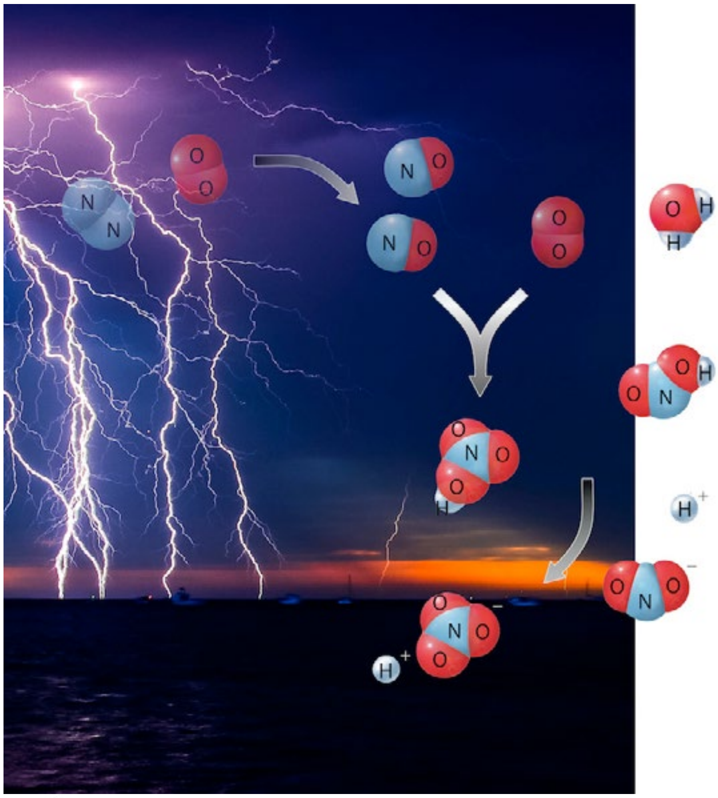
Chapter 9

How Chemicals React



THE MAIN IDEA

Atoms change partners during a chemical reaction.

9.5 Entropy and Chemical Reactions

Energy tends to disperse. It flows from where it is concentrated to where it is spread out. The energy of a hot pan, for example, does not stay concentrated in the pan once the pan is taken off the stove. Instead, the energy spreads away from the pan into the cooler surroundings. Similarly, the concentrated chemical energy in gasoline disperses, when ignited, in the formation of many very hot smaller molecules that scatter explosively. Some of this released thermal energy is used by the engine to get the car moving. The rest spreads into the engine block and radiator fluid and out the exhaust pipe.

Scientists consider this tendency of energy to disperse to be one of the central reasons for both physical and chemical changes. In other words, changes that result in energy spreading out tend to occur on their own—they are favored. This includes the cooling down of a hot pan or the burning of ignited gasoline. In both cases, there is a dispersal of energy to the environment.

READING CHECK

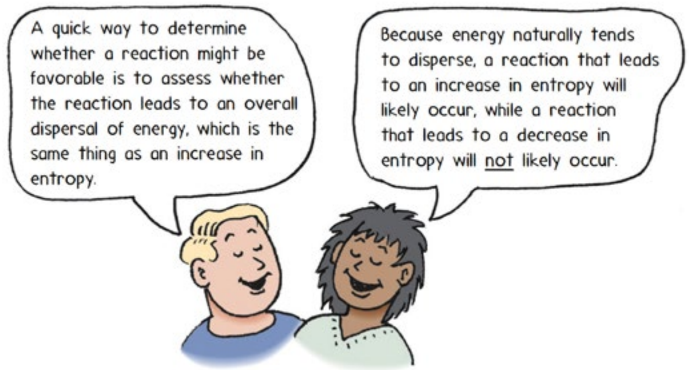
What is one of the central reasons for the occurrence of any physical or chemical change?

The opposite holds true, too. Changes that result in the concentration of energy do *not* tend to occur—they are not favored. Heat from the room, for example, will never spontaneously move into a pan to heat it up. Likewise, low-energy exhaust molecules coming out of a car's tailpipe will not spontaneously come back together to form higher-energy gasoline molecules. The natural flow of energy is always a one-way trip from where it is concentrated to where it is less concentrated, or "spread out."

That energy tends to disperse is spelled out by the *second law of thermodynamics*, which can be paraphrased as follows:

> *Any process that happens by itself results in the net dispersal of energy. For example, heat naturally flows from a higher-temperature object to a lower-temperature object because in doing so, energy is dispersed from where it is concentrated (a hot pan) to where it is spread out (the cooler kitchen).*

Second Law of Thermodynamics



Entropy is a measure of this natural spreading of energy. Wherever there is a spreading of energy, there is a corresponding *increase* in entropy. Applied to chemistry, entropy helps us to answer a most fundamental question: if you take two materials and put them together, will they react to form

$$\text{sunlight} + \underset{\text{carbon dioxide}}{6\,CO_2} + \underset{\text{water}}{6\,H_2O} \rightarrow \underset{\text{carbohydrate}}{C_6H_{12}O_6} + \underset{\text{oxygen}}{6\,O_2}$$

new materials? If the reaction results in the dispersal of energy (an overall increase in entropy), then the answer is yes. Conversely, if the reaction results in the concentration of energy (an overall decrease in entropy), then the reaction will not occur by itself. Instead, such a reaction will occur only if an external source of energy is supplied to it.

Using this concept of entropy, you are now in a position to understand why exothermic reactions are self-sustaining—occurring on their own without need of external help—while most endothermic reactions need a continual prodding. Exothermic reactions spread energy out to the surroundings, much like a cooling hot pan. This is an increase in entropy; hence, exothermic reactions are favored to occur. An endothermic reaction, by contrast, requires that energy from the surroundings be absorbed by the reactants. This is a concentration of energy, which is counter to energy's natural tendency to disperse. Endothermic reactions, therefore, can progress from reactants to products only with the continual input of energy. But from where might this energy come? The answer is "from some self-sustaining exothermic reaction occurring elsewhere."

CONCEPT **CHECK**

Sugar crystals form naturally within a supersaturated solution of sugar water. Does the formation of these crystals result in an increase or a decrease in entropy?

CHECK YOUR ANSWER

The formation of these sugar crystals results in an increase in entropy. Your clue to an increase in entropy here is that the crystals form "on their own," a spontaneous process and thus one that must result in an entropy increase. Recall from Section 8.6 that energy is released when molecules come together to form a solid (the heat of freezing). This release of heat involves the spreading out of energy, which is, by definition, an increase in entropy.

The classic example is photosynthesis, which is an endothermic reaction by which plants use solar energy to create carbohydrates and oxygen from carbon dioxide and water, as represented by the following equation:

In photosynthesis, energy dispersed from the Sun becomes contained within the carbohydrate and oxygen products, which, of course, are the primary fuels of living organisms (**Figure 9.10**). Likewise, most modern materials, such as plastics, synthetic fibers, pharmaceuticals, fertilizers, and metals such as iron and aluminum, are made or purified using endothermic reactions. Our ability to produce these new and useful materials has been the hallmark of modern chemistry. Creating these products, however, necessarily requires the input of energy, which we must obtain from some external source, such as electricity from a power plant that burns fossil or nuclear fuels.

While on the subject of the second law of thermodynamics, we would be remiss not to discuss the close relationship between entropy and our psychological sense of time. That energy tends to spread out is part of our human experience. We *expect* a hot pan to cool, just as we *expect* hot gases to come out of an exhaust pipe. But what if we saw the reverse? For example, what would we think if we saw smoke moving *into* a smokestack? Or what if we saw a diver fly out of the water and rise upward to the diving platform? If we were watching these energy-concentrating events on video, we would quickly conclude that the video was running backward. However, if in real life we actually saw such things—if we could survive the shock—we would immediately sense that time itself was running backward. Thus, when we watch smoke shoot out of a smokestack and a diver diving into water, as shown in **Figure 9.11,** we have the sense that time is moving forward. The second law of thermodynamics, therefore, gives us our psychological sense of time; it is the "arrow of time."

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There are examples of endothermic reactions that proceed spontaneously absorbing heat from the environment. A classic example is the mixing of ions (salt) in water, as presented as one of the Quick Activities for this chapter. In such cases, the environment disperses energy to the dissolving ions, which then spread this energy more widely into the volume of the solvent.

Figure 9.10

The Sun is truly a "hothouse"—dispersing enormous amounts of energy from exothermic nuclear reactions. A tiny fraction of the Sun's energy is used to drive photosynthesis, which is vital for plants and plant-eating creatures like us.

Figure 9.11

As the diver dives, her potential energy is converted into kinetic energy. As she splashes into the water, this kinetic energy is spread to make the water molecules move faster and to heat up just a little. Will this dissipated energy reconcentrate itself to push her back through the air up to the cliff? Our common experience with the second law of thermodynamics says no.

CHEMICAL CONNECTIONS

How is the dispersal of energy related to the concept of time?

Students often state the laws of thermodynamics this way: you can't win because you can't get any more energy out of a system than you put into it. You can't break even because no matter what you do, some of your energy will be dispersed as ambient heat. Finally, you can't get out of the game because you depend on entropy-increasing processes, such as solar thermonuclear fusion, to remain alive.

CONCEPT **CHECK**

The energy of a diver diving into a pool is dispersed as lots of moving water and a little heat after the diver hits the water. How, then, can the diver get back up to the platform?

CHECK YOUR ANSWER

As a living organism, the diver has a supply of biochemical energy, obtained ultimately from photosynthesis, that she can tap to climb upward against gravity to get back to the diving platform.