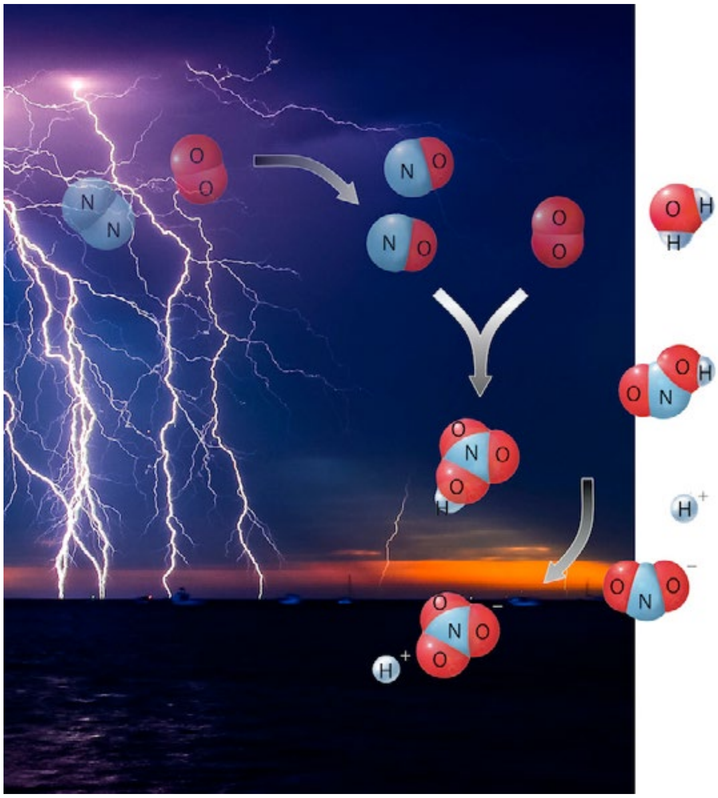


Chapter 9

How Chemicals React

THE MAIN IDEA

Atoms change partners during a chemical reaction.

9.1 Chemical Equations
9.2 Measuring Molecules
9.3 Grams to Moles
9.4 Exothermic or Endothermic
9.5 Entropy and Chemical Reactions
9.6 Chemical Kinetics
9.7 Chemical Catalysts
9.8 Chemical Equilibrium

9.4 Exothermic or Endothermic

Once a reaction is complete, there may be either a net release or a net absorption of energy. Reactions in which there is a net release of energy are called **exothermic**. Rocket ships lift into space and campfires glow red hot as a result of exothermic reactions. Reactions in which there is a net absorption of energy are called **endothermic**. Photosynthesis, for example, involves a series of endothermic reactions that are driven by the energy of sunlight. Both exothermic and endothermic reactions, illustrated in **Figure 9.6**, can be understood through the concept of bond energy.

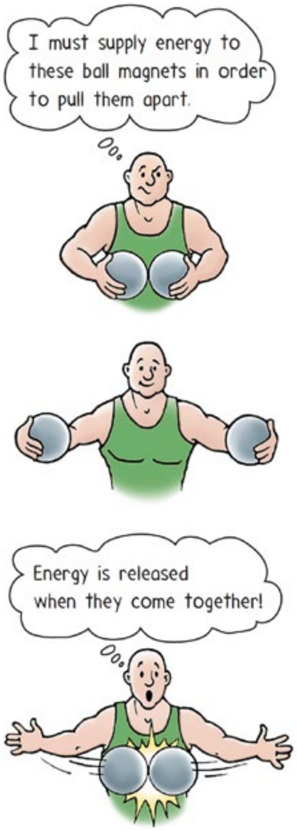
< Figure 9.6

For the chemical reactions that occur in a photosynthetic plant, there is a net absorption of energy. For the chemical reactions that occur when wood is burning, there is a net release of energy.

READING CHECK

What do the breaking and forming of chemical bonds involve?

During a chemical reaction, chemical bonds are broken and atoms rearranged to form new chemical bonds. Such breaking and forming of chemical bonds involves changes in energy. As an analogy, consider a pair of magnets. To separate them requires an input of "muscle energy." Conversely, when the two separated magnets collide, they become slightly warmer than they had been, and this warmth is evidence of energy released. Energy must be absorbed by the magnets if they are to move apart, and energy is released as they come together. The same principle applies to atoms. To pull bonded atoms apart requires an energy input. When atoms combine, there is an energy output, usually in the form of faster-moving atoms and molecules, electromagnetic radiation, or both.



The amount of energy required to pull two bonded atoms apart is the same as the amount released when they are brought together. This energy is called **bond energy**. Each chemical bond has its own characteristic bond energy. The hydrogen–hydrogen bond energy, for example, is 436 kilojoules per mole. This means that 436 kilojoules of energy is absorbed as 1 mole of hydrogen–hydrogen bonds break apart and 436 kilojoules of energy is released upon the formation of 1 mole of hydrogen–hydrogen bonds. Different bonds involving different elements have different bond energies, as **Table 9.1** shows. You can refer to the table as you study this section, but please do not memorize these bond energies. Instead, focus on understanding what they mean.

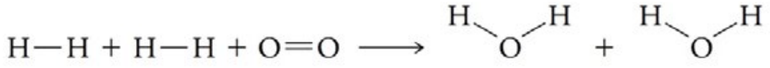
By convention, a positive bond energy represents the amount of energy absorbed as a bond breaks and a negative bond energy represents the amount of energy released as a bond forms. Thus, when you are calculating the net energy released or absorbed during a reaction, you need to be careful about plus and minus signs. It is standard practice when doing such calculations to assign a plus sign to energy absorbed and a minus sign to energy released. For instance, when dealing with a reaction in which 1 mole of H–H bonds are broken, you write +436 kilojoules to indicate energy absorbed. The positive sign indicates that the molecules gained energy, which was used to break the bonds. When dealing with the formation of 1 mole of H–H bonds, you write –436 kilojoules to indicate energy released. The negative sign indicates that the molecules lost energy, which was released to the environment. We'll do some sample calculations in a moment.

TABLE 9.1 Selected Bond Energies

BOND	BOND ENERGY (KJ/MOLE)	BOND	BOND ENERGY (KJ/MOLE)
H–H	436	N–N	159
H–C	414	O–O	138
H–N	389	Cl–Cl	243
H–O	464	C=O	803
H–F	569	N=O	631
H–Cl	431	O=O	498
C–O	351	C≡C	837
C–C	347	N≡N	946

An Exothermic Reaction: A Net Release of Energy

For most chemical reactions, the total amount of energy absorbed in breaking bonds in reactants is different from the total amount of the energy released as bonds form in the products. Consider the reaction in which hydrogen and oxygen react to form water:



In the reactants, hydrogen atoms are bonded to hydrogen atoms and oxygen atoms are double-bonded to oxygen atoms. The total amount of energy absorbed as these bonds break is +1370 kilojoules. Note that we use the plus sign to indicate the amount of energy *absorbed* to break bonds.

Type of bond	Number of bonds	Bond energy	Total energy
H—H	2 moles	+436 kJ/mole	+872 kJ
O=O	1 mole	+498 kJ/mole	+498 kJ
		Total energy absorbed:	+1370 kJ

In the products, there are four moles of hydrogen–oxygen bonds. The total amount of energy released as these bonds form is –1856 kilojoules. Note that we use the minus sign to indicate the amount of energy *released* as bonds are formed.

Type of bond	Number of bonds	Bond energy	Total energy
H—O	4 moles	–464 kJ/mole	–1856 kJ
		Total energy released:	–1856 kJ

The amount of energy released in this reaction exceeds the amount of energy absorbed. The net energy of the reaction is found by adding the two quantities:

$$\begin{aligned}\text{net energy of reaction} &= \text{energy absorbed} + \text{energy released}\\ &= +1370\ \text{kJ} + (-1856\ \text{kJ})\\ &= -486\ \text{kJ}\end{aligned}$$

The negative sign on the net energy indicates that there is a net release of energy, so the reaction is exothermic. For any exothermic reaction, energy can be considered a product and is thus sometimes included after the arrow of the chemical equation:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O + \text{energy}$$

In an exothermic reaction, the potential energy of atoms in the product molecules is lower than their potential energy in the reactant molecules. This is illustrated in the reaction profile shown in Figure 9.7. The lowered potential energy of the atoms in the product molecules is due to their being more tightly held together. This is analogous to two attracting magnets, whose potential energy decreases as they come closer together. The loss of potential energy is balanced by a gain in kinetic energy. Like two free-floating magnets coming together and accelerating to higher speeds, the potential energy of the reactants is converted to faster-moving atoms and molecules, electromagnetic radiation, or both. This kinetic energy released by the reaction is equal to the difference between the potential energy of the reactants and the potential energy of the products, as is indicated in **Figure 9.7**.

FOR YOUR INFORMATION

The bonds that form in the product molecules are not the same bonds that broke in the reactant molecules. The amount of energy released upon product formation, therefore, will not be the same as the amount of energy consumed in reactant deformation.

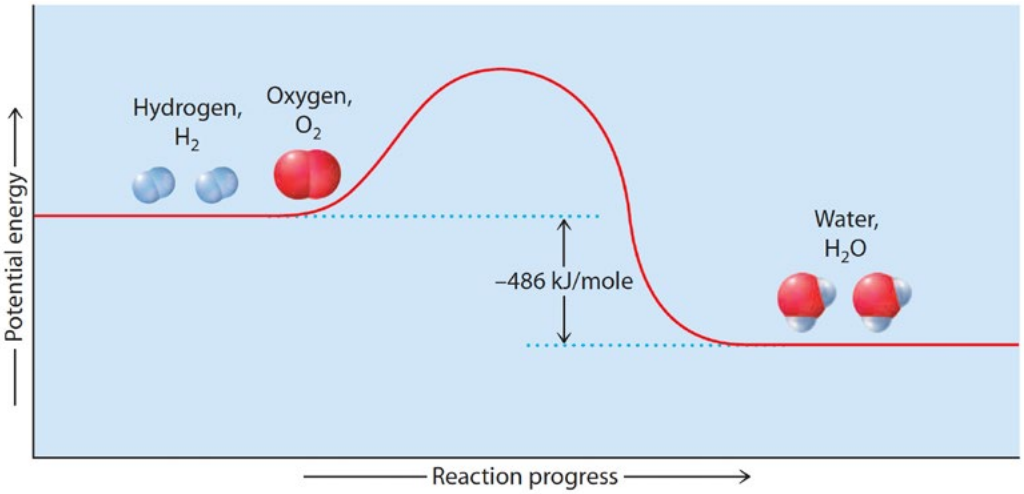


Figure 9.7 >

In an exothermic reaction, the product molecules are at a lower potential energy than the reactant molecules. The net amount of energy released by the reaction is equal to the difference in the potential energies of the reactants and the products. In Section 9.6, we explore why graphs such as this have a bump in the middle.

The total amount of energy released in an exothermic reaction depends on the amounts of the reactants. The reaction of large amounts of hydrogen and oxygen, for example, provided the energy to lift the Space Shuttle shown in **Figure 9.8** into orbit. There were two compartments in the large central tank, to which the orbiter was attached—one filled with liquid hydrogen and the other filled with liquid oxygen. Upon ignition, these two liquids mixed and reacted chemically to form water vapor, which produced the needed thrust as it is expelled the rocket cones. Additional thrust was obtained from a pair of solid-fuel rocket boosters containing a mixture of ammonium perchlorate, NH_4ClO_4, and powdered aluminum, Al. Upon ignition, these chemicals reacted to form products that were expelled at the rear of the rocket. The balanced equation representing this aluminum reaction is

$$3\ NH_4ClO_4 + 3\ Al \longrightarrow Al_2O_3 + AlCl_3 + 3\ NO + 6\ H_2O + \text{energy}$$

< Figure 9.8

Space rockets use exothermic chemical reactions to lift off from the Earth's surface.

CONCEPT **CHECK**

Where does the net energy released in an exothermic reaction go?

CHECK YOUR ANSWER

This energy goes into increasing the speeds of reactant atoms and molecules and often into electromagnetic radiation such as light.

An Endothermic Reaction: A Net Absorption of Energy

When the amount of energy released in product formation is less than the amount of energy absorbed when reactant bonds break, the reaction is endothermic. An example is the reaction of atmospheric nitrogen and oxygen to form nitrogen monoxide:

$$N \equiv N + O = O \rightarrow N = O + N = O$$

The amount of energy absorbed as the chemical bonds in the reactants break is

Type of bond	Number of bonds	Bond energy	Total energy
$N \equiv N$	1 mole	+946 kJ/mole	+946 kJ
$O = O$	1 mole	+498 kJ/mole	+498 kJ
		Total energy absorbed:	+1444 kJ

The amount of energy released upon the formation of bonds in the products is

Type of bond	Number of bonds	Bond energy	Total energy
$N = O$	2 moles	−631 kJ/mole	−1262 kJ
		Total energy released:	−1262 kJ

As before, the net energy of the reaction is found by adding the two quantities:

$$\begin{aligned} \text{net energy of reaction} &= \text{energy absorbed} + \text{energy released} \\ &= +1444 \text{ kJ} + (-1262 \text{ kJ}) \\ &= +182 \text{ kJ} \end{aligned}$$

The positive sign indicates that there is a net absorption of energy, meaning the reaction is endothermic. For any endothermic reaction, energy can be considered a reactant and is thus sometimes included before the arrow of the chemical equation:

$$\text{energy} + N_2 + O_2 \longrightarrow 2\,NO$$

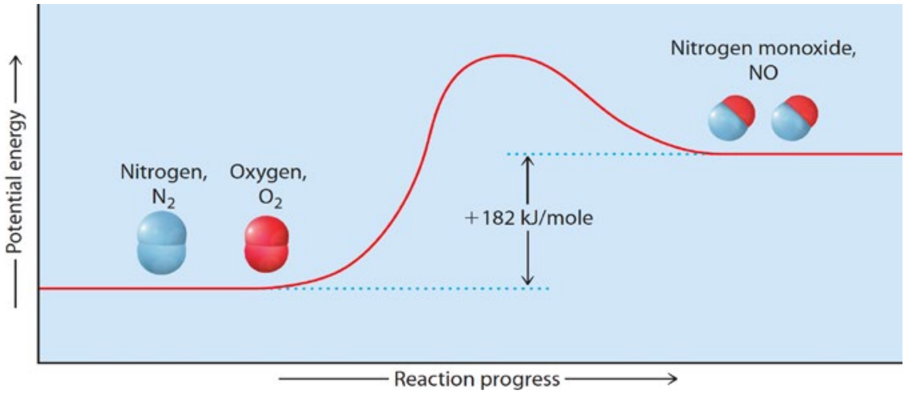
In an endothermic reaction, the potential energy of atoms in the product molecules is higher than their potential energy in the reactant molecules. This is illustrated in the reaction profile shown in **Figure 9.9**. Raising the potential energy of the atoms in the product molecules requires a net input of energy, which must come from some external source, such as electromagnetic radiation, electricity, or heat. Nitrogen and oxygen react to form nitrogen monoxide with the application of large amounts of heat, as occurs adjacent to a lightning bolt or in an internal-combustion engine.

FOR YOUR INFORMATION

NASA scientists routinely test various materials for their durability against atomic oxygen, O, which is abundant in low orbit. They discovered that atomic oxygen effectively transforms surface organic materials into gaseous carbon dioxide. The scientists realized atomic oxygen's usefulness for restoring fine art paintings damaged by smoke or other organic contaminants. Together with art conservationists, they used atomic oxygen to restore certain damaged paintings, and it worked spectacularly.

Figure 9.9 >

In an endothermic reaction, the product molecules are at a higher potential energy than the reactant molecules. The net amount of energy absorbed by the reaction is equal to the difference in the potential energies of the reactants and the products.



CONCEPT **CHECK**

Should the following reaction be endothermic or exothermic?

$O_2NNO_2 \rightarrow O_2N + NO_2$

CHECK YOUR ANSWER

No calculations are necessary. This reaction is endothermic because it involves only the breaking of a chemical bond. For practice with examples requiring calculations, see the questions in the Chapter Review.

Energy Is Conserved in a Chemical Reaction

We have been focusing on the key role energy plays in chemical reactions. This is an area of science known as **thermodynamics**, which stems from Greek words meaning "movement of heat." The concepts of exothermic and endothermic reactions fit neatly within what is known as the *first law of thermodynamics*, which can be paraphrased as follows:

First Law of Thermodynamics

> *Energy is conserved. It may be converted from one form to another, say, from potential to kinetic energy, but the total amount of energy remains the same. The energy that an exothermic reaction releases always goes somewhere into the environment, often in the form of thermal energy (heat), but other forms, such as light energy or electric energy, are also possible. Likewise, the energy that an endothermic reaction absorbs always comes from somewhere in the environment, again, in various forms.*

This is a common sense type of law, from which we derive the expression "You can't get something for nothing." Energy doesn't just appear or disappear. It either comes from somewhere or goes to somewhere. In the case of an exothermic reaction, energy comes from the formation of bonds in which atoms are held more tightly but vibrate faster. This is a downhill transformation of potential energy into kinetic energy. In the case of an endothermic reaction, energy is absorbed in the formation of bonds in which atoms are held more loosely and vibrate slower. This is an uphill transformation of kinetic energy into potential energy.

The first law of thermodynamics tells us that energy can be neither created nor destroyed. This is an important law to understand, but it does not tell us the whole picture. Why, for example, do reactants react to form products? By doing nothing instead, they are following the first law of thermodynamics quite perfectly. What then compels them to move forward in the formation of products? The answer to this question is aptly provided by the *second law of thermodynamics*, which we explore next.