CHAPTER

4

Chemistry of the Troposphere

- **Indoor Air Pollution**

- **Additional Sources of Information**

- **Keywords**

- **Questions and Problems**

AN **AIR POLLUTANT** IS DEFINED AS A SUBSTANCE THAT IS PRESENT IN THE ATMOSPHERE AT A CONCENTRATION THAT IS SUFFICIENT TO CAUSE HARM TO HUMANS, OTHER ANIMALS, VEGETATION, OR MATERIALS. Each day humans inhale approximately 20,000 L (5300 gallons) of air. If harmful gases or fine toxic particles are present in the air, they are also drawn into the lungs, where they may cause serious respiratory diseases and other health problems.

Approximately 90% of all air pollution in the United States is caused by five **primary air pollutants**: carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen oxides (NO_x), **volatile organic compounds** (**VOCs;** mostly hydrocarbons [HCs]), and suspended particles. Their major sources and the relative contribution of each to air pollution nationwide are shown in Figure 4.1. Emissions of all five are now regulated in the United States.

The transportation industry is responsible for nearly 50% of all air pollution from anthropogenic sources. In addition to CO, automobiles emit NO_x and HCs. The burning of fossil fuels by stationary sources (power plants and industrial plants) accounts for approximately one-third of air pollutants, mainly
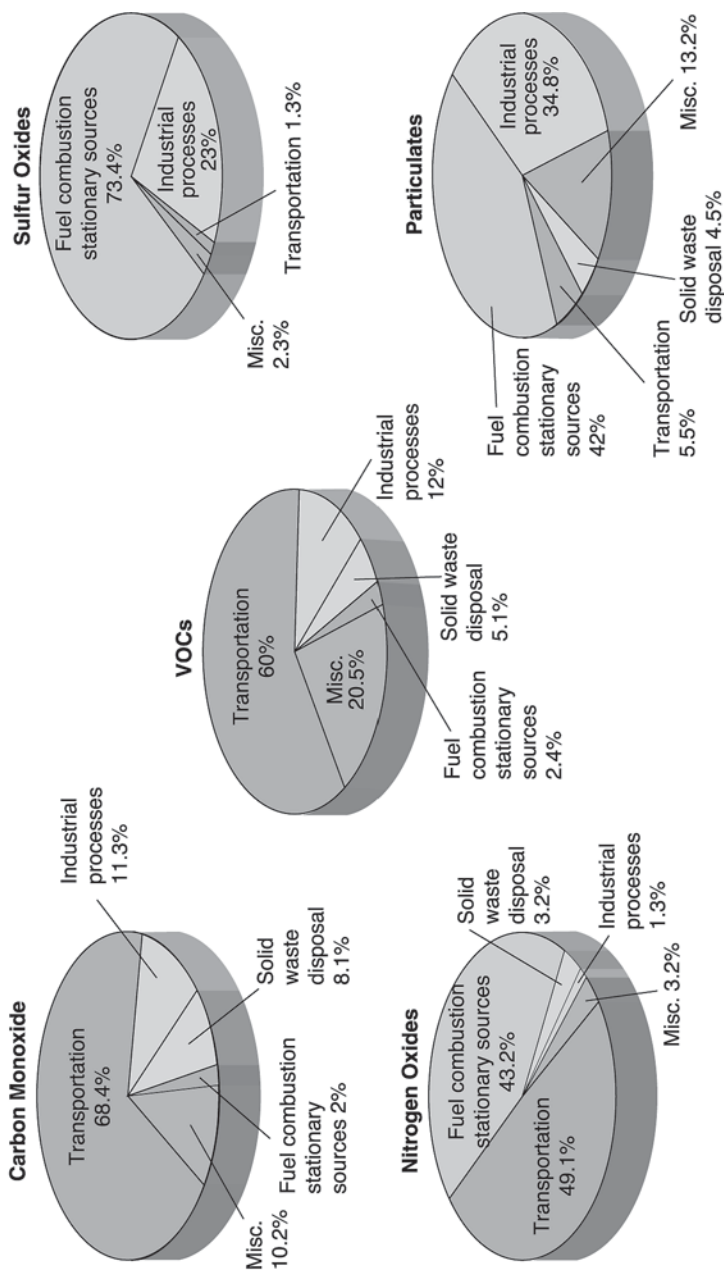
Sulfur Oxides

Fuel combustion stationary sources 73.4%

Industrial processes 23%

Transportation 1.3%

Misc. 2.3%

Particulates

Industrial processes 34.8%

Misc. 13.2%

Fuel combustion stationary sources 42%

Transportation 5.5%

Solid waste disposal 4.5%

VOCs

Industrial processes 12%

Transportation 60%

Solid waste disposal 5.1%

Misc. 20.5%

Fuel combustion stationary sources 2.4%

Carbon Monoxide

Industrial processes 11.3%

Transportation 68.4%

Solid waste disposal 8.1%

Fuel combustion stationary sources 2%

Misc. 10.2%

Nitrogen Oxides

Solid waste disposal 3.2%

Fuel combustion stationary sources 43.2%

Industrial processes 1.3%

Transportation 49.1%

Misc. 3.2%

Figure 4.1 Nationwide emissions of primary air pollutants according to source.

2ND REVISE

in the form of sulfur oxides. Other industrial activities, along with a variety of processes, including incineration of solid wastes, contribute smaller amounts.

If air pollutants were distributed evenly over the entire country, their harmful effects would be greatly reduced. Because the pollutants tend to be concentrated in urban areas, where industry is more common and automobile traffic is congested, large segments of the population are exposed to their harmful effects, particularly during daily rush hours.

In addition to the five primary air pollutants, the atmosphere is contaminated with **secondary air pollutants**, which are harmful substances produced by chemical reactions between primary pollutants and other constituents of the atmosphere. Secondary pollutants include sulfuric acid, nitric acid, sulfates and nitrates (which contribute to acid deposition), and **ozone** and other photochemical oxidants (which contribute to photochemical smog).

This chapter first identifies the sources and fate of the major pollutants of the troposphere: CO, NO_x, VOCs, and SO_2. Next, the chemistry of photochemical smog and importance of the hydroxyl radical are presented. Finally, indoor air pollution and the impact of government regulation on air pollution are presented.

■ Chemical Reactions in the Atmosphere

In the atmosphere, species called **free radicals** (often referred to simply as radicals) are often formed under the influence of solar radiation. Radicals are uncharged fragments of molecules that, unlike ordinary chemical species, have an unpaired electron. As a result, radicals are highly reactive and are very short-lived. They are responsible for many of the complex, often poorly understood reactions that occur in the normal and polluted atmosphere.

Central to the chemistry of the troposphere is the **hydroxyl radical.** The hydroxyl radical ($\cdot$ OH) is uncharged and thus quite different from the negatively charged hydroxide ion (OH^-). It is written with a dot ($\cdot$) beside it to indicate an unpaired electron.

$$:\overset{..}{\underset{..}{O}}:H^- \qquad\qquad :\overset{..}{\underset{..}{O}}:H \quad \leftarrow \text{ unpaired electron}$$

hydroxide ion hydroxyl radical
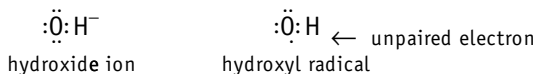
Hydroxyl radicals are continually formed and consumed in the troposphere and are produced as the result of a series of complex reactions primarily involving ozone, water, and nitrogen dioxide (NO_2), which are described later in the chapter. They play a role in the removal of

2ND REVISE

CO and HCs from the atmosphere and in the formation of nitric acid, sulfuric acid, and photochemical smog from atmospheric gases.

■ Carbon Monoxide (CO)

Sources of CO

The main anthropogenic source of CO is the combustion of gasoline in automobile engines (Figure 4.1). Gasoline is a complex mixture of HCs. If it is ignited in an adequate supply of oxygen, the products are carbon dioxide and water, as shown here for octane (C_8H_{18}), a representative gasoline HC.
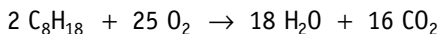
$$2\ C_8H_{18}\ +\ 25\ O_2\ \rightarrow\ 18\ H_2O\ +\ 16\ CO_2$$

In the confined space of the internal combustion engine, however, atmospheric oxygen is in limited supply, and combustion is incomplete. CO is formed and released to the atmosphere in automobile exhaust.

$$2\ C_8H_{18}\ +\ 17\ O_2\ \rightarrow\ 18\ H_2O\ +\ 16\ CO$$
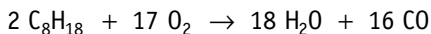
Since the introduction of the catalytic converter (described later in this chapter), CO emissions have been greatly reduced. In addition to the automobile, other anthropogenic sources of CO are combustion processes that are used by the electric power industry, various industrial processes, and solid-waste disposal.

It is perhaps surprising to discover that natural sources release approximately 10 times more CO into the atmosphere than all of the anthropogenic sources combined. The main natural source is methane gas, which is released during the anaerobic decay of plant materials in swamps, rice paddies, and other wetlands, where vegetation is submerged in oxygen-depleted water. Methane is also produced in the stomachs of ruminants (cattle and sheep) and the intestines of termites. Cattle, as they digest food, produce methane in their intestines. The gas then enters the bloodstream, and when the blood reaches the lungs, the methane is released and exhaled in normal breathing. Oxygen in the atmosphere oxidizes the methane to CO.

$$2\ CH_4\ +\ 3\ O_2\ \rightarrow\ 2\ CO\ +\ 4\ H_2O$$
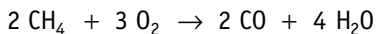
Unlike anthropogenic sources, natural emissions of CO are dispersed over the entire surface of the Earth. Two mechanisms are believed to be at work to maintain the average global level constant at approximately 0.1 parts per million (ppm): (1) the conversion of CO to carbon dioxide in reactions involving hydroxyl radicals and (2) the removal of CO from the atmosphere by microorganisms in soil. In cities, where soil has been largely replaced with asphalt and concrete and where emissions are very concentrated, nature's natural defense mechanism is overwhelmed, and atmospheric CO levels increase.

Effects of CO on Human Health

Although CO is the most abundant air pollutant, it is not very toxic at the levels usually found in the atmosphere; however, if allowed to build up in a confined space, it can cause serious health problems.

2ND REVISE

CO interferes with the oxygen-carrying capacity of blood. Normally, **hemoglobin (Hb)** in red blood cells combines with oxygen in the lungs to form oxyhemoglobin (HbO_2). The HbO_2 is carried in the bloodstream to the various parts of the body, where the oxygen is released to the tissues.

CO binds much more strongly to Hb than oxygen. If CO is present in the lungs, it displaces oxygen from Hb and thus reduces the amount of oxygen that can be delivered to the tissues.

$$HbO_2 \;\; + \;\; CO \;\; \rightarrow \;\; HbCO \;\; + \;\; O_2$$

oxyhemoglobin   carboxyhemoglobin
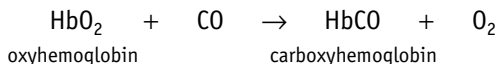
Treatment for CO poisoning is inhalation of pure oxygen, which reverses the direction of this reaction. The symptoms of CO poisoning are those of oxygen deprivation: headache, dizziness, impaired judgment, drowsiness, slowed reflexes, respiratory failure, and eventually loss of consciousness and death. Prolonged exposure to CO levels as low as 10 ppm can be harmful. The danger from CO is heightened by the fact that the gas is colorless, tasteless, and odorless; people succumb to its effects before they are aware of its presence. On busy city streets, the CO concentration may reach 50 ppm and may be much higher in underground garages and traffic jams.

■ Nitrogen Oxides (NO_x)

Nitrogen dioxide (NO_2) is the major NO_x pollutant in the atmosphere and is formed from nitric oxide (NO). Collectively, these related **nitrogen oxides** are designated as NO_x.

Sources of NO_x

Practically all anthropogenic NO_x enter the atmosphere from the combustion of fossil fuels by automobiles, aircraft, and power plants (see Figure 4.1). At normal atmospheric temperatures, nitrogen and oxygen—the two main components of air—do not react with each other; however, at the very high temperatures that exist in the internal combustion engine and in industrial furnaces, normally unreactive atmospheric nitrogen reacts with oxygen. In a series of complex reactions, the two gases combine to form NO:

$$N_2 \; + \; O_2 \; \rightarrow \; 2\,NO$$
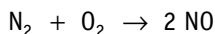
When released to the atmosphere, NO combines rapidly with atmospheric oxygen to form NO_2. NO is another molecule that like the hydroxyl radical has an unpaired electron and can be written as NO$\cdot$.

$$2\,NO \; + \; O_2 \; \rightarrow \; 2\,NO_2$$
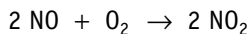
As is the case with CO, far more NO_x are released to the atmosphere by natural processes than by human activities. During electrical storms, atmospheric nitrogen and oxygen react to form NO, which then rapidly combines with more atmospheric oxygen to form NO_2, as shown in the previous equations. Bacterial decomposition of nitrogen-containing organic

2ND REVISE

matter in soil is another natural source of NO_x. Because emissions from natural processes are widely dispersed, they do not have an adverse effect on the environment.

Fate of Atmospheric NO_x

NO_2, regardless of its source, is ultimately removed from the atmosphere as nitric acid and nitrates in dust and rainfall (discussed in Chapter 7). In a series of complex reactions involving hydroxyl radicals, NO_2 combines with water vapor to form nitric acid. The simplified overall reaction can be written as follows:

$$4\ NO_2\ +\ 2\ H_2O\ +\ O_2\ \rightarrow\ 4\ HNO_3$$
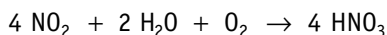
Much of the nitric acid in the atmosphere is formed within aqueous aerosols. If weather conditions are right, the aerosols coalesce into larger droplets in clouds, and the result is **acid rain.** Some of the nitric acid formed reacts with ammonia and metallic particles in the atmosphere to form nitrates. Ammonium nitrate is formed as follows:

$$HNO_3\ +\ NH_3\ \rightarrow\ NH_4NO_3$$
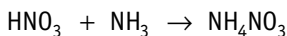
Nitrates dissolve in rain and snow or settle as particles. The combined fallout contributes to acid deposition.

Effects of NO_x on Human Health and the Environment

NO_2 is a red-brown toxic gas that has a very unpleasant acrid odor. It can cause irritation of the eyes, inflammation of lung tissue, and emphysema. Even in badly polluted areas, however, its concentration in the atmosphere is rarely high enough to produce these symptoms. NO_x is a serious health problem because of its role in the formation of the secondary pollutants associated with photochemical smog (discussed later in this chapter).

Emissions from stationary fuel combustion sources are difficult to control. Lowering the combustion temperature of the furnace decreases formation of NO, but it decreases efficiency at the same time. Most research has concentrated on reducing automobile emissions by means of the catalytic converter.

■ Volatile Organic Compounds (VOCs)

A great variety of VOCs, including many HCs, enter the atmosphere from both natural and anthropogenic sources (see Figure 4.1). Most are not pollutants themselves but create problems when they react with other substances in the atmosphere to form the secondary air pollutants associated with photochemical smog.

The petroleum industry is the main anthropogenic source of HCs in the atmosphere. Gasoline is a complex mixture of many volatile HCs, and in urban areas, gasoline vapors can escape into the atmosphere in several ways: when gas is pumped at gas stations, during filling of storage tanks, and as unburned gasoline in exhaust from automobiles and small combustion engines, such as weed whackers and lawn mowers.

In the natural world, the pleasant aroma of pine, eucalyptus, and sandalwood trees is caused by the evaporation of VOCs called **terpenes** from their leaves. Natural sources account for approximately 85% of total emissions of volatile HCs. The remaining 15% comes from anthropogenic sources, which are of concern because unlike natural sources they are not evenly distributed but are concentrated in urban areas.

Automobile Four-Cycle Internal Combustion Engine

In more developed countries, the gasoline-powered **four-cycle internal combustion engine** is predominant. To understand why pollutants such as NO_x, CO, and HCs are produced by the automobile's four-cycle gasoline engine requires an insight into how this engine works. As shown in Figure 4.2, there are four steps in one complete cycle (two revolutions of the crank shaft) of the gasoline engine. If the combustion of gasoline were carried out in an open vessel exposed to the atmosphere, there would be much less air pollutants produced than are produced in the automobile engine. In the confined space of the internal combustion engine, however, atmospheric oxygen is in limited supply, and combustion is incomplete. CO is formed and released to the atmosphere in automobile exhaust.

The combination of the high temperature and pressure of the internal combustion engine increases the pollutants that are emitted from the engine. In the combustion cylinder, normally unreactive atmospheric nitrogen reacts with oxygen. In a series of complex reactions, the two gases combine to form NO. Not all of the gasoline vapor is burned. Walls of the combustion cylinder are cooler than the rest of the cylinder and cause the explosive flame to be extinguished in the area adjacent to the cylinder walls. The unburned HCs are emitted with the burned gas as pollutant VOCs.

The air/fuel ratio has a dramatic effect on the emission of pollutants from the four-cycle engine. During an engine tune-up, adjustment of the carburetor or the fuel injection system
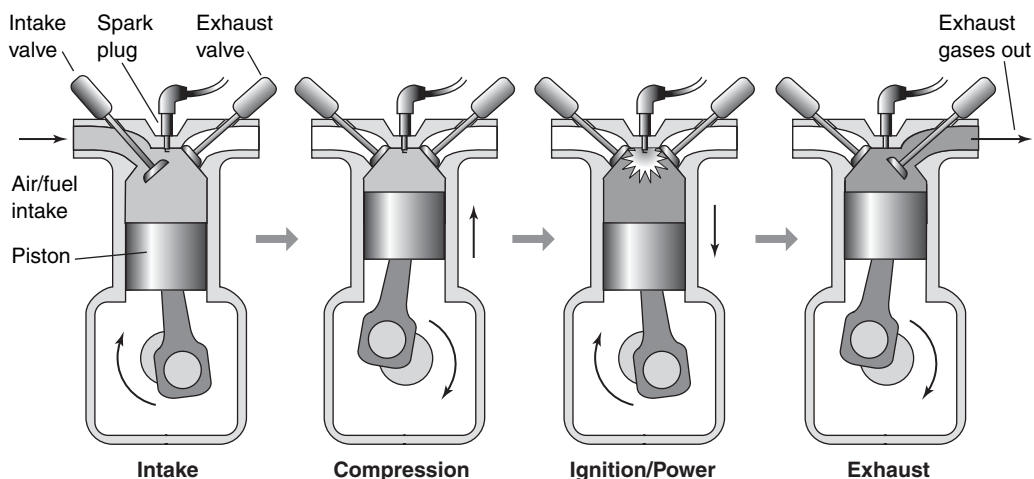

Figure 4.2 The steps in one complete cycle of a four-cycle internal combustion engine. Gasoline vapor has been mixed with the intake air.

2ND REVISE

can greatly reduce emission of pollutants. Figure 4.3 shows that the ideal, stoichiometric air/fuel ratio is 14.5. Adjustment to a more fuel-rich (lower air/fuel) ratio makes the car easier to start and decreases the emissions of NO_x and HCs. Unfortunately, it also decreases fuel efficiency, and the car will get fewer miles per gallon. The emission of CO also is increased with a fuel-rich ratio because less air is available. Adjustment to a more air-rich (higher air/fuel) ratio will make the car harder to start. Although it increases fuel efficiency, the emission of NO_x is increased. The ideal ratio is a compromise between fuel efficiency and the emission of the lowest collective amount of pollutants.

Gasoline Powered Two-Cycle Engines

The **two-cycle engine** is used to power motor scooters, mopeds, snowmobiles, marine outboard motors, and lawncare equipment such as weed whackers and leaf blowers. Because it is a less complicated device than the four-cycle engine, it can be made to be much lighter than a four-cycle engine. It is also much less expensive; however, and unlike automobile engines, which have been continuously modified for decades to increase efficiency and reduce emissions, the two-cycle gasoline engine has not been improved significantly since it was introduced in the 1940s.

The two-cycle gasoline engine, which can be seen in Figure 4.4, takes in fuel, releases exhaust in the same stroke, and emits from 25% to 30% of the fuel consumed as unburned HCs. Notice that the two-cycle engine has no valves and that power is produced in one of two steps rather than one in four steps. This means that the two-cycle engine runs faster (higher rpm) and hotter than the four-cycle engine.

Gasoline that is used in two-cycle engines is mixed with motor oil in a 40:1 ratio. The fuel is also used to lubricate the internal parts of the engine. Motor oil has a higher molecular weight than gasoline; gasoline is a mixture of C_6 to C_{10} HCs, whereas motor oil is a mixture of C_{18} to C_{25} HCs. Another facet of the two-cycle engine is that combustion takes place at a lower temperature than the four-cycle engine. Because of its high molecular weight, the
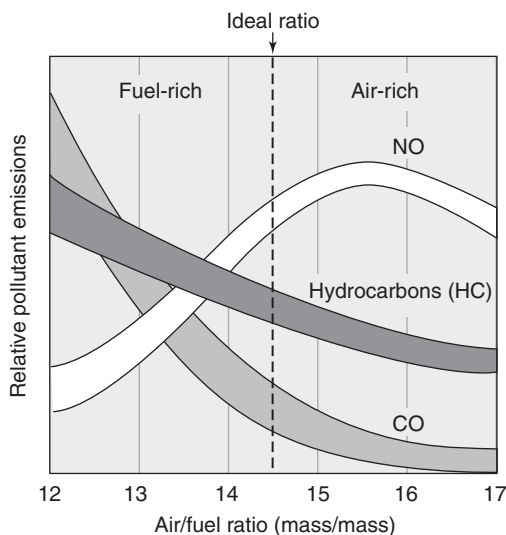

Figure 4.3 Emission of air pollutants from four-cycle internal combustion engine as the air/fuel ratio is varied.
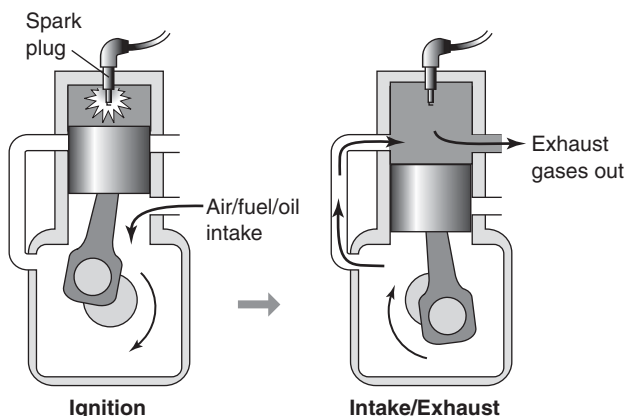
2ND REVISE

Figure 4.4 The steps in one complete cycle of a two-cycle internal combustion engine. Lubricating-oil is added to gasoline in a 1:40 ratio.

motor oil is not vaporized and burned as efficiently as the gasoline. The two-step cycle requires that the exhaust gases from combustion are leaving the cylinder through the exhaust port while the fresh air/fuel mixture for the next power stroke is simultaneously entering the cylinder from the side arm. All of these factors act together to produce exhaust gases that have a very high unburned HC concentration.

A comparison of the emissions from marine outboard two- and four-cycle engines of the same horsepower was made. The results of those tests (Table 4.1) show that the exhaust of a two-cycle engine contained more than 12 times the amount of HCs than a four-cycle engine of the same power.

The U.S. Environmental Protection Agency (EPA) estimates that gasoline-burning engines in recreational vehicles such as snowmobiles, all-terrain vehicles, boats, and personal watercraft are responsible for approximately 13% of the HCs that mobile sources emit. In 2008, EPA issued new regulations intended to reduce emissions from small engines used in

Table 4.1

Emissions from Marine Outboard Engines

Type of Marine Outboard Engine	CO(g)	NO_x(g)	HC(g)
Two-cycle engine	165	0.3	89
Four-cycle engine	127	0.7	7

Source: Juttner FD et al. Emissions of two- and four-stroke outboard engines-1: quantification of gases and VOC. *Water Research* 1995;29:1976–1982.

2ND REVISE

newly manufactured lawnmowers, power garden equipment, and outboard marine engines by 35%. The new standards will take effect in 2011 for smaller engines or 2012 for larger engines. EPA estimates that by 2030, the annual reduction to be 600,000 tons of HCs, 130 tons of NO_x and 5,500 tons of particulates ($PM_{2.5}$) as a result of the new regulation.

■ Automobile Pollutants and the Catalytic Converter

Motor vehicles are a major source of CO, NO_x, and volatile HCs. Since 1975, when all new cars in the United States were required by law to be equipped with a catalytic converter, emissions of those pollutants have been reduced significantly. Table 4.2 shows that today's cars emit 95% less pollutants than pre-1970 vehicles, despite the fact that the number of miles traveled has almost doubled in the last 20 years.

NO$_x$ emissions are difficult to reduce. As was stated before, the amount of NO_x produced by a four-cycle engine is near its maximum at the ideal, stoichiometric air/fuel ratio. One approach to lowering both NO and HC is by a two-stage combustion process. The first step is to operate the system rich in fuel, and the second step is rich in air. This system burns the fuel completely, but not at a high enough temperature to produce as much NO_x. The "stratified-charge" engine uses this design to make modest reductions in NO_x emissions.
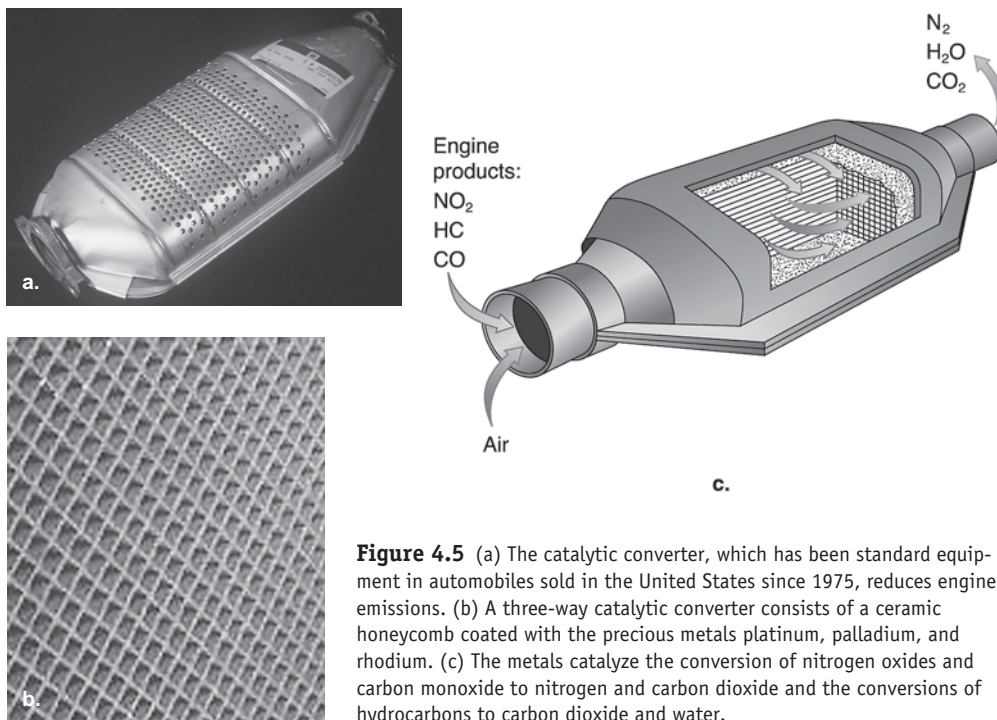
Another way to reduce emissions is by use of the three-way **catalytic converter** (in use since 1981), so named because it simultaneously reduces the amount of HC, NO_x, and CO in the exhaust stream. Hot exhaust gases from the engine pass through the converter before they enter the muffler. The converter is a very fine honeycomb structure made of ceramic coated with the precious metals platinum (Pt), palladium (Pd), and rhodium (Rh), which act as catalysts (Figure 4.5).

Table 4.2

Emission Standards for Light-Duty Vehicles (Passenger Cars)

Year	Federal Standards				California Standards			
	HCs	CO	NO$_x$	Evaporative HCs	HCs	CO	NO$_x$	Evaporative HCs
<1970	10.6	84	4.1	>45	10.6	84	4.1	>45
1970	4.1	34			4.1	34		
1975	1.5	15	3.1	2	0.9	9	2.0	2
1980	0.41	7.0	2.0	2	0.39	9	1.0	2
1985	0.41	3.4	1.0	2	0.39	7	0.4	2
1990	0.41	3.4	1.0	2	0.39	7	0.4	2
1993	0.41	3.4	1.0	2	0.25	3.4	0.4	2
2000	0.41	3.4	0.4	2	0.25	3.4	0.4	2

All values reported in grams per mile except for evaporative HCs, which are expressed as grams per test.

2ND REVISE

Figure 4.5 (a) The catalytic converter, which has been standard equipment in automobiles sold in the United States since 1975, reduces engine emissions. (b) A three-way catalytic converter consists of a ceramic honeycomb coated with the precious metals platinum, palladium, and rhodium. (c) The metals catalyze the conversion of nitrogen oxides and carbon monoxide to nitrogen and carbon dioxide and the conversions of hydrocarbons to carbon dioxide and water.

The catalytic converter has two chambers in succession. As the gases enter, Rh catalyzes the reduction of NO_x to nitrogen gas by hydrogen, which is generated at the surface of the Rh catalyst by the reaction of water on unburned HC molecules.

$$HCs + H_2O \rightarrow H_2 + CO$$

$$2\ NO + 2\ H_2 \rightarrow N_2 + 2\ H_2O$$
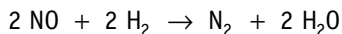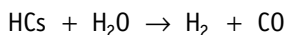
Then air is injected into the exhaust stream to provide oxygen that, in the presence of the Pt and Pd catalysts, oxidizes CO to carbon dioxide and HCs to water and carbon dioxide.

$$2\ CO + O_2 \rightarrow 2\ CO_2$$

$$HC + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$$
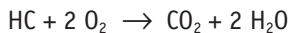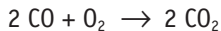
The overall reaction for the reduction of NO and the oxidation of CO can be written as follows:

$$2\ NO + 2\ CO \xrightarrow{\text{Rh, Pt, Pd catalysts}} N_2 + 2\ CO_2$$
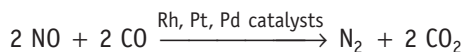
The oxidation of a typical gasoline HC, octane, occurs as follows:

$$2\ C_8H_{18} + 25\ O_2 \xrightarrow{\text{Pt, Pd catalysts}} 16\ CO_2 + 18\ H_2O$$
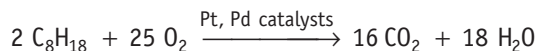
Automobiles using catalytic converters must have their air/fuel ratio set at 14.8:1. If the amount of air is increased (leaner), then CO and HCs are converted efficiently, but NO_x is not. If the amount of air is reduced (richer), the reverse is true.

Under normal driving conditions, the exhaust gases heat the catalytic converter. It operates at optimum efficiency in a temperature range of 350°C to 600°C. At 25°C, the efficiency of the catalytic converter is near zero. This means, of course, that the catalytic converter is ineffective when starting a cold engine and that its efficiency is low during engine warm-up.

Pt and Rh are very expensive, but because they are not used up, the small amounts needed last a long time. Replacement of a catalytic converter can cost more than $1000. Lead-free gasoline must be used in cars fitted with catalytic converters because lead coats and inactivates the catalysts.

Federal standards for automotive emissions became law in 1970. Table 4.2 lists the emission standards and the year that they were required. Notice that the amount of emissions allowed in the year 2000 for HC and CO are only one-tenth of what the original 1970 standard allowed. The catalytic converter has been credited with bringing significant reductions in automotive emissions. Today's catalytic converters remove 96% of CO and HCs and 76% of NO_x from auto exhausts. Even better results will have to be achieved in the future to meet the requirements of the 1990 Clean Air Act Amendments.

■ Sulfur Dioxide (SO_2)

Sources of SO_2

The release of SO_2 to the atmosphere is the primary cause of acid rain in the United States. Fossil fuel combustion at electric power-generating plants accounts for about 70% of the emissions; industrial sources contribute approximately 23% (Figure 4.1).

Coal, oil, and all other fossil fuels naturally contain some sulfur because the plant materials from which they were formed included sulfur-containing compounds. Coal frequently contains additional sulfur in the form of the mineral pyrite (FeS). Coal mined in the United States is typically between 1% and 4% (by weight) sulfur. The percentage is lower in coal from the western states than in coal mined in the central and eastern states. When sulfur-containing coal is burned, the sulfur is oxidized to SO_2:

$$S + O_2 \rightarrow SO_2$$
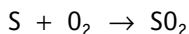
Natural sources account for approximately half of all SO_2 emissions. Table 4.3 shows that hydrogen sulfide produced as an end product of the anaerobic decomposition of sulfur-containing organic matter by microorganisms is the main source. After entering the atmosphere, hydrogen sulfide is oxidized to SO_2:
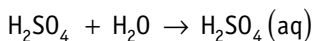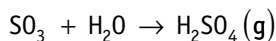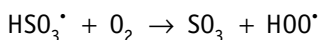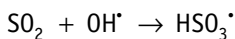
$$2 H_2S + 3 O_2 \rightarrow 2 SO_2 + 2 H_2O$$
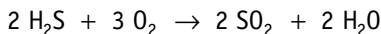
Volcanic eruptions are another more localized natural source of SO_2. It has been estimated that the eruption of Mt. Pinatubo in the Philippines in June 1991 (Figure 4.6) injected as much as 25 million tons of SO_2 into the stratosphere, where it was converted into sulfuric acid aerosols.

2ND REVISE

Table 4.3

End Products of Decomposition of Organic Compounds under Aerobic and Anaerobic Conditions

Element in Organic Compound	End Product(s) of Decomposition	
	Aerobic conditions	Anaerobic conditions
Carbon (C)	CO_2	CH_4
Nitrogen (N)	NO_3^-	NH_3 and amines
Sulfur (S)	SO_4^{2-}	H_2S
Phosphorus (P)	PO_4^{3-}	PH_3 and other phosphorus compounds

Fate of Atmospheric SO_2: Acid Rain

SO_2 in the atmosphere reacts with oxygen to form sulfur trioxide (SO_3), which then reacts readily with water vapor or water droplets to form sulfuric acid. The mechanism involves hydroxyl radicals, and the sequence of reactions can be written as follows:

$$SO_2 + OH^{\bullet} \rightarrow HSO_3^{\bullet}$$

$$HSO_3^{\bullet} + O_2 \rightarrow SO_3 + HOO^{\bullet}$$

$$SO_3 + H_2O \rightarrow H_2SO_4\,(g)$$

$$H_2SO_4 + H_2O \rightarrow H_2SO_4\,(aq)$$

Sulfuric acid in the atmosphere becomes concentrated near the base of clouds, where pH levels as low as 3 (approximately the same pH as orange juice) have been recorded. Thus,

Figure 4.6 The eruption of Mt. Pinatubo in the Philippines in June 1991 ejected huge quantities of sulfur dioxide and ash into the atmosphere.

2ND REVISE

cloud-enshrouded, high-altitude trees and vegetation may be exposed to unusually high acidity. Because rain is made of moisture from all cloud levels, it is less acidic than moisture at the lower cloud levels.

Some of the atmospheric SO_2 dissolves if there is a significant amount of water in the air. In this case, most of the oxidation of SO_2 to H_2SO_4 occurs in the liquid phase rather than the gas phase. When SO_2 dissolves in water, some of it forms sulfurous acid (H_2SO_3):

$$SO_2(g) + H_2O(aq) \rightleftharpoons H_2SO_3(aq)$$
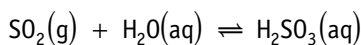
The concentration of H_2SO_3 is determined by the equilibrium constant for this reaction. Whenever gases are dissolved in water, the equilibrium constant is expressed as a Henry's law constant K_H, which for this case is equal to 1.0 M/atm at 25°C and is defined as follows:

$$K_H = \left[H_2SO_3(aq)\right]/P$$

Where P is the atmospheric partial pressure of SO_2 (which is usually approximately 0.1 ppm), which at atmospheric pressure is a partial pressure of 1.0×10^{-7} atm. Thus,

$$1.0 \times 10^{-7} \text{ M} = \left[H_2SO_3(aq)\right] = PK_H$$

Although technically a weak acid, H_2SO_3 has a large enough Ka (1.7×10^{-2}) that in the atmospheric aerosols it subsequent ionizes to HSO_3^-, bisulfite ion:

$$H_2SO_3(aq) \rightleftharpoons HSO_3^-(aq) + H^+(aq)$$
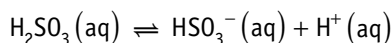
Because of the equilibrium between gaseous SO_2 and dissolved $H_2SO_3(aq)$, the $[H_2SO_3(aq)]$ corresponds to only the H_2SO_3 that does not ionize to bisulfite, and it remains at a constant 1.0×10^{-7} M.

If the equilibrium xy is the only source of acid, then it follows that

$$\left[HSO_3^-\right] = \left[H^+\right]$$

and

$$Ka = 1.7 \times 10^{-2} = \frac{\left[HSO_3^-\right]\left[H^+\right]}{\left[H_2SO_3\right]} = \frac{\left[HSO_3^-\right]^2}{1.0 \times 10^{-7}}$$

$$\left[HSO_3^-\right] = 4.1 \times 10^{-5} \text{ M}$$

Thus, the ratio of HSO_3^- to H_2SO_3 is 410:1 ($4.1 \times 10^{-5}/1.0 \times 10^{-7}$). Because

$$\left[HSO_3^-\right] = \left[H^+\right] = 4.1 \times 10^{-5} \text{ M}$$

The pH of the aerosol droplets is therefore 4.4.

2ND REVISE

On the other hand, if strong acids are present in the aerosol, they will control the pH. If strong acids are also present in the droplet, the bisulfite concentration can be easily calculated:

$$\left[HSO_3^-\right] = \frac{\left(1.7\times10^{-2}\right)\left(1.0\times10^{-7}\right)}{\left[H^+\right]}$$

because $[H^+]$ is controlled by the release of H^+ from strong acids and the $[HSO_3^-]$ is inversely proportional to $[H^+]$.

The dissolved SO_2 is oxidized by trace amount of hydrogen peroxide (H_2O_2) and ozone that are also present in the aerosol droplets to sulfate ion (SO_4^{2-}). In the next section, ozone and H_2O_2 are the products of photodissociation reactions in photochemical smog.

The bisulfite is oxidized by either H_2O_2 or ozone to produce bisulfate (HSO_4^-) ion. The reaction with H_2O_2 can be written as follows:

$$HSO_3^- + H_2O_2 \rightarrow H_2O + HSO_4^-$$
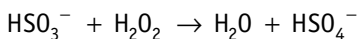
This reaction is acid catalyzed. The reaction with ozone, on the other hand, is not acid sensitive:

$$HSO_3^- + O_3 \rightarrow O_2 + HSO_4^-$$
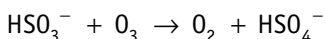
Oxidation of bisulfite in acidic aerosols (pH of less than 5) proceeds primarily by the acid-catalyzed oxidation by H_2O_2. In aerosols with higher pH, the oxidation is accomplished by O_3.

Ash particles are usually emitted together with SO_2 from electric power-generating plants. Sulfur oxides become adsorbed onto particle surfaces and may be carried many miles from their source before settling or being washed out by precipitation. Like nitric acid and nitrates formed from NO_x, sulfuric acid, sulfates, and particulates, all contribute to acid deposition.

## Effects of SO_2 on Human Health and the Environment

SO_2 is a colorless, toxic gas with a sharp, acrid odor. Exposure to it causes irritation of the eyes and respiratory passages and aggravates symptoms of respiratory disease. Children and the elderly are especially susceptible to its effects.

SO_2 is also harmful to plants. Crops such as barley, alfalfa, cotton, and wheat are particularly likely to be adversely affected. In Sudbury, Ontario, tall smokestacks (1200 feet high) are used to protect local agriculture from the release of SO_2. Unfortunately, this only produces a problem elsewhere; SO_2 emissions from North America have been detected as far away as Greenland.

Methods for Controlling Emissions of SO_2

As a result of the Clean Air Act of 1970 and amendments made to it in 1990, coal-fired electric power plants were required to make significant reductions in their emissions of SO_2. Reductions can be achieved in two ways: (1) Sulfur can be removed from coal before combustion, or (2) SO_2 can be removed from the smokestack after combustion—but before it reaches the atmosphere. The second, cheaper approach is generally chosen.

The most commonly used method is **flue-gas desulfurization (FGD)** in which sulfur-containing compounds are washed out (or scrubbed) by passing the chimney (flue) gases through a slurry of water mixed with finely ground limestone ($CaCO_3$) or dolomite [$Ca \cdot Mg(CO_3)_2$] or both. On heating, the basic calcium carbonate reacts with acidic SO_2 and oxygen to form calcium sulfate ($CaSO_4$):

$$2\ SO_2\ +\ 2\ CaCO_2\ +\ O_2\ \rightarrow\ 2\ CaSO_4\ +\ 2\ CO_2$$
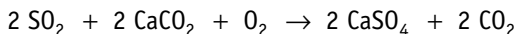
Scrubbers, which remove up to 90% of the SO_2 in the flue gas, can be quite easily and inexpensively retrofitted onto existing power plants.

A promising newer method is **fluidized bed combustion (FBC)**, a process in which a mixture of pulverized coal and powdered limestone is burned, with air being introduced to keep the mixture in a semifluid state. The limestone is converted to $CaSO_4$ according to the previous equation. In this process, however, because the coal is so finely divided, the reaction occurs at a lower temperature than in FGD, and as a result, the quantity of NO_x emitted is much lower. The disadvantage of FBC is that it cannot be added to existing power plants, but it is the preferred technology for installing in a new power plant. Both FGD and FBC have the problem of disposing of large quantities of $CaSO_4$.

Legislation to Control Emissions of SO_2

Before the passage of the Clean Air Act Amendments of 1990, the electric utility industry was unwilling to take steps to reduce its emissions of SO_2 because of cost considerations. The law required that total emissions of SO_2 be reduced to 10 million tons per year for the next ten years. Power companies could meet this requirement by installing efficient scrubbers or by switching to low-sulfur western coal, a move that would mean a loss of jobs and great economic hardship for the high-sulfur coal miners of the Ohio Valley and West Virginia. The law gave each power plant an emissions allowance that permits it to release a certain amount of SO_2 per year. To make it easier for the industry to reach the required overall reduction, the EPA introduced a free-market system of emissions trading, which allowed a plant emitting less SO_2 than its allowance to sell the difference to a plant that is emitting more than its allowance. This trading of pollution reduction credits allowed the lower overall emission levels required by law to be achieved, but the disadvantage is that the oldest and dirtiest plants can continue to release unacceptably high levels of pollution by buying credits from newer, cleaner plants.

Between 1983 and 2002, emissions of SO_2 from burning fossil fuels fell by almost 50% in Europe and by 33% in the United States. During this same period, however, emissions in the developing countries more than doubled and are expected to rise further as populations in these countries increase and they become more industrialized. China released 25 million tons of SO_2 in 2005 and is now the largest producer of atmospheric SO_2. China's SO_2 emissions have increased 27% in the period 2000 to 2006.

■ Industrial Smog

Particulate matter and SO_2 can be a deadly combination. Released into the atmosphere together when coal is burned, they can form **industrial smog** (sometimes called *London smog*), a mixture of fly ash, soot, SO_2, and some VOCs.

In the 19th and 20th centuries, industrial smog was common in the industrial centers of Europe and the United States. It formed in winter, typically in cities where the weather was cold and wet. Visibility was often reduced to a few yards, and people in factory towns lived under a pall of black smoke (Figure 4.7).

Photochemical Smog

The origin of **photochemical smog** is quite different from that of industrial smog. Typically, photochemical smog develops as a yellow-brown haze in hot sunny weather in cities, such as Los Angeles, where automobile traffic is congested (Figure 4.8). The reactions that led to its formation are initiated by sunlight and involve the HCs and NO_x emitted in automobile exhaust. NO_2 is responsible for the brownish color of the haze.

Figure 4.7 Industrial smog is created by the burning of coal and is made up primarily of fly ash, soot, and sulfur dioxide.

Production of Hydroxyl Radicals

It is well understood that solar energy is required for smog production. By the time sunlight reaches the surface of the Earth, all of the high-energy UV light has been absorbed in the stratosphere. As can be seen in Figure 4.9, NO_2 is the only automobile emission that is capable of absorbing visible light that reaches the Earth's surface.
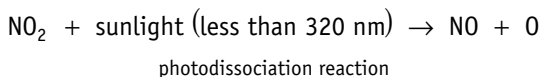
$$NO_2 + \text{sunlight (less than 320 nm)} \rightarrow NO + O$$

photodissociation reaction

Figure 4.8 Photochemical smog forms in cities such as Los Angeles when nitrogen oxides and hydrocarbons in the air interact in the presence of sunlight to form a yellow-brown haze.
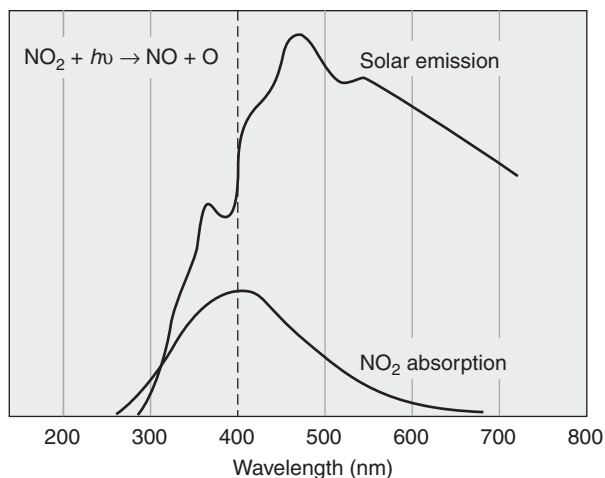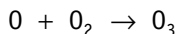
2ND REVISE

**Figure 4.9** At $\lambda < 400$ nm, NO_2 absorbs sunlight to produce oxygen atoms.

The O atoms react immediately with atmospheric oxygen, O_2, producing ozone, O_3, in the lower stratosphere.

$$O + O_2 \rightarrow O_3$$

Because each molecule of ozone formed requires a NO_2 to photodissociate, this pathway cannot produce ozone concentrations that are higher than that of the NO_2 itself. Furthermore, the NO produced from the photodissociation reaction can react with the ozone to reduce its concentration even more as it reacts to produce more NO_2.

$$O_3 + NO \rightarrow NO_2 + O_2$$
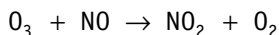
The ozone produced absorbs light in the blue region of the visible spectrum (less than 310 nm) and photodissociates:
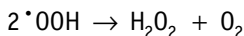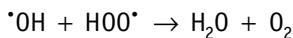
$$O_3 \rightarrow O_2 + O$$
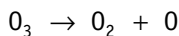
The oxygen atom produced (which has six electrons) reacts with water vapor in the atmosphere and abstracts a hydrogen atom (with its electron), producing a hydroxyl radical (seven electrons).

$$O + H_2O \rightarrow 2\ ^{\cdot}OH\ \left(\text{hydroxyl radical}\right)$$
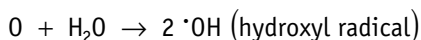
By this pathway, one NO_2 molecule produces two hydroxyl radicals.

The concentration of hydroxyl radicals does not continue to increase out of control because there are termination reactions that remove it from the troposphere. It can react with other radical species in the troposphere:

2ND REVISE

$$\cdot OH + \cdot NO_2 \rightarrow HNO_3$$

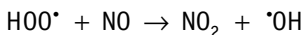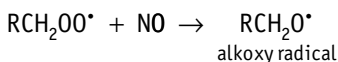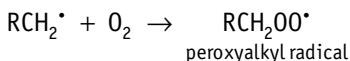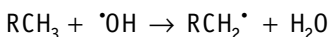$$\cdot OH + HOO\cdot \rightarrow H_2O + O_2$$

$$2\cdot OOH \rightarrow H_2O_2 + O_2$$
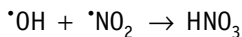
The products of these reactions are very soluble in water and are removed from the troposphere during precipitation. Because hydroxyl radical production is a photochemical reaction, nightfall also causes the reaction sequence to stop.

Unburned HCs in automobile exhaust (represented by RCH_3 in the following equation) react with hydroxyl radicals to form a number of secondary pollutants, including the HC radical $RO_2\cdot$. This radical then reacts with NO to form aldehydes and the hydroperoxide radical ($HO_2\cdot$). The step wise mechanism is as follows:

$$RCH_3 + \cdot OH \rightarrow RCH_2\cdot + H_2O$$

$$RCH_2\cdot + O_2 \rightarrow \quad RCH_2OO\cdot$$
$$\text{peroxyalkyl radical}$$

$$RCH_2OO\cdot + NO \rightarrow \quad RCH_2O\cdot$$
$$\text{alkoxy radical}$$

$$RCH_2O\cdot + O_2 \rightarrow \quad RCHO \quad + \quad \cdot OOH$$
$$\text{aldehyde} \quad \text{hydroperoxyl}$$

$$HOO\cdot + NO \rightarrow NO_2 + \cdot OH$$

Each step in this reaction produces a radical. The overall reaction is obtained by summing these individual steps.

$$RCH_3 + 2 O_2 + 2 NO \rightarrow RCHO + 2 NO_2 + H_2O$$
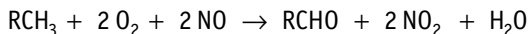
One NO_2 produces two hydroxyl radicals by the following equation:

$$NO_2 + H_2O \rightarrow NO + 2\cdot OH$$
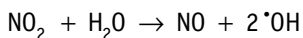
Multiply this equation by 2 and add it to the previous equation and the following is obtained:

$$RCH_3 + 2 O_2 + H_2O \rightarrow RCHO + 4\cdot OH$$
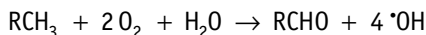
This reaction produces four hydroxyl radicals for every HC reacted. This is a catalytic reaction. A very small number of radicals can produce a large amount of product through the production of four radicals per cycle.

Reactions of Hydroxyl Radicals with HCs

Abstraction of Hydrogen

Hydroxyl radicals will react with certain unburned HCs from the automobile's exhaust depending on the number and type of C—H bonds in the HC. Not all C—H bonds are equally

reactive. To compare the reactivity of HC molecules, the dissociation energy of the C—H bond must be known. The dissociation reaction can be written as follows:

R — H → R˙ + H˙
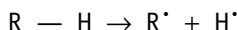
The stability of the R radical depends on its structure. An unpaired electron on a carbon atom is stabilized if that carbon atom is attached to other carbon substituents. For this reason, a tertiary C—H bond is more easily dissociated than is a secondary C—H bond, and the secondary is more easily dissociated than a primary C—H bond. Table 4.4 lists the dissociation energy of certain C—H bonds.

Aromatic HCs, such as benzene, have a high C—H dissociation energy because of hybridization. The hybridization on the aromatic carbons is sp^2, not the sp^3, of aliphatic carbons. The aromatic sp^2 C—H bonds are shorter and stronger because they have more character.

Because the dissociation energy is the highest for benzene and HCs with mostly methyl C—H (ethanol, methanol, ethane) bonds, the reaction rate with hydroxyl radical is the lowest for these HCs. As the number of secondary C—H bonds increase (more methylenes), the rate of the reaction increases, and the rate of reaction follows the trend, n-butane < pentane < n-hexane < n-heptane < n-octane. Higher reaction rates are observed for methyl substituted benzenes, such as toluene and xylene. The methylene radicals formed by the abstraction of hydrogen by the hydroxyl radical are stabilized by the aromatic ring. The free electron on the methyl carbon, which is adjacent to the benzene ring, is delocalized over the entire benzene pi orbital system.

Addition to Double Bonds

The reaction of hydroxyl radicals with alkenes proceeds at even a faster rate than the hydrogen abstraction reactions for HCs. This reaction is not a hydrogen atom extraction but rather an addition of the hydroxyl radical to the double bond. The pi electrons in the double bond are not as tightly bound and offer a site for interaction with radicals. The mechanism shown here is for the addition reaction of hydroxyl radical with propene (propylene).

Table 4.4		
Dissociation Energy of C—H Bonds		
Compound	**Bond**	**Energy (kJ/mol)**
Methane	$H_3C—H$	427
Ethane	$H_3CH_2C—H$	406
Propane (methylene)	$(H_3C)_2HC—H$	393
Methanol	$HOH_2C—H$	393
Benzene	$H_5C_5C—H$	427
Toluene	$H_5C_6H_2C—H$	326

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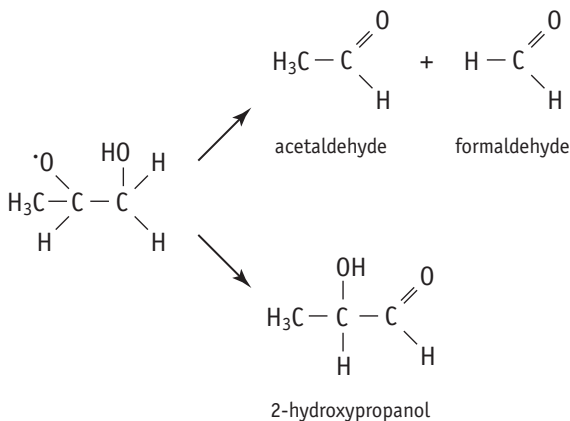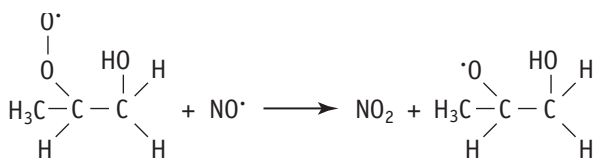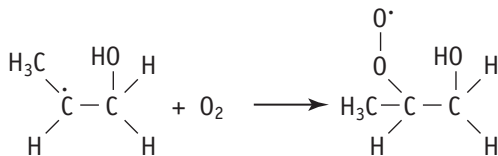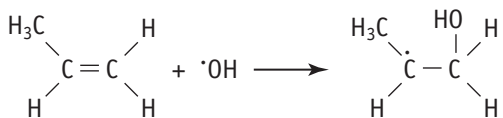
The NO_2 produced in this reaction can go on to make more ozone, and the products of this addition reaction, acetaldehyde, formaldehyde, and 2-hydroxypropanol, all go on to form other pollutants in secondary smog-forming reactions.

Secondary Smog-Forming Reactions

In the previous reaction sequences, aldehydes were one of the products produced by the attack of hydroxyl radicals on HCs. Once formed, these primary reaction products can undergo further reaction in the troposphere. The following reaction sequence takes place for all aldehydes formed. Acetaldehyde is used as an example.

2ND REVISE

$$CH_3CHO + {}^{\bullet}OH \rightarrow CH_3\overset{\bullet}{C}O + H_2O$$

$$CH_3\overset{\bullet}{C}O + O_2 \rightarrow CH_3COOO^{\bullet}$$

$$CH_3COOO^{\bullet} + {}^{\bullet}NO2 \longleftrightarrow CH_3COONO_2$$
$$\text{PAN}$$
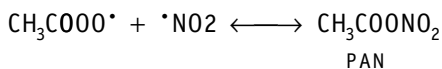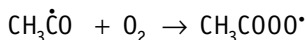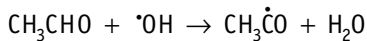
The drawn-out structure of **peroxyacetyl nitrate (PAN)** is as follows:

$$\overset{\displaystyle O}{\underset{\displaystyle CH_3-C-O-O-NO_2}{\|}}$$
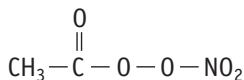
PAN is the component of smog that causes major eye irritation. PANs are relatively stable molecules and have long lifetimes in cooler air. Because of this, they may travel long distances. In warmer climates, the PANs break down to release NO_2 and can begin the cycle described previously producing additional ozone and hydroxyl radicals. In this way, PANs can be considered a reservoir for NO_x species. Ozone, aldehydes, and PANs all contribute to the harmful effects of photochemical smog, but ozone—the pollutant produced in greatest quantity—causes the most serious problems.

Ozone: A Pollutant in the Troposphere

Ozone in the stratosphere protects us from damaging ultraviolet radiation from the sun, but ozone in the troposphere is a dangerous pollutant. Ozone is a powerful oxidizing agent. It is a colorless, pungent, very reactive gas that irritates the eyes and nasal passages. People with asthma or heart disease are particularly susceptible to its harmful effects. Exposure to ozone levels as low as 0.3 ppm for one to two hours can cause fatigue and respiratory difficulties. In Los Angeles, school children are kept indoors if ozone levels reach 0.35 ppm. Fortunately, because of pollution controls, today these levels are rarely reached.

Ozone is also very toxic to plants. In California, crop damage caused by ozone and other photochemical pollutants costs the state millions of dollars a year. Ozone also damages fabrics and the rubber in tires and windshield wiper blades.

■ Temperature Inversions and Smog

Certain meteorologic and geographic conditions favor the formation of both industrial and photochemical smog. Normally, air temperature in the troposphere decreases with increasing altitude (see Figure 2.1). Warm air at the Earth's surface expands, becomes less dense, and rises. As it does so, cooler air from above flows in to replace it. In turn, the cooler air is warmed and rises. Through this process, the air is continually renewed, and pollutants are dispersed by vertical currents and prevailing winds (Figure 4.10a).

A reversal of the usual temperature pattern, called a **temperature inversion**, sometimes occurs; after an initial decrease, the air temperature, instead of continuing to decrease with increasing altitude, begins to increase. A lid of warm air forms over cooler air near the Earth's surface (Figure 4.10b). The cooler, denser layer cannot rise through the warm lid of air above it and becomes trapped, sometimes for days. There is no vertical circulation, and pollutants accumulate.
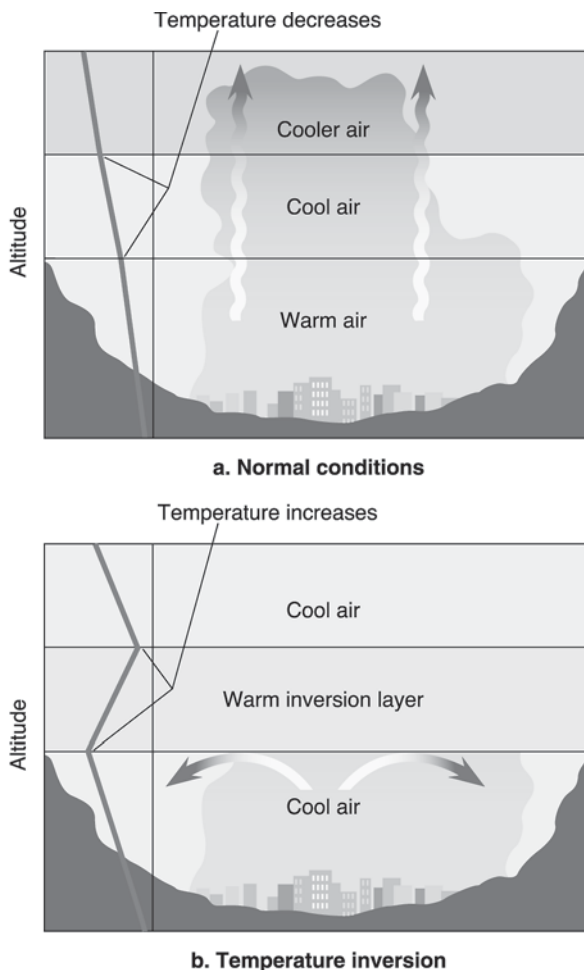
Figure 4.10 (a) Under normal atmospheric conditions, air warmed at Earth's surface rises and mixes with cooler air above. Any pollutants are dispersed upward. (b) When a temperature inversion occurs, a layer of warm air settles over cooler air, preventing it from rising. Any pollutants become trapped under the warm lid until atmospheric conditions change.

A particularly serious incident occurred in 1948 in the Donora Valley, an industrial area in Pennsylvania. As a result of a temperature inversion, industrial smog settled over the valley for five days. Many people died, and almost half of the population suffered from respiratory ailments. In 1952, a similar incident in London resulted in 4000 deaths. In that case, smoke from coal burned for heat in homes and workplaces was the main cause of the air pollution.

If a temperature inversion occurs in an area partly surrounded by mountains (e.g., Los Angeles, Denver, or Salt Lake City), photochemical smog buildup is particularly serious. Because of the encircling mountains, the pollutants cannot be dispersed horizontally. They remain in a blanket over the city until the weather changes and the wind disperses the polluted air.

2ND REVISE

■ Regulating Air Pollution

The Clean Air Act of 1970 mandated air quality standards for five air pollutants: suspended particles, SO_2, CO, NO_x, and ozone. A few years later, lead was added to the list. Until a phaseout began in 1975, lead was added to gasoline to prevent knocking, and large quantities of lead were released to the atmosphere in engine exhausts, causing serious problems in urban areas. Despite great improvements in air quality, including a dramatic drop in lead emissions (Figure 4.11), many urban areas were not meeting the desired standards by the late 1980s. Thus, in 1990, tougher standards were established in the Clean Air Act Amendments.

A significant problem not addressed by the original Act was the emission by industry of thousands of tons of unregulated hazardous chemicals, many of which are suspected of being carcinogens. The 1990 amendments require that industries emitting any of 189 specifically named toxic chemicals install control devices that are capable of reducing these emissions by at least 90%.

As noted earlier, the 1990 amendments include other important provisions: Coal-burning power plants must reduce annual SO_2 emissions to 10 million tons by 2000, and new cars will have to meet increasingly strict emission standards. Currently, light trucks (sport utility
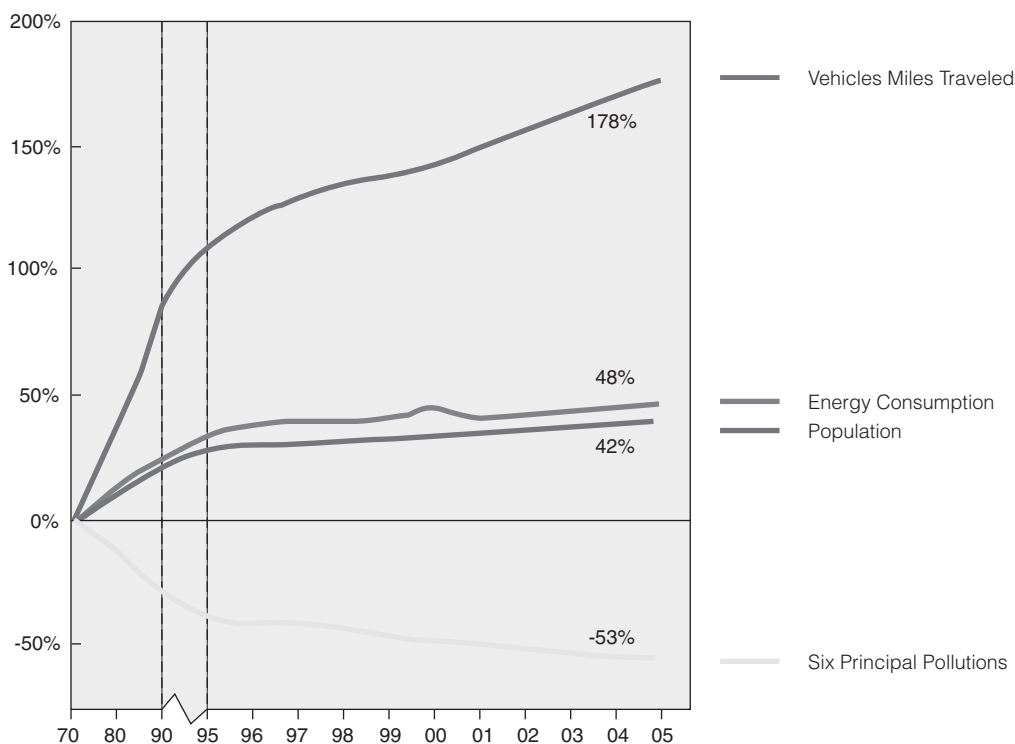

Figure 4.11 Reductions in six air pollutants, using 1977 values as 100% levels. The most dramatic reduction was in lead emissions. Adapted from B. J. Nebel, Environmental Science: The Way the World Works, 3rd ed. (Englewood Cliffs, NJ: Prentice Hall, 1990).

2ND REVISE

vehicles, minivans, and pickups) emit three times as much pollution as the average passenger car because they are not required to meet the same emissions standards. In May of 2007, President George W. Bush issued an executive order that would cut greenhouse gas emissions (GHGs) released by motor vehicles. The executive order was issued in response to a Supreme Court order to the EPA requiring the EPA to take action under the Clear Air Act to regulate GHGs from motor vehicles. The Bush order proposed a 20-in-10 regulation, which is a mandate to reduce gasoline consumption by 20% over the next ten years. The Bush proposal would set a mandatory fuel standard that requires 35 billion gallons of renewable (ethanol) and alternate fuels to be available by 2017, which would replace 15% of the projected annual gasoline use in the United States. In addition, he proposed to increase fuel efficiency by "reforming and modernizing" the Corporate Average Fuel Economy (CAFE) standards for cars and by extending the current Light Truck Rule. These rule changes were intended to bring another 5% reduction in gasoline consumption. Late in 2008, the White House announced the Bush administration would not implement the executive order by the end of the Bush presidency. This announcement caused the *Washington Post* to suggest that the acronym EPA should stand for the "Emitters Protection Agency."

Since 1992, cities with unacceptably high emissions of CO have been required to sell gasoline containing 2.7% oxygen during the winter months to reduce these emissions. The oxygen content can be increased by adding ethanol or methanol, but MTBE (methyl *t*-butyl ether) is preferred because of its higher octane rating. As a result of its increased oxygen content, this reformulated gasoline emits less CO when it is burned than does regular gasoline. However, MTBE—a known animal carcinogen—has been detected in groundwater in several states after gasoline spills and leaks from underground storage tanks. Both California and Maine began phasing out the use of MTBE, and in 1999, the EPA recommended a substantial reduction in its use because of the threat to human health.

The Clean Air Act and its amendments required the EPA to establish National Ambient Air Quality Standards for the major pollutants (Table 4.5). For each pollutant, these standards specified a concentration, averaged over a specified time period, which must not be exceeded. At the end of 1996, the EPA proposed even more stringent standards for ozone and particulates: The allowable level for ozone was lowered from 0.12 to 0.08 ppm, and the size (diameter) of particulates covered by the standards was reduced from 10 to 2.5 μm. Because of the costs involved and questions about the potential health benefits, the tougher standards are opposed by industry, state governors, and cities, and have not been adopted.

In 1998, the EPA announced further new rules, this time aimed at reducing the flow of smog-causing emissions from 22 industrial eastern states across state borders. Power plants in the targeted states would have to limit emissions of oxides of NO_x, which are precursors of both ozone and photochemical smog.

Air pollution is a worldwide problem that is far more serious in many other countries than it is in the United States. For example, in Mexico City, São Paulo (Brazil), and many industrial cities in China, Eastern Europe, and the former Soviet Union, people live under a pall of toxic smog. The sun is obscured. Severe respiratory ailments are common, and infant mortality rates are high; often there are few complaints because the smog and pollution mean jobs.

Cleaning the atmosphere will be costly, and economic priorities will need to be readjusted, particularly for the developing countries of the world. However, the alternative of continuing to pour pollutants into the air will have far more serious consequences.

Table 4.5

National Ambient Air Quality Standards

Pollutant	Time Period*	Limit Set in 1992	2009 Limit[†]
Carbon monoxide	8 hours	9 ppm	no change
	1 hour	35 ppm	no change
Lead	3 months	1.5 µg/m^3	no change
Nitrogen oxides	1 year	0.05	no change
Ozone	1 hour	0.12 ppm	no change
	8 hours	none	0.08 ppm
Sulfur dioxide	1 year	0.03 ppm	no change
	24 hours	0.14 ppm	no change
Inhalable Particulates 10 µm diameter or less (PM10)	1 year	50 µg/m^3	no change
	24 hours	150 µg/m^3	no change
Inhalable Particulates 2.5 µm diameter or less (PM10)	1 year	none	15 µg/m^3
	24 hours	none	35 µg/m^3

* Period over which the concentrations are measured and averaged.
[†] New standards set in 2006.
Source: www.epa.gov.

■ Indoor Air Pollution

You might expect to be safer from air pollutants indoors, but in today's well-sealed homes and offices, this is often not the case. In buildings where there is little or no circulation of fresh air, pollutants may accumulate to dangerous levels. Figure 4.12 shows sources of the major indoor pollutants.

Smoking is a particularly dangerous cause of indoor air pollution. In addition to nicotine, **environmental tobacco smoke** contains high levels of all the primary pollutants (CO, NO_2) and particulates associated with combustion. Tobacco smoke contains many VOCs such as aldehydes (formaldehyde), ketones (acetone), HCs, and organic acids. Because the tobacco is tightly paced inside a paper wrapper, air cannot reach the burning tobacco easily, and the combustion process takes place at a lower temperature unless the smoker draws the air through the cigarette. Consequently, sidestream smoke (emitted when the cigarette is burning but not being drawn on) actually contains more products of incomplete combustion than does the smoke that is inhaled. For this reason, many localities have issued smoking bans in restaurants and public buildings to limit the exposure of their customers to second hand smoke. Of increasing concern is the risk of smoking to nonsmokers.

Because of the low temperature of combustion, cigarette smoke contains tar, which contains particulates consisting of large HC molecules and nicotine. Smoking also contributes
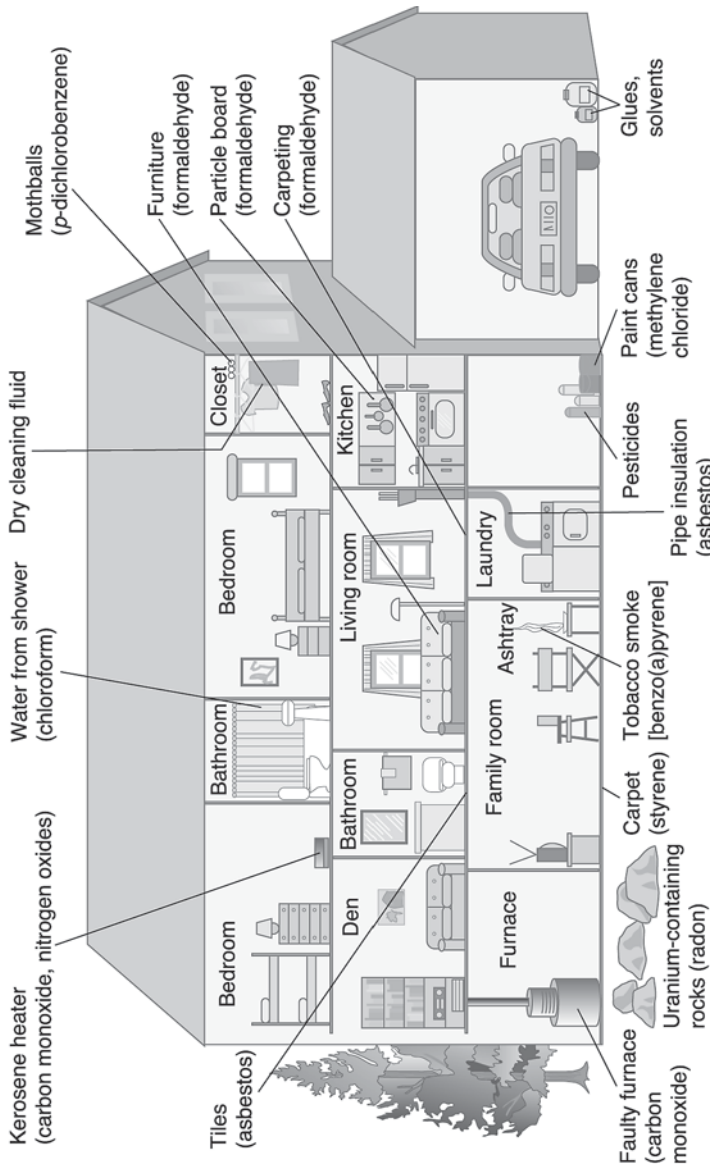
2ND REVISE

Figure 4.12 Sources of major indoor air pollutants.

to the amount of respirable particulate matter inside a room. Studies have established a relationship between the level of indoor $PM_{2.5}$ (particulate matter 2.5 μm or less in diameter from all sources) and respiratory illness. Young children of smokers, for example, are more likely to suffer from asthma and bronchitis than are children of nonsmokers. Smoking causes emphysema, lung cancer, and coronary heart disease.

Gas stoves, kerosene heaters, wood stoves, and faulty furnaces are potential sources of NO_x and CO. Polynuclear aromatic hydrocarbons (PAHs) are also released by the combustion of organic material (biomass). Because there are many individual PAH molecules, measuring the concentration of one PAH, benzo(a)pyrene, is often used to indicate the collective concentration of all PAHs in the air. Homes with wood stoves or open fireplaces often have elevated levels benzo(a)pyrene.

Paint, paint strippers and thinners, gasoline, and pesticides, which many people store in their basements, release harmful vapors and dust particles. Formaldehyde, a toxic and irritating gas, is released from the polymers that are used to manufacture certain types of insulation foam and furniture stuffing and from newly installed carpeting and paneling. Clothes brought home from the dry cleaners may also cause a problem, as traces of harmful volatile solvents used in the cleaning process are retained by the garments and later released into the atmosphere. Even taking a hot shower or bath may be harmful because chloroform can be released from chlorine-treated water.

Another particularly insidious indoor air pollutant is radon (discussed in Chapter 11). It is released through the foundation walls into basements from uranium-containing minerals in the ground. Asbestos (discussed in detail in Chapter 17) is an inhalation hazard that is still present in some older homes, where it was used as an insulating material for furnaces and pipes.

Apart from preventing pollutants from entering a building in the first place, one way to control indoor air pollution is to install air-to-air heat exchangers that circulate fresh air without adversely upsetting the temperature of the indoor air. Air conditioners, smoke removers, and vacuum cleaners all help to reduce indoor air pollutants.

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■ Keywords

acid rain	environmental tobacco smoke
air pollutant	flue-gas desulfurization (FGD)
carbon monoxide	fluidized bed combustion (FBC)
catalytic converter	four-cycle internal combustion engine

2ND REVISE

free radicals
hemoglobin (Hb)
hydroxyl radical
industrial smog
nitrogen oxides
operation of the two-cycle engine
operation of the four-cycle internal
   combustion engine

ozone
peroxyacetyl nitrate (PAN)
photochemical smog
primary and secondary air pollutants
sulfur dioxide
temperature inversion
terpenes
volatile organic compounds (VOCs)

■ Questions and Problems

1. Define primary air pollutant. List the five primary air pollutants.
2. List the five substances that are responsible for more than 90% of air pollution in the United States. What is the major source for each of these pollutants?
3. What are the major air pollutants produced by the following industries?
   a. Trucking
   b. Electric power generation
4. Define a secondary air pollutant. List five secondary air pollutants.
5. What is a free radical? How does hydroxyl radical differ from hydroxide ion?
6. Write chemical equations to show how CO and CO_2 are formed during the burning of fossil fuels. Which gas (CO or CO_2) is produced in each of the following situations?
   a. Gasoline is burned in an automobile engine.
   b. Coal is burned in an open fireplace.
7. Assume that gasoline is octane, C_8H_{18}. Calculate the stoichiometric mass of air that is required to burn 1.0 kg of octane. Assume that air is 20% oxygen. Compute the optimum fuel/air ratio.
8. Do anthropogenic or natural sources release more CO into the troposphere?
   a. List the natural sources of CO.
   b. Describe natural processes that remove CO from the troposphere.
   c. List two reasons that CO concentrations are higher in cities than rural areas.
9. Why do almost all of the anthropogenic NO_x emissions come from combustion in internal combustion engines? Write reactions that show how NO_2 is formed from O_2 and N_2 in the engine.
10. Draw the Lewis electron dot structure for N_2O. Should it be written $N_2O^\bullet$?
11. Draw the Lewis electron dot structure for NO. Why is it written $NO^\bullet$?
12. Using chemical reactions, describe the fate of tropospheric NO_2.
13. Using schematics, describe the following:
   a. a four-cycle internal combustion engine
   b. a two-cycle internal combustion engine
14. Compare a two-cycle versus a four-cycle engine:
   a. revolutions per minute
   b. temperature of operation
   c. HC emissions
   d. Cost
15. What is the ideal air/fuel ratio for a four-cycle engine?
   a. What happens to HC emissions if the ratio is made more lean?

2ND REVISE

    b. What happens to NO_x emissions if the ratio is made more rich?

    c. What happens to fuel economy if the ratio is made more lean?

16. You are having trouble starting you car. Your auto mechanic suggests that he or she should adjust your engine so that it has a more fuel rich mixture, which will make it start easier. What effect will this have on your engine's emission of HC, NO_x, and CO?

17. Compare the emission of HC, NO_x, and CO coming from two- and four-cycle engines.

18. Why is the catalytic converter called a three-way catalytic converter?

19. Draw a diagram of a catalytic converter and describe how it reduces pollutants in automobile exhausts. Catalytic converters reduce automobile emissions by 95%. Why are there calls for devices with greater efficiency?

20. Write the following catalytic chemical reactions that occur in the catalytic converter:

    a. The removal of CO from the exhaust stream

    b. The removal of unburned octane from the exhaust stream

    c. The removal of NO from the exhaust stream

21. List the catalysts that are used in the catalytic converter. Why are they coated on a ceramic honeycomb structure?

22. Why will the use of leaded gasoline in an automobile destroy the effectiveness of its catalytic converter?

23. By how much have catalytic converters reduced the amount of CO, NO_x, and HC in automobile exhaust since 1975?

24. What are the main anthropogenic sources of SO_2? Why does the burning of coal release SO_2? Write equations to show how SO_2 reacts in the atmosphere.

25. Calculate the pH of rainwater that is in equilibrium with air that has an SO_2 concentration of 2 ppm.

26. You have measured the pH of rainwater on your campus to be 4.2. Assuming that the acidity in the rainwater is cause by SO_2, calculate the concentration of SO_2 that must be in the air in the vicinity of your campus.

27. What is the pH of an aerosol that is saturated with air that has a $[CO_2]$ concentration of 250 ppm? The $K_H = 3.4 \times 10^{-2}$ mol/L atm at 25°C.

28. Calculate the pH of rainwater that is in equilibrium with air that has an SO_2 concentration of 5.

29. What adverse effects does SO_2 have on human health?

30. Describe two methods for removing SO_2 from smokestack emissions.

31. In your opinion, is the installation of very tall smokestacks a good way to deal with hazardous industrial emissions? Explain.

32. Describe how the flue gas desulfurization process removes SO_2 from chimney gases.

33. What is FBC?

34. List two uses for the $CaSO_4$ produced from the FGD process.

35. Describe how the SO_2 emissions changed during the 1980s

    a. in the United States

    b. in Europe

    c. in developing countries

36. What two air pollutants are responsible for photochemical smog?

37. Using chemical reactions, show how tropospheric ozone is formed from the reaction of NO_2 and sunlight. Next show how the hydroxyl radical is formed.

2ND REVISE

38. How many hydroxyl radicals are produced for every HC reacted in the troposphere?
39. Write two reactions that show how the hydroxyl radical is removed from the troposphere.
40. If the concentration of OH· in air is 5×10^{-6} molecules/cm^3, calculate its concentration in ppbv and pptv (parts per trillion).
41. Write the mechanism for the production of hydroxyl radical in unpolluted air.
42. Assume that there is unburned pentane (C_5H_{12}) in automobile exhaust. Write the reaction that would occur between pentane and hydroxyl radical. Is the reaction that you wrote an addition or an abstraction reaction?
43. Which of the following HCs would react faster with hydroxyl radical? Why?
    a. Butane
    b. Octane
44. Which of the following aromatics would react faster with hydroxyl radical?
    a. Benzene
    b. Xylene
45. Assume that there is unburned 2-pentene in automobile exhaust. Write the stepwise mechanism of the reaction that would occur between 2-pentene and hydroxyl radical. What reaction products are formed?
46. Does the reaction of 2-octene and a hydroxyl radical proceed at a faster rate than the reaction between octane and hydroxyl radical? If 2-octene does react faster, by how much is the rate increased and why?
47. Write the reaction that occurs between propanol and hydroxyl radical. What products are formed?
48. Draw the structure of PAN.
49. Describe the following about PAN:
    a. Lifetime in the troposphere
    b. Breakdown products in warmer air
    c. Why it is a reservoir for NO_x?
50. What chemical is responsible for giving smog an orange brown color?
51. Use a diagram to show how a temperature inversion occurs. What geographic features promote the formation of an inversion?
52. In what year was the Clean Air Act first enacted? It mandated air pollution standards for what five air pollutants?
53. The 1990 amendments to the Clean Air Act tightened emission standards for what air pollutants?
54. What are the National Ambient Air Quality Standards?
55. Since 1992, what new EPA regulations have been mandated for cities with high levels of tropospheric CO.
56. List three chemicals that can be added to gasoline to increase its oxygen content.
57. Draw the structure of MTBE. Why is it no longer being used in gasoline in California?
58. List four classes of chemicals that are components of cigarette smoke.
59. Describe the risk to nonsmokers who inhale secondhand cigarette smoke.
60. How is the PAH concentration in indoor air measured?
61. Formaldehyde is known to irritate the eyes and cause bronchial problems. List two sources of formaldehyde in indoor air.

2ND REVISE