling points than substances composed of nonpolar molecules, as **Table 6.3** shows. Water, for example, boils at 100°C, whereas carbon dioxide boils at –79°C. This 179°C difference is quite dramatic when you consider that a carbon dioxide molecule is more than twice as massive as a water molecule.

Because molecular "stickiness" can play a lead role in determining a substance's macroscopic properties, molecular polarity is a central concept of chemistry. Figure 6.37 helps bring to mind, in a tragic way, the fact that oil (both petroleum-based oil and cooking oil) and water don't mix. It's not, however, that oil and water repel each other. Rather, water molecules are so attracted to them- selves because of their polarity that they pull themselves together. The nonpolar oil molecules are thus excluded and left to themselves. We see this in a bottle of oil and vinegar salad dressing. After the bottle is shaken vigorously, the water molecules of the vinegar cling together, excluding the oil molecules, which separate into their own layer. Being less dense than water, the oil rises to the top.

The shape of a molecule, as determined by VSEPR, plays a major role in determining the polarity of that molecule. A molecule's polarity, in turn, has a great influence on macroscopic behavior. Consider what the world would be like if the oxygen atom in a water molecule did not have its two nonbonding pairs of electrons. Instead of being bent, each water molecule would be linear, much like carbon dioxide. The dipoles of the two hydrogen–oxygen bonds would cancel each other, which would make water a nonpolar substance and give it a relatively low boiling point. Water would not be a liquid at the ambient temperatures of our planet, and we in turn would not be here discussing these concepts. We should be thankful that the oxygen within water has two nonbonding pairs. That's good chemistry.

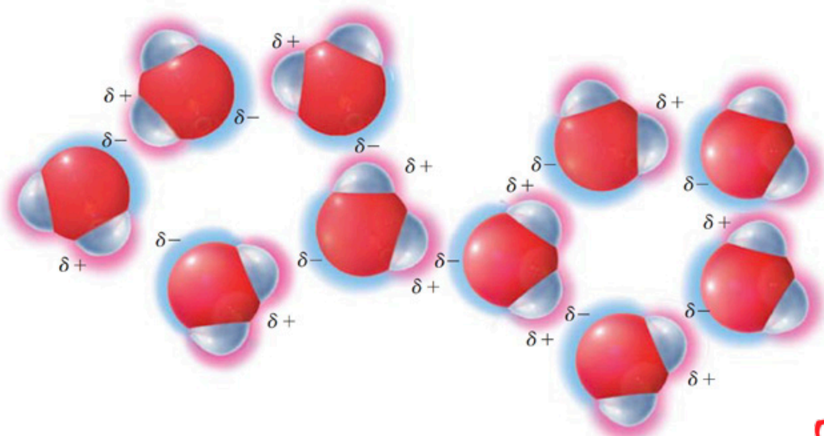


Figure 6.36 >
Water molecules attract one another because each contains a slightly positive side and a slightly negative side. The molecules position themselves in such a way that the positive side of one faces the negative side of a neighbor.

TABLE 6.3 Boiling Points of Some Polar and Nonpolar Substances

SUBSTANCE	BOILING POINT (°C)
Polar	
Hydrogen fluoride, HF	20
Water, H_2O	100
Ammonia, NH_3	–33
Nonpolar	
Hydrogen, H_2	–253
Oxygen, O_2	–183
Nitrogen, N_2	–196
Boron trifluoride, BF_3	–100
Carbon dioxide, CO_2	–79

Λ Figure 6.37
Oil and water are difficult to mix, as is evident from these photo of the Deepwater Horizon oil spill of 2010 in the Gulf of Mexico—the largest accidental oil spill in human history. The oil came from a sea- floor oil gusher that released an estimated 53,000 barrels every day for three months before it was finally capped. Petroleum- based oil molecules are not able to compete with the attraction water molecules have for themselves, which is why the oil and water don't mix.

< Figure 6.38
All species on our planet depend upon water, H_2O, for survival.