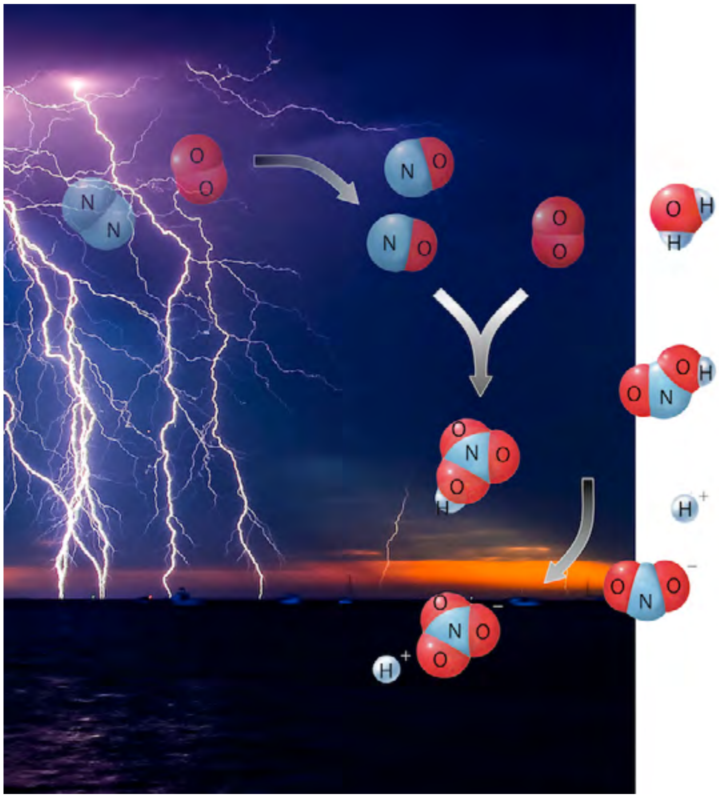


Chapter 9

How Chemicals React

THE MAIN IDEA

Atoms change partners during a chemical reaction.

9.7 Chemical Catalysts

As discussed in the previous section, a chemical reaction can be made to go faster by increasing the concentration of the reactants or by increasing the temperature. A third way to increase the speed of a reaction is to add a **catalyst**, which is any substance that increases the rate of a chemical reaction without itself being consumed.

To learn how catalysts work, let's consider some chemical reactions that take place in our atmosphere. One of the most important reactions occurs at altitudes higher than 20 km, within a region known as the *stratosphere*. Here the Sun's ultraviolet (UV) rays cause oxygen molecules to transform into ozone molecules, as follows:

$$\underset{\text{molecular oxygen}}{3\,O_2(g)} + UV \rightarrow \underset{\text{ozone}}{2\,O_3(g)}$$

Furthermore, the ozone itself, once formed, is able to transform ultraviolet light into heat:

$$\underset{\text{ozone}}{O_3(g)} + UV \rightarrow \underset{\text{ozone}}{O_3(g)} + \text{heat}$$

In all, these ozone reactions prevent about 95 percent of the ultraviolet rays that come to our planet from the Sun from reaching its surface. This is of great benefit to life on the Earth because ultraviolet rays are most harmful to living tissue. Stratospheric ozone is our planet's safety shield.

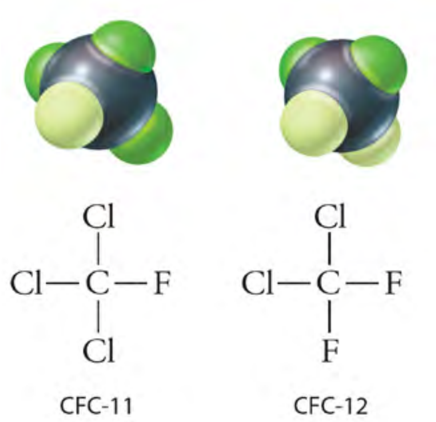
Starting in the 1970s, scientists began to recognize that human-made chlorofluorocarbons, also known as CFCs, posed a significant threat to stratospheric ozone. Because CFCs are inert gases, they were once commonly

READING CHECK

A catalyst speeds up a chemical reaction by lowering what?

FOR YOUR INFORMATION

The stratospheric ozone layer is about 10 kilometers thick, but the concentration of ozone, O_3, within the layer is quite low. If this ozone layer were brought down to Earth's surface, atmospheric pressure would squeeze it to a thickness of only 3 millimeters. Not much ozone is up there protecting us. But thankfully, even small amounts of ozone are very good at shading us from solar ultraviolet light.



Λ Figure 9.20

Two of the most common CFCs, also known as freons, were CFC-11, trichlorofluoromethane, and CFC-12, dichlorodifluoromethane. At the height of CFC production in 1988, some 1.13 million tons was produced worldwide. Because of their inertness, CFCs were once thought to pose little threat to the environment.

used in air conditioners and aerosol propellants. Two of the most frequently used CFCs are shown in **Figure 9.20.**

The CFCs, it was discovered, drift their way to the stratosphere, where the intense ultraviolet rays break apart these molecules, producing chlorine atoms. The chlorine atoms, in turn, speed up the rate at which ozone molecules are destroyed. They do this by offering a reaction pathway that has a lower activation energy, as shown in **Figure 9.21**.

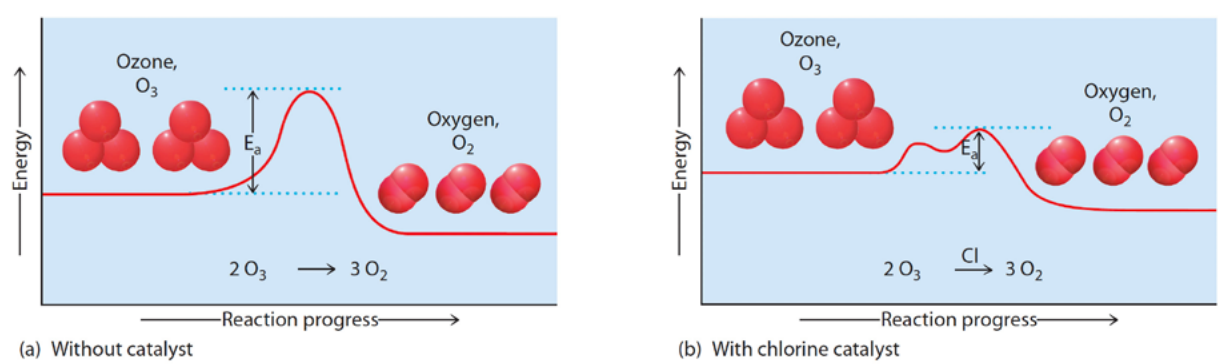
Chlorine atoms provide an alternate pathway involving intermediate reactions, each having a lower activation energy than the uncatalyzed reaction. This alternate pathway involves two steps. Initially, the chlorine reacts with the ozone to form chlorine monoxide and oxygen:

$$\underset{\text{Chlorine}}{Cl} + \underset{\text{Ozone}}{O_3} \longrightarrow \underset{\text{Chlorine monoxide}}{ClO} + \underset{\text{Oxygen}}{O_2}$$

The chlorine monoxide then reacts with another ozone molecule to re-form the chlorine atom, as well as to produce two additional oxygen molecules:

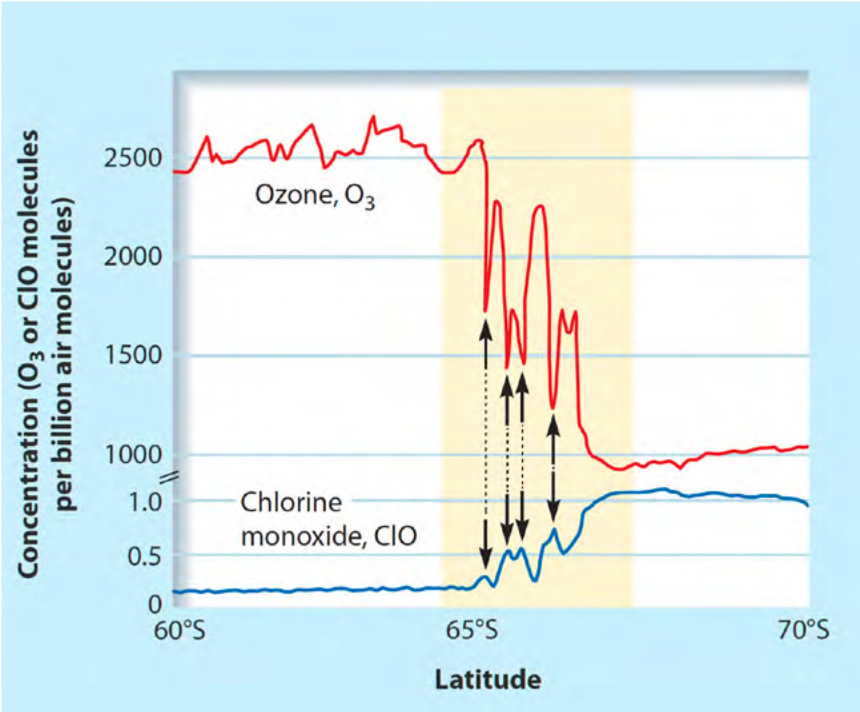
$$\underset{\text{Chlorine monoxide}}{ClO} + \underset{\text{Ozone}}{O_3} \longrightarrow \underset{\text{Chlorine}}{Cl} + \underset{\text{Oxygen}}{2\,O_2}$$

A catalyst speeds up a chemical reaction, but interestingly, it is not destroyed by the reaction it catalyzes. Notice that although chlorine is depleted in the first reaction, it is regenerated in the second reaction. As a result, there is no net consumption of chlorine. Instead, it survives; so, it can speed up the reaction repeatedly. One chlorine atom in the ozone layer, for example, can catalyze the transformation of 100,000 ozone molecules to oxygen molecules in the one or two years before the chlorine atom is removed by natural processes. In short, chlorine is bad news for stratospheric ozone, which is bad news for life on the Earth.



Λ Figure 9.21

(a) The high activation energy indicates that only the most energetic ozone molecules can react to form oxygen molecules. (b) The presence of chlorine atoms allows conversion of ozone to oxygen with a lower activation energy, which means more ozone molecules have sufficient energy to form the product. (Note that the convention is to write the catalyst above the reaction arrow.)



< Figure 9.22

Concentrations of stratospheric ozone and chlorine monoxide in southern latitudes. As chlorine monoxide levels increase, ozone levels decrease. The yellow highlighting shows where small fluctuations in ClO concentrations result in large fluctuations in O_3 concentrations. This is consistent with catalytic behavior.

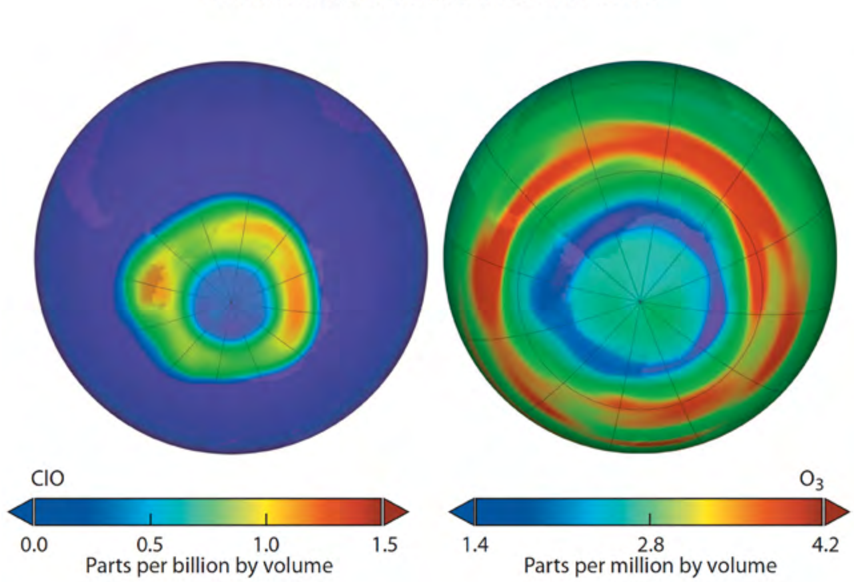
The fragility of stratospheric ozone came to the world's attention in 1985, with the discovery of a seasonal depletion of stratospheric ozone over the Antarctic continent, a phenomenon known as the *ozone hole*. The fact that chlorine atoms play an active role in the destruction of Antarctic ozone is revealed by measuring chlorine monoxide concentrations over this region, as shown in **Figure 9.22**. Furthermore, the satellite images show that the shape of the ozone hole typically matches the shape of a map showing chlorine monoxide distribution (**Figure 9.23**).

There has been an unprecedented level of international cooperation toward banning ozone-destroying substances such as CFCs. As a result, stratospheric concentrations of chlorine have been declining. Even with these treaties in place, however, the ozone-destroying actions of CFCs will be with us for some time. Atmospheric CFC levels are not expected to drop back to the levels found before the ozone hole was formed until sometime in the 22nd century.

FOR YOUR INFORMATION

Numerous oil-drilling sites in Siberia were once allowed to vent natural gas freely into the atmosphere. After the fall of the Soviet Union, these wells were capped to prevent this venting. Within weeks, instruments at the Mauna Loa weather observatory on the other side of the planet noted a significant drop in atmospheric levels of methane and its by-product, carbon dioxide. The effect that we humans have on global atmospheric conditions is very measurable.

Chlorine Monoxide and the Ozone Hole



< Figure 9.23

Satellite images of the southern hemisphere showing concentrations of chlorine monoxide adjacent to concentrations of stratospheric ozone.

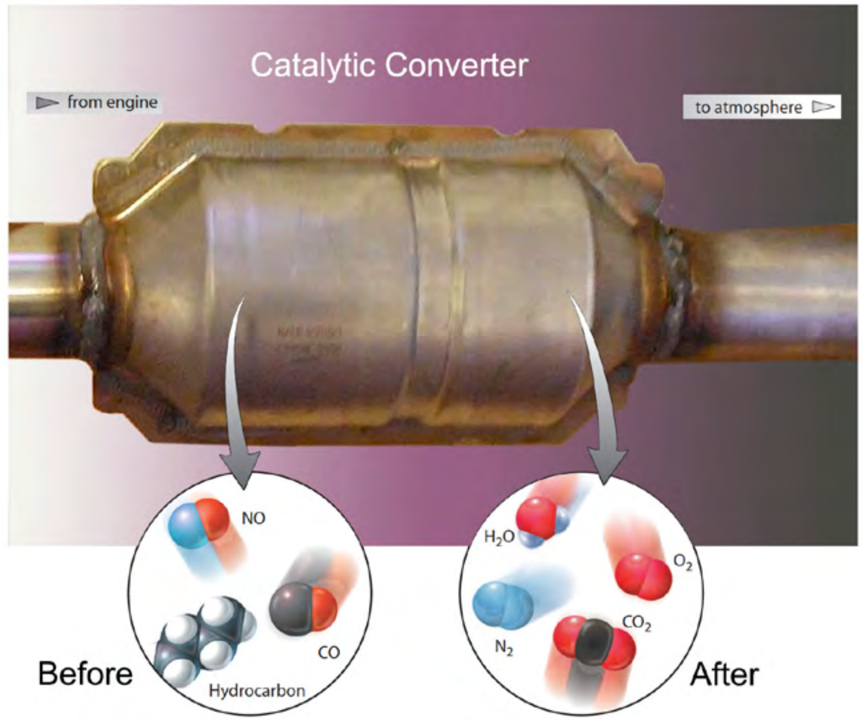


Figure 9.24 >

A catalytic converter reduces the pollution caused by automobile exhaust by converting such harmful combustion products as NO, CO, and hydrocarbons to harmless N_2, O_2, CO_2, and H_2O. The catalyst is typically platinum, Pt; palladium, Pd; or rhodium, Rd.

Catalysts are also Most Beneficial

Chemists have been able to harness the power of catalysts for numerous beneficial purposes. The exhaust that comes from an automobile engine, for example, contains a wide assortment of pollutants, such as nitrogen monoxide, carbon monoxide, and uncombusted fuel vapors (hydrocarbons). To reduce the amount of these pollutants entering the atmosphere, most automobiles are equipped with *catalytic converters*, as shown in **Figure 9.24**. Metal catalysts in a converter speed up reactions that convert exhaust pollutants to less toxic substances. Nitrogen monoxide is transformed to nitrogen and oxygen, carbon monoxide is transformed to carbon dioxide, and unburned fuel is converted to carbon dioxide and water vapor. Because catalysts are not consumed by the reactions they speed up, a single catalytic converter may continue to operate effectively for the lifetime of the car.

Catalytic converters, along with microchip-controlled fuel–air ratios, have led to a significant drop in the per-vehicle emission of pollutants. This improvement, however, has been offset by an increase in the number of cars being driven, as exemplified by the traffic jam shown in **Figure 9.25**.

FOR YOUR INFORMATION

Chlorofluorocarbons are distributed fairly evenly across the Earth's stratosphere. Over the poles, however, stratospheric clouds are able to form during the dark and extremely cold winters. CFC molecules bind to ice crystals within these clouds. When hit by sunlight in the spring, the crystal-bound CFC molecules break apart, producing a large dose of ozone-destroying chlorine atoms. In Antarctica, this process reaches a peak in September, which is when the largest ozone holes are typically observed. The ozone hole over the South Pole is typically more intense than the one over the North Pole. The reason is because the geography of the Southern Ocean favors a stable vortex around the South Pole, which, in turn, favors the formation of the stratospheric clouds.

Figure 9.25 >

The exhaust from automobiles today is much cleaner than before the advent of the catalytic converter, but there are many more cars on the road. In 1960, there were about 74 million registered motor vehicles in the United States. By 2020, there were more than 276 million.

Catalysts lower manufacturing costs by lowering required temperatures and by providing greater product yields without being consumed. Indeed, more than 90 percent of all manufactured goods are produced with the assistance of catalysts. The production of polymer plastics, as described in Chapter 12, is particularly dependent upon catalysts. Also, without catalysts, the price of gasoline would be much higher, as would be the price of such consumer goods as rubber, pharmaceuticals, automobile parts, clothing, and food grown with chemical fertilizers. Living organisms rely on special types of catalysts known as *enzymes*, which allow exceedingly complex biochemical reactions to occur with ease.

CONCEPT **CHECK**

How is a catalyst different from a chemical reactant?

CHECK YOUR ANSWER

A catalyst is not used up during a chemical reaction. Instead, it is released as its original self. The catalyst can then serve to catalyze more reactions. A chemical reactant, by contrast, is consumed during a reaction as it is transformed into a chemical product.