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11 GASEOUS INORGANIC AIR POLLUTANTS

11.1 INORGANIC POLLUTANT GASES

A number of gaseous inorganic pollutants enter the atmosphere as the result of human activities. Those added in the greatest quantities are CO, SO₂, NO, and NO₂. (These quantities are relatively small compared to the amount of CO₂ in the atmosphere. The possible environmental effects of increased atmospheric CO₂ levels are discussed in Chapter 14.) Other inorganic pollutant gases include NH₃, N₂O, N₂O₅, H₂S, Cl₂, HCl, and HF. Substantial quantities of some of these gases are added to the atmosphere each year by human activities. Globally, atmospheric emissions of carbon monoxide, sulfur oxides, and nitrogen oxides are of the order of one to several hundred million tons per year.

11.2. PRODUCTION AND CONTROL OF CARBON MONOXIDE

Carbon monoxide, CO, causes problems in cases of locally high concentrations because of its toxicity (see Chapter 23). The overall atmospheric concentration of carbon monoxide is about 0.1 ppm corresponding to a burden in the earth's atmosphere of approximately 500 million metric tons of CO with an average residence time ranging from 36 to 110 days. Much of this CO is present as an intermediate in the oxidation of methane by hydroxyl radical (see Section 9.8, Reaction 9.8.17). From Table 9.1 it may be seen that the methane content of the atmosphere is about 1.6 ppm, more than 10 times the concentration of CO. Therefore, any oxidation process for methane that produces carbon monoxide as an intermediate is certain to contribute substantially to the overall carbon monoxide burden, probably around two-thirds of the total CO.

Degradation of chlorophyll during the autumn months releases CO, amounting to perhaps as much as 20% of the total annual release. Anthropogenic sources account for about 6% of CO emissions. The remainder of atmospheric CO comes from largely unknown sources. These include some plants and marine organisms known

as siphonophores, an order of Hydrozoa. Carbon monoxide is also produced by decay of plant matter other than chlorophyll.

Because of carbon monoxide emissions from internal combustion engines, the highest levels of this toxic gas tend to occur in congested urban areas at times when the maximum number of people are exposed, such as during rush hours. At such times, carbon monoxide levels in the atmosphere have become as high as 50-100 ppm.

Atmospheric levels of carbon monoxide in urban areas show a positive correlation with the density of vehicular traffic, and a negative correlation with wind speed. Urban atmospheres may show average carbon monoxide levels of the order of several ppm, much higher than those in remote areas.

Control of Carbon Monoxide Emissions

Since the internal combustion engine is the primary source of localized pollutant carbon monoxide emissions, control measures have been concentrated on the automobile. Carbon monoxide emissions may be lowered by employing a leaner air-fuel mixture, that is, one in which the weight ratio of air to fuel is relatively high. At air-fuel (weight:weight) ratios exceeding approximately 16:1, an internal combustion engine emits very little carbon monoxide.

Modern automobiles use catalytic exhaust reactors to cut down on carbon monoxide emissions. Excess air is pumped into the exhaust gas, and the mixture is passed through a catalytic converter in the exhaust system, resulting in oxidation of CO to CO_2 .

11.3. FATE OF ATMOSPHERIC CO

It is generally agreed that carbon monoxide is removed from the atmosphere by reaction with hydroxyl radical, HO•:

$$CO + HO \bullet CO_2 + H$$
 (11.3.1)

The reaction produces hydroperoxyl radical as a product:

$$O_2 + H + M$$
 HOO• + M (11.3.2)

HO• is regenerated from HOO• by the following reactions:

$$HOO \bullet + NO \qquad HO \bullet + NO_2 \tag{11.3.3}$$

$$HOO \bullet + HOO \bullet \quad H_2O_2 + O_2 \tag{11.3.4}$$

The latter reaction is followed by photochemical dissociation of H_2O_2 to regenerate HO•:

$$H_2O_2 + h$$
 2HO• (11.3.5)

Methane is also involved through the atmospheric CO/HO \cdot / CH₄ cycle.

Soil microorganisms act to remove CO from the atmosphere. Therefore, soil is a sink for carbon monoxide.

11.4. SULFUR DIOXIDE SOURCES AND THE SULFUR CYCLE

Figure 11.1 shows the main aspects of the global sulfur cycle. This cycle involves primarily H_2S , $(CH_3)_2S$, SO_2 , SO_3 , and sulfates. There are many uncertainties regarding the sources, reactions, and fates of these atmospheric sulfur species. On a global basis, sulfur compounds enter the atmosphere to a very large extent through human activities. Approximately 100 million metric tons of sulfur per year enters the global atmosphere through anthropogenic activities, primarily as SO_2 from the com-



Figure 11.1. The global atmospheric sulfur cycle. Fluxes of sulfur represented by the arrows are in millions of metric tons per year. Those marked with a question mark are uncertain, but large, probably of the order of 100 million metric tons per year.

bustion of coal and residual fuel oil. The greatest uncertainties in the cycle have to do with nonanthropogenic sulfur, which enters the atmosphere largely as SO_2 and H_2S from volcanoes,¹ and as $(CH_3)_2S$ and H_2S from the biological decay of organic matter and reduction of sulfate. The single largest source of natural sulfur discharged to the atmosphere is now believed to be biogenic dimethyl sulfide, $(CH_3)_2S$, from marine sources.² Any H_2S that does get into the atmosphere is converted rapidly to SO_2 by the following overall process:

$$H_2S + \frac{3}{2}O_2 = SO_2 + H_2O$$
 (11.4.1)

The initial reaction is hydrogen ion abstraction by hydroxyl radical,

$$H_2S + HO \bullet \qquad HS \bullet + H_2O \tag{11.4.2}$$

followed by the following two reactions to give SO₂:

$$HS\bullet + O_2 \qquad HO\bullet + SO \tag{11.4.3}$$

$$SO + O_2 = SO_2 + O$$
 (11.4.4)

The primary source of anthropogenic sulfur dioxide is coal, from which sulfur must be removed at great expense to keep sulfur dioxide emissions at acceptable levels. Approximately half of the sulfur in coal is in some form of pyrite, FeS_2 , and the other half is organic sulfur. The production of sulfur dioxide by the combustion of pyrite is given by the following reaction:

$$4\text{FeS}_2 + 11\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$$
 (11.4.5)

Essentially all of the sulfur is converted to SO₂ and only 1 or 2% to SO₃.

11.5. SULFUR DIOXIDE REACTIONS IN THE ATMOSPHERE

Many factors, including temperature, humidity, light intensity, atmospheric transport, and surface characteristics of particulate matter, may influence the atmospheric chemical reactions of sulfur dioxide. Like many other gaseous pollutants, sulfur dioxide reacts to form particulate matter, which then settles or is scavenged from the atmosphere by rainfall or other processes. It is known that high levels of air pollution normally are accompanied by a marked increase in aerosol particles and a consequent reduction in visibility. Reaction products of sulfur dioxide are thought to be responsible for some aerosol formation. Whatever the processes involved, much of the sulfur dioxide in the atmosphere is ultimately oxidized to sulfuric acid and sulfate salts, particularly ammonium sulfate and ammonium hydrogen sulfate. In fact, it is likely that these sulfates account for the turbid haze that covers much of the eastern part of the U.S. under all atmospheric conditions except those characterized by massive intrusions of Arctic air masses during the winter months. The potential of sulfates to induce climatic change is high and must be taken into account when considering control of sulfur dioxide.

Some of the possible ways in which sulfur dioxide may react in the atmosphere are (1) photochemical reactions; (2) photochemical and chemical reactions in the presence of nitrogen oxides and/or hydrocarbons, particularly alkenes; (3) chemical processes in water droplets, particularly those containing metal salts and ammonia; and (4) reactions on solid particles in the atmosphere. It should be kept in mind that the atmosphere is a highly dynamic system with great variations in temperature, composition, humidity, and intensity of sunlight; therefore, different processes may predominate under various atmospheric conditions.

Photochemical reactions are probably involved in some of the processes resulting in the atmospheric oxidation of SO_2 . Light with wavelengths above 218 nm is not sufficiently energetic to bring about the photodissociation of SO_2 , so direct

photochemical reactions in the troposphere are of no significance. The oxidation of sulfur dioxide at the parts-per-million level in an otherwise unpolluted atmosphere is a slow process. Therefore, other pollutant species must be involved in the process in atmospheres polluted with SO₂.

The presence of hydrocarbons and nitrogen oxides greatly increases the oxidation rate of atmospheric SO_2 . As discussed in Chapter 13, hydrocarbons, nitrogen oxides, and ultraviolet light are the ingredients necessary for the formation of photochemical smog. This disagreeable condition is characterized by high levels of various oxidizing species (photochemical oxidants) capable of oxidizing SO_2 . In the smog-prone Los Angeles area, the oxidation of SO_2 ranges up to 5-10% per hour. Among the oxidizing species present which could bring about this fast reaction are HO•, HOO•, O, O₃, NO₃, N₂O₅, ROO•, and RO•. As discussed in Chapters 12 and 13, the latter two species are reactive organic free radicals containing oxygen. Although ozone, O₃, is an important product of photochemical smog, it is believed that the oxidation of SO_2 by ozone in the gas phase is too slow to be appreciable, but it is probably significant in water droplets.

The most important gas-phase reaction leading to the oxidation of SO_2 is the addition of HO• radical,³

$$HO^{\bullet} + SO_2 \qquad HOSO_2^{\bullet} \tag{11.5.1}$$

forming a reactive free radical which is eventually converted to a form of sulfate.

In all but relatively dry atmospheres, it is probable that sulfur dioxide is oxidized by reactions occurring inside water aerosol droplets. The overall process of sulfur dioxide oxidation in the aqueous phase is rather complicated. It involves the transport of gaseous SO₂ and oxidant to the aqueous phase, diffusion of species in the aqueous droplet, hydrolysis and ionization of SO₂, and oxidation of SO₂ by the following overall process, where {O} represents an oxidizing agent such as H₂O₂, HO•, or O₃ and S(IV) is SO₂(*aq*), HSO₃⁻(*aq*), and SO₃²⁻(*aq*).

$$\{O\}(aq) + S(IV)(aq) = 2H^{+} + SO_{4}^{2-}$$
 (unbalanced) (11.5.2)

In the absence of catalytic species, the reaction with dissolved molecular O_2 ,

$$\frac{1}{2}O_2(aq) + SO_2(aq) + H_2O + H_2SO_4(aq)$$
 (11.5.3)

is too slow to be significant. Hydrogen peroxide is an important oxidizing agent in the atmosphere. It reacts with dissolved sulfur dioxide through the overall reaction,

$$SO_2(aq) + H_2O_2(aq) = H_2SO_4(aq)$$
 (11.5.4)

to produce sulfuric acid. The major reaction is thought to be between hydrogen peroxide and HSO_3^- ion with peroxymonosulfurous acid, $HOOSO_2^-$, as an intermediate.

Ozone, O_3 , oxidizes sulfur dioxide in water. The fastest reaction is with sulfite ion;

$$SO_3^{2-}(aq) + O_3(aq) = SO_4^{2-}(aq) + O_2$$
 (11.5.5)

reactions are slower with $HSO_3(aq)$ and $SO_2(aq)$. The rate of oxidation of aqueous SO_2 species by ozone increases with increasing pH. The oxidation of sulfur dioxide in water droplets is faster in the presence of ammonia, which reacts with sulfur dioxide to produce bisulfite ion and sulfite ion in solution:

$$NH_3 + SO_2 + H_2O = NH_4^+ + HSO_3^-$$
 (11.5.6)

Some solutes dissolved in water catalyze the oxidation of aqueous SO_2 . Both iron(III) and Mn(II) have this effect. The reactions catalyzed by these two ions are faster with increasing pH. Dissolved nitrogen species, NO_2 and HNO_2 , oxidize aqueous sulfur dioxide in the laboratory. As noted in Section 10.10, nitrite dissolved in water droplets may react photochemically to produce HO• radical, and this species in turn could act to oxidize dissolved sulfite.

Heterogeneous reactions on solid particles may also play a role in the removal of sulfur dioxide from the atmosphere. In atmospheric photochemical reactions, such particles may function as nucleation centers. Thus, they act as catalysts and grow in size by accumulating reaction products. The final result would be production of an aerosol with a composition unlike that of the original particle. Soot particles, which consist of elemental carbon contaminated with polynuclear aromatic hydrocarbons (see Chapter 10, Section 10.4) produced in the incomplete combustion of carbonaceous fuels, can catalyze the oxidation of sulfur dioxide to sulfate as indicated by the presence of sulfate on the soot particles. Soot particles are very common in polluted atmospheres, so it is very likely that they are strongly involved in catalyzing the oxidation of sulfur dioxide.

Oxides of metals such as aluminum, calcium, chromium, iron, lead, or vanadium may also be catalysts for the heterogenous oxidation of sulfur dioxide. These oxides may also adsorb sulfur dioxide. However, the total surface area of oxide particulate matter in the atmosphere is very low so that the fraction of sulfur dioxide oxidized on metal oxide surfaces is relatively small.

Effects of Atmospheric Sulfur Dioxide

Though not terribly toxic to most people, low levels of sulfur dioxide in air do have some health effects. Its primary effect is upon the respiratory tract, producing irritation and increasing airway resistance, especially to people with respiratory weaknesses and sensitized asthmatics. Therefore, exposure to the gas may increase the effort required to breathe. Mucus secretion is also stimulated by exposure to air contaminated by sulfur dioxide. Although SO₂ causes death in humans at 500 ppm, it has not been found to harm laboratory animals at 5 ppm.

Sulfur dioxide has been at least partially implicated in several acute incidents of air pollution. In December 1930 a thermal inversion trapped waste products from a number of industrial sources in the narrow Meuse River Valley of Belgium. Sulfur dioxide levels reached 38 ppm. Approximately 60 people died in the episode, and some cattle were killed. In October 1948 a similar incident caused illness in over 40% of the population of Donora, Pennsylvania, and 20 people died. Sulfur dioxide concentrations of 2 ppm were recorded. During a five-day period marked by a temperature inversion and fog in London in December 1952, approximately 3500-4000 deaths in excess of normal occurred. Levels of SO₂ reached 1.3 ppm. Autopsies

revealed irritation of the respiratory tract, and high levels of sulfur dioxide were suspected of contributing to excess mortality.

Atmospheric sulfur dioxide is harmful to plants, some species of which are affected more than others. Acute exposure to high levels of the gas kills leaf tissue, a condition called leaf necrosis. The edges of the leaves and the areas between the leaf veins show characteristic damage. Chronic exposure of plants to sulfur dioxide causes chlorosis, a bleaching or yellowing of the normally green portions of the leaf. Plant injury increases with increasing relative humidity. Plants incur most injury from sulfur dioxide when their stomata (small openings in plant surface tissue that allow interchange of gases with the atmosphere) are open. For most plants, the stomata are open during the daylight hours, and most damage from sulfur dioxide occurs then. Long-term, low-level exposure to sulfur dioxide can reduce the yields of grain crops such as wheat or barley. Sulfur dioxide in the atmosphere is converted to sulfuric acid, so that in areas with high levels of sulfur dioxide pollution, plants may be damaged by sulfuric acid aerosols. Such damage appears as small spots where sulfuric acid droplets have impinged on leaves.

One of the more costly effects of sulfur dioxide pollution is deterioration of building materials. Limestone, marble, and dolomite are calcium and/or magnesium carbonate minerals that are attacked by atmospheric sulfur dioxide to form products that are either water-soluble or composed of poorly adherent solid crusts on the rock's surface, adversely affecting the appearance, structural integrity, and life of the building. Although both SO₂ and NO_x attack such stone, chemical analysis of the crusts shows predominantly sulfate salts. Dolomite, a calcium/magnesium carbonate mineral, reacts with atmospheric sulfur dioxide as follows:

$$CaCO_{3} \cdot MgCO_{3} + 2SO_{2} + O_{2} + 9H_{2}O$$

 $CaSO_{4} \cdot 2H_{2}O + MgSO_{4} \cdot 7H_{2}O + 2CO_{2}$ (11.5.7)

Sulfur Dioxide Removal

A number of processes are being used to remove sulfur and sulfur oxides from fuel before combustion and from stack gas after combustion. Most of these efforts concentrate on coal, since it is the major source of sulfur oxides pollution. Physical separation techniques may be used to remove discrete particles of pyritic sulfur from coal. Chemical methods may also be employed for removal of sulfur from coal. Fluidized bed combustion of coal promises to eliminate SO_2 emissions at the point of combustion. The process consists of burning granular coal in a bed of finely divided limestone or dolomite maintained in a fluid-like condition by air injection. Heat calcines the limestone,

$$CaCO_3 \qquad CaO + CO_2 \tag{11.5.8}$$

and the lime produced absorbs SO₂:

$$CaO + SO_2$$
 $CaSO_3$ (Which may be oxidized to $CaSO_4$) (11.5.9)

Many processes have been proposed or studied for the removal of sulfur dioxide from stack gas. Table 11.1 summarizes major stack gas scrubbing systems including

Process	Reaction	Significant advantages or disadvantages
Lime slurry scrubbing ²	$Ca(OH)_2 + SO_2 $ $CaSO_3 + H_2O$	Up to 200 kg of lime are needed per metric ton of coal, producing huge quantities of wastes
Limestone slurry scrubbing ²	$CaCO_3 + SO_2$ $CaSO_3 + CO_2(g)$	Lower pH than lime slurry, not so efficient
Magnesium oxide scrubbing	$\begin{array}{l} Mg(OH)_2(slurry) + SO_2 \\ MgSO_3 + H_2O \end{array}$	The sorbent can be regen- erated, which can be done off site, if desired.
Sodium-base scrubbing	$\begin{array}{ll} Na_2SO_3 + H_2O + SO_2 & 2NaHSO_3\\ 2NaHSO_3 + heat & Na_2SO_3 + \\ H_2O + SO_2 \ (regeneration) \end{array}$	No major technological limitations. Relatively high annual costs.
Double alkali ²	$2\text{NaOH} + \text{SO}_2 \qquad \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \\ \text{Ca(OH)}_2 + \text{Na}_2\text{SO}_3 \qquad \text{CaSO}_3(s) + \\ 2\text{NaOH} \text{ (regeneration of NaOH)}$	Allows for regeneration of expensive sodium alkali solution with inexpensive lime.

Table 11.1. Major Stack Gas Scrubbing Systems¹

 $^2\,$ These processes have also been adapted to produce a gypsum product by oxidation of ${\rm CaSO}_3$ in the spent scrubber medium:

$$CaSO_3 + \frac{1}{2}O_2 + 2H_2O = CaSO_4 \cdot 2H_2O(s)$$

Gypsum has some commercial value, such as in the manufacture of plasterboard, and makes a relatively settleable waste product.

throwaway and recovery systems as well as wet and dry systems. A dry throwaway system used with only limited success involves injection of dry limestone or dolomite into the boiler followed by recovery of dry lime, sulfites, and sulfates. The overall reaction, shown here for dolomite, is the following:

$$CaCO_{3}MgCO_{3} + SO_{2} + \frac{1}{2}O_{2} = CaSO_{4} + MgO + 2CO_{2}$$
 (11.5.10)

The solid sulfate and oxide products are removed by electrostatic precipitators or cyclone separators. The process has an efficiency of 50% or less for the removal of sulfur oxides.

As may be noted from the chemical reactions shown in Table 11.1, all sulfur dioxide removal processes, except for catalytic oxidation, depend upon absorption of SO_2 by an acid-base reaction. The first two processes listed are throwaway processes

For details regarding these and more advanced processes see (1) Satriana, M., New Developments in Flue Gas Desulfurization Technology, Noyes Data Corp., Park Ridge, NJ, 1982, and (2) Takeshita, Mitsuru, and Herminé Soud, FGD Performance and Experience on Coal-Fired Plants, Gemini House, London, 1993.

yielding large quantities of wastes; the others provide for some sort of sulfur product recovery.

Lime or limestone slurry scrubbing for SO_2 removal involves acid-base reactions with SO_2 . Since they were introduced during the late 1960s, wet lime flue gas desulfurization processes have been the most widely used means for removing sulfur dioxide from flue gas and are likely to remain so for the foreseeable future.⁴

When sulfur dioxide dissolves in water as part of a wet scrubbing process, equilibrium is established between SO_2 gas and dissolved SO_2 :

$$SO_2(g) = SO_2(aq)$$
 (11.5.11)

This equilibrium is described by Henry's law (Section 5.3),

$$[\mathrm{SO}_2(aq)] = \mathrm{K} \times \mathrm{P}_{\mathrm{SO}_2} \tag{11.5.12}$$

where $[SO_2(aq)]$ is the concentration of dissolved molecular sulfur dioxide; K is the Henry's law constant for SO₂; and P_{SO2} is the partial pressure of sulfur dioxide gas. In the presence of base, Reaction 11.5.11 is shifted strongly to the right by the following reactions:

$$H_2O + SO_2(aq) = H^+ + HSO_3^-$$
 (11.5.13)

$$HSO_3^ H^+ + SO_3^{-2-}$$
 (11.5.14)

In the presence of calcium carbonate slurry (as in limestone slurry scrubbing), hydrogen ion is taken up by the reaction

$$CaCO_3 + H^+$$
 $Ca^{2+} + HCO_3^-$ (11.5.15)

The reaction of calcium carbonate with carbon dioxide from stack gas,

$$CaCO_3 + CO_2 + H_2O$$
 $Ca^{2+} + 2HCO_3$ (11.5.16)

results in some sorption of CO_2 . The reaction of sulfite and calcium ion to form highly insoluble calcium sulfite hemihydrate

$$Ca^{2+} + SO_3^{2-} + \frac{1}{2}H_2O$$
 $CaSO_3 \cdot \frac{1}{2}H_2O(s)$ (11.5.17)

also shifts Reactions 11.5.13 and 11.5.14 to the right. Gypsum is formed in the scrubbing process by the oxidation of sulfite,

$$SO_3^{2-} + \frac{1}{2}O_2 \qquad SO_4^{2-}$$
 (11.5.18)

followed by reaction of sulfate ion with calcium ion:

$$Ca^{2+} + SO_4^{2-} + 2H_2O$$
 $CaSO_4 \cdot 2H_2O(s)$ (11.5.19)

Formation of gypsum in the scrubber is undesirable because it creates scale in the scrubber equipment. However, gypsum is sometimes produced deliberately in the spent scrubber liquid downstream from the scrubber.

When lime, $Ca(OH)_2$, is used in place of limestone (lime slurry scrubbing), a source of hydroxide ions is provided for direct reaction with H^+ :

$$H^+ + OH^- H_2O$$
 (11.5.20)

The reactions involving sulfur species in a lime slurry scrubber are essentially the same as those just discussed for limestone slurry scrubbing. The pH of a lime slurry is higher than that of a limestone slurry, so that the former has more of a tendency to react with CO_2 , resulting in the absorption of that gas:

$$CO_2 + OH^- HCO_3^-$$
 (11.5.21)

Current practice with lime and limestone scrubber systems calls for injection of the slurry into the scrubber loop beyond the boilers. A number of power plants are now operating with this kind of system. Experience to date has shown that these scrubbers remove well over 90% of both SO_2 and fly ash when operating properly. (Fly ash is fuel combustion ash normally carried up the stack with flue gas, see Chapter 10.) In addition to corrosion and scaling problems, disposal of lime sludge poses formidable obstacles. The quantity of this sludge may be appreciated by considering that approximately one ton of limestone is required for each five tons of coal. The sludge is normally disposed of in large ponds, which can present some disposal problems. Water seeping through the sludge beds becomes laden with calcium sulfate and other salts. It is difficult to stabilize this sludge as a structurally stable, nonleachable solid.

Recovery systems in which sulfur dioxide or elemental sulfur are removed from the spent sorbing material, which is recycled, are much more desirable from an environmental viewpoint than are throwaway systems.⁵ Many kinds of recovery processes have been investigated, including those that involve scrubbing with magnesium oxide slurry, sodium hydroxide solution, sodium sulfite solution, ammonia solution, or sodium citrate solution.

Sulfur dioxide trapped in a stack-gas-scrubbing process can be converted to hydrogen sulfide by reaction with synthesis gas (H_2, CO, CH_4) ,

$$SO_2 + (H_2, CO, CH_4) = H_2S + CO_2(H_2O)$$
 (11.5.22)

The Claus reaction is then employed to produce elemental sulfur:

$$2H_2S + SO_2 = 2H_2O + 3S$$
 (11.5.23)

11.6. NITROGEN OXIDES IN THE ATMOSPHERE

The three oxides of nitrogen normally encountered in the atmosphere are nitrous oxide (N₂O), nitric oxide (NO), and nitrogen dioxide (NO₂). Nitrous oxide, a commonly used anesthetic known as "laughing gas," is produced by microbiological processes and is a component of the unpolluted atmosphere at a level of approx-

imately 0.3 ppm (see Table 9.1). This gas is relatively unreactive and probably does not significantly influence important chemical reactions in the lower atmosphere. Its concentration decreases rapidly with altitude in the stratosphere due to the photochemical reaction

$$N_2O + h = N_2 + O$$
 (11.6.1)

and some reaction with singlet atomic oxygen:

$$N_2O + O = N_2 + O_2$$
 (11.6.2)

$$N_2O + O = 2NO$$
 (11.6.3)

These reactions are significant in terms of depletion of the ozone layer. Increased global fixation of nitrogen, accompanied by increased microbial production of N_2O , could contribute to ozone layer depletion.

Colorless, odorless nitric oxide (NO) and pungent red-brown nitrogen dioxide (NO₂) are very important in polluted air. Collectively designated NO_x, these gases enter the atmosphere from natural sources, such as lightning and biological processes, and from pollutant sources. The latter are much more significant because of regionally high NO₂ concentrations which can cause severe air quality deterioration. Practically all anthropogenic NO_x enters the atmosphere as a result of the combustion of fossil fuels in both stationary and mobile sources. Globally, somewhat less than 100 million metric tons of nitrogen oxides are emitted to the atmosphere from these sources each year, compared to several times that much from widely dispersed natural sources. United States production of nitrogen oxides is of the order of 20 million metric tons per year. The contribution of automobiles to nitric oxide production in the U.S. has become somewhat lower in the last decade as newer automobiles have replaced older models.

Most NO_X entering the atmosphere from pollution sources does so as NO generated from internal combustion engines. At very high temperatures, the following reaction occurs:

$$N_2 + O_2 = 2NO$$
 (11.6.4)

The speed with which this reaction takes place increases steeply with temperature. The equilibrium concentration of NO in a mixture of 3% O_2 and 75% N_2 , typical of that which occurs in the combustion chamber of an internal combustion engine, is shown as a function of temperature in Figure 11.2. At room temperature (27°C) the equilibrium concentration of NO is only 1.1 x 10⁻¹⁰ ppm, whereas at high temperatures it is much higher. Therefore, high temperatures favor both a high equilibrium concentration and a rapid rate of formation of NO. Rapid cooling of the exhaust gas from combustion "freezes" NO at a relatively high concentration because equilibrium is not maintained. Thus, by its very nature, the combustion process both in the internal combustion engine and in furnaces produces high levels of NO in the combustion products. The mechanism for formation of nitrogen oxides from N_2 and O_2 during combustion is a complicated process. Both oxygen and nitrogen atoms are formed at the very high combustion temperatures by the reactions

$$O_2 + M = O + O + M$$
 (11.6.5)

$$N_2 + M \qquad N^{\bullet} + N^{\bullet} + M \qquad (11.6.6)$$



Figure 11.2. Log of equilibrium NO concentration as a function of temperature in a mixture containing 75% N_2 and 3% $O_2.$

where M is a highly energetic third body that imparts enough energy to the molecular N_2 and O_2 to break their chemical bonds. The energies required for these reactions are quite high because breakage of the oxygen bond requires 118 kcal/mole and breakage of the nitrogen bond requires 225 kcal/mole. Once formed, O and N atoms participate in the following chain reaction for the formation of nitric oxide from nitrogen and oxygen:

$$N_2 + O = NO + N$$
 (11.6.7)

$$N + O_2 = NO + O$$
 (11.6.8)

$$N_2 + O_2 = 2NO$$
 (11.6.9)

There are, of course, many other species present in the combustion mixture besides those shown. The oxygen atoms are especially reactive toward hydrocarbon fragments by reactions such as the following:

$$\mathbf{RH} + \mathbf{O} \qquad \mathbf{R}^{\bullet} + \mathbf{HO}^{\bullet} \tag{11.6.10}$$

where RH represents a hydrocarbon fragment with an extractable hydrogen atom. These fragments compete with N_2 for oxygen atoms. It is partly for this reason that the formation of NO is appreciably higher at air/fuel ratios exceeding the stoichiometric ratio (lean mixture), as shown in Figure 13.3.

The hydroxyl radical itself can participate in the formation of NO. The reaction is

 $N + HO^{\bullet} = NO + H^{\bullet}$ (11.6.11)

Nitric oxide, NO, is a product of the combustion of coal and petroleum containing chemically bound nitrogen. Production of NO by this route occurs at much lower temperatures than those required for "thermal" NO, discussed previously.

Atmospheric Reactions of NO_x

Atmospheric chemical reactions convert NO_x to nitric acid, inorganic nitrate salts, organic nitrates, and peroxyacetyl nitrate (see Chapter 13). The principal reactive nitrogen oxide species in the troposphere are NO, NO_2 , and HNO_3 . These species cycle among each other, as shown in Figure 11.3. Although NO is the primary form in which NO_x is released to the atmosphere, the conversion of NO to NO_2 is relatively rapid in the troposphere.



Figure 11.3. Principal reactions among NO, NO₂, and HNO₃ in the atmosphere. ROO• represents an organic peroxyl radical, such as the methylperoxyl radical, CH_3OO •.

Nitrogen dioxide is a very reactive and significant species in the atmosphere. It absorbs light throughout the ultraviolet and visible spectrum penetrating the troposphere. At wavelengths below 398 nm, photodissociation occurs,

$$NO_2 + h$$
 $NO + O$ (11.6.12)

to produce ground state oxygen atoms. Above 430 nm, only excited molecules are formed,

$$NO_2 + h = NO_2^*$$
 (11.6.13)

whereas at wavelengths between 398 nm and 430 nm, either process may occur. Photodissociation at these wavelengths requires input of rotational energy from rotation of the NO₂ molecule. The tendency of NO₂ to photodissociate is shown clearly by the fact that in direct sunlight the half-life of NO₂ is much shorter than that of any other common molecular atmospheric species. The photodissociation of nitrogen dioxide can give rise to the following significant inorganic reactions in addition to a host of atmospheric reactions involving organic species:

$$O + O_2 + M$$
(third body) $O_3 + M$ (11.6.14)

 $NO + O_3 = NO_2 + O_2$ (11.6.15)

 $NO_2 + O_3 \qquad NO_3 + O_2$ (11.6.16)

$$O + NO_2$$
 NO + O_2 (11.6.17)

$$O + NO_2 + M = NO_3 + M$$
 (11.6.18)

$$NO_2 + NO_3 \qquad N_2O_5$$
 (11.6.19)

$$NO + NO_3 = 2NO_2$$
 (11.6.20)

$$O + NO + M$$
 $NO_2 + M$ (11.6.21)

Nitrogen dioxide ultimately is removed from the atmosphere as nitric acid, nitrates, or (in atmospheres where photochemical smog is formed) as organic nitrogen. Dinitrogen pentoxide formed in Reaction 11.6.19 is the anhydride of nitric acid, which it forms by reacting with water:

$$N_2O_5 + H_2O = 2HNO_3$$
 (11.6.22)

In the stratosphere, nitrogen dioxide reacts with hydroxyl radicals to produce nitric acid:

$$HO \bullet + NO_2 \qquad HNO_3 \tag{11.6.23}$$

In this region, the nitric acid can also be destroyed by hydroxyl radicals,

$$HO_{\bullet} + HNO_{3} = H_{2}O_{2} + NO_{3}$$
 (11.6.24)

or by a photochemical reaction,

$$HNO_3 + h \qquad HO\bullet + NO_2 \tag{11.6.25}$$

so that HNO_3 serves as a temporary sink for NO_2 in the stratosphere. Nitric acid produced from NO_2 is removed as precipitation, or reacts with bases (ammonia, particulate lime) to produce particulate nitrates.

Harmful Effects of Nitrogen Oxides

Nitric oxide, NO, is less toxic than NO_2 . Like carbon monoxide and nitrite, NO attaches to hemoglobin and reduces oxygen transport efficiency. However, in a polluted atmosphere, the concentration of nitric oxide normally is much lower than that of carbon monoxide so that the effect on hemoglobin is much less.

Acute exposure to NO_2 can be quite harmful to human health. For exposures ranging from several minutes to one hour, a level of 50-100 ppm of NO_2 causes inflammation of lung tissue for a period of 6-8 weeks, after which time the subject normally recovers. Exposure of the subject to 150-200 ppm of NO_2 causes *bronchiolitis fibrosa obliterans*, a condition fatal within 3-5 weeks after exposure. Death generally results within 2-10 days after exposure to 500 ppm or more of NO_2 . "Silo-filler's disease," caused by NO_2 generated by the fermentation of ensilage containing nitrate, is a particularly striking example of nitrogen dioxide poisoning. Deaths have resulted from the inhalation of NO_2 -containing gases from burning celluloid and nitrocellulose film, and from spillage of NO_2 oxidant (used with liquid hydrazine fuel) from missile rocket motors.

Although extensive damage to plants is observed in areas receiving heavy exposure to NO_2 , most of this damage probably comes from secondary products of nitrogen oxides, such as PAN formed in smog (see Chapter 14). Exposure of plants to several parts per million of NO_2 in the laboratory causes leaf spotting and breakdown of plant tissue. Exposure to 10 ppm of NO causes a reversible decrease in the rate of photosynthesis. The effect on plants of long-term exposure to a few tenths of a part per million of NO_2 is less certain.

Nitrogen oxides are known to cause fading of dyes and inks used in some textiles. This has been observed in gas clothes dryers and is due to NO_x formed in the dryer flame. Much of the damage to materials caused by NO_x comes from secondary nitrates and nitric acid. For example, stress-corrosion cracking of springs used in telephone relays occurs far below the yield strength of the nickel-brass spring metal because of the action of particulate nitrates and aerosol nitric acid formed from NO_x .

Concern has been expressed about the possibility that NO_x emitted to the atmosphere by supersonic transport planes could catalyze the partial destruction of the stratospheric ozone layer that absorbs damaging short-wavelength (240-300 nm) ultraviolet radiation. Detailed consideration of this effect is quite complicated, and only the main features are considered here.

In the upper stratosphere and in the mesosphere, molecular oxygen is photodissociated by ultraviolet light of less than 242-nm wavelength:

$$O_2 + h = O + O$$
 (11.6.26)

In the presence of energy-absorbing third bodies, the atomic oxygen reacts with molecular oxygen to produce ozone:

$$O_2 + O + M = O_3 + M$$
 (11.6.27)

Ozone can be destroyed by reaction with atomic oxygen,

$$O_3 + O = O_2 + O_2$$
 (11.6.28)

and its formation can be prevented by recombination of oxygen atoms:

$$O + O + M = O_2 + M$$
 (11.6.29)

Addition of the reaction of nitric oxide with ozone,

$$NO + O_3 \qquad NO_2 + O_2$$
 (11.6.30)

to the reaction of nitrogen dioxide with atomic oxygen,

$$NO_2 + O$$
 $NO + O_2$ (11.6.31)

results in a net reaction for the destruction of ozone:

$$O + O_3 \qquad O_2 + O_2$$
 (11.6.32)

Along with NO_x , water vapor is also emitted into the atmosphere by aircraft exhausts, which could accelerate ozone depletion by the following two reactions:

$$O + H_2O$$
 $HO^{\bullet} + HO^{\bullet}$ (11.6.33)

$$HO^{\bullet} + O_3 \qquad HOO^{\bullet} + O_2$$
 (11.6.34)

However, there are many natural stratospheric buffering reactions which tend to mitigate the potential ozone destruction from those reactions outlined above. Atomic oxygen capable of regenerating ozone is produced by the photochemical reaction,

$$NO_2 + h$$
 $NO + O$ (< 420 nm) (11.6.35)

A competing reaction removing catalytic NO is

$$NO + HOO^{\bullet} \qquad NO_2 + HO^{\bullet} \qquad (11.6.36)$$

Current belief is that supersonic aircraft emissions will not cause nearly as much damage to the ozone layer as chlorofluorocarbons.

Control of Nitrogen Oxides

The level of NO_x emitted from stationary sources such as power plant furnaces generally falls within the range of 50-1000 ppm. NO production is favored both kinetically and thermodynamically by high temperatures and by high excess oxygen concentrations. These factors must be considered in reducing NO emissions from stationary sources. Reduction of flame temperature to prevent NO formation is accomplished by adding recirculated exhaust gas, cool air, or inert gases. Unfortunately, this decreases the efficiency of energy conversion as calculated by the Carnot equation (see Chapter 18).

Low-excess-air firing is effective in reducing NO_x emissions during the combustion of fossil fuels. As the term implies, low-excess-air firing uses the minimum amount of excess air required for oxidation of the fuel, so that less oxygen is available for the reaction

$$N_2 + O_2 = 2NO$$
 (11.6.37)

in the high temperature region of the flame. Incomplete fuel burnout with the emission of hydrocarbons, soot, and CO is an obvious problem with low-excess-air firing. This may be overcome by a two-stage combustion process consisting of the following steps:

- 1. A first stage in which the fuel is fired at a relatively high temperature with a substoichiometric amount of air, for example, 90-95% of the stoichiometric requirement. NO formation is limited by the absence of excess oxygen.
- 2. A second stage in which fuel burnout is completed at a relatively low temperature in excess air. The low temperature prevents formation of NO.

In some power plants fired with gas, the emission of NO has been reduced by as much as 90% by a two-stage combustion process.

Removal of NO_x from stack gas presents some formidable problems. These problems arise largely from the low water solubility of NO, the predominant nitrogen oxide species in stack gas. Possible approaches to NO_x removal are catalytic decomposition of nitrogen oxides, catalytic reduction of nitrogen oxides, and sorption of NO_x by liquids or solids. Uptake of NO_x is facilitated by oxidation of NO to more water-soluble species including NO₂, N₂O₃, N₂O₄, HNO₂, and HNO₃.

A typical catalytic reduction of NO in stack gas involves methane:

$$CH_4 + 4NO = 2N_2 + CO_2 + 2H_2O$$
 (11.6.38)

Production of undesirable by-products is a major concern in these processes. For example, sulfur dioxide reacts with carbon monoxide used to reduce NO to produce toxic carbonyl sulfide, COS:

$$SO_2 + 3CO = 2CO_2 + COS$$
 (11.6.39)

Most sorption processes have been aimed at the simultaneous removal of both nitrogen oxides and sulfur oxides. Sulfuric acid solutions or alkaline scrubbing solutions containing $Ca(OH)_2$ or $Mg(OH)_2$ may be used. The species N_2O_3 produced by the reaction

$$NO_2 + NO = N_2O_3$$
 (11.6.40)

is most efficiently absorbed. Therefore, since NO is the primary combustion product, the introduction of NO_2 into the flue gas is required to produce the N_2O_3 , which is absorbed efficiently.

11.7. ACID RAIN

As discussed in this chapter, much of the sulfur and nitrogen oxides entering the atmosphere are converted to sulfuric and nitric acids, respectively. When combined with hydrochloric acid arising from hydrogen chloride emissions, these acids cause acidic precipitation (acid rain) that is now a major pollution problem in some areas.

Headwater streams and high-altitude lakes are especially susceptible to the effects of acid rain and may sustain loss of fish and other aquatic life. Other effects

include reductions in forest and crop productivity; leaching of nutrient cations and heavy metals from soils, rocks, and the sediments of lakes and streams; dissolution of metals such as lead and copper from water distribution pipes; corrosion of exposed metal; and dissolution of the surfaces of limestone buildings and monuments.

As a result of its widespread distribution and effects, acid rain is an air pollutant that may pose a threat to the global atmosphere. Therefore, it is discussed in greater detail in Chapter 14.

11.8 AMMONIA IN THE ATMOSPHERE

Ammonia is present even in unpolluted air as a result of natural biochemical and chemical processes. Among the various sources of atmospheric ammonia are microorganisms, decay of animal wastes, sewage treatment, coke manufacture, ammonia manufacture, and leakage from ammonia-based refrigeration systems. High concentrations of ammonia gas in the atmosphere are generally indicative of accidental release of the gas.

Ammonia is removed from the atmosphere by its affinity for water and by its action as a base. It is a key species in the formation and neutralization of nitrate and sulfate aerosols in polluted atmospheres. Ammonia reacts with these acidic aerosols to form ammonium salts:

$$\mathrm{NH}_3 + \mathrm{HNO}_3 \qquad \mathrm{NH}_4\mathrm{NO}_3 \tag{11.8.1}$$

$$NH_3 + H_2SO_4 \qquad NH_4HSO_4 \tag{11.8.2}$$

Ammonium salts are among the more corrosive salts in atmospheric aerosols.

11.9. FLUORINE, CHLORINE, AND THEIR GASEOUS COMPOUNDS

Fluorine, hydrogen fluoride, and other volatile fluorides are produced in the manufacture of aluminum, and hydrogen fluoride is a by-product in the conversion of fluorapatite (rock phosphate) to phosphoric acid, superphosphate fertilizers, and other phosphorus products. The wet process for the production of phosphoric acid involves the reaction of fluorapatite, $Ca_5F(PO_4)_3$, with sulfuric acid:

$$Ca_5F(PO_4)_3 + 5H_2SO_4 + 10H_2O = 5CaSO_4 \cdot 2H_2O + HF + 3H_3PO_4$$
 (11.9.1)

It is necessary to recover most of the by-product fluorine from rock phosphate processing to avoid severe pollution problems. Recovery as fluorosilicic acid, H_2SiF_6 , is normally practiced.

Hydrogen fluoride gas is a dangerous substance that is so corrosive it even reacts with glass. It is irritating to body tissues, and the respiratory tract is very sensitive to it. Brief exposure to HF vapors at the part-per-thousand level may be fatal. The acute toxicity of F_2 is even higher than that of HF. Chronic exposure to high levels of fluorides causes fluorosis, the symptoms of which include mottled teeth and pathological bone conditions.

Plants are particularly susceptible to the effects of gaseous fluorides. Fluorides from the atmosphere appear to enter the leaf tissue through the stomata. Fluoride is a cumulative poison in plants, and exposure of sensitive plants to even very low levels of fluorides for prolonged periods results in damage. Characteristic symptoms of fluoride poisoning are chlorosis (fading of green color due to conditions other than the absence of light), edge burn, and tip burn. Conifers (such as pine trees) afflicted with fluoride poisoning may have reddish-brown, necrotic needle tips. The sensitivity of some conifers to fluoride poisoning is illustrated by the fact that fluorine produced by aluminum plants in Norway has destroyed forests of *Pinus sylvestris* up to 8 miles distant; trees were damaged at distances as great as 20 miles from the plant.

Silicon tetrafluoride gas, SiF_4 , is another gaseous fluoride pollutant produced during some steel and metal smelting operations that employ CaF_2 , fluorspar. Fluorspar reacts with silicon dioxide (sand), releasing SiF_4 gas:

 $2CaF_2 + 3SiO_2 \qquad 2CaSiO_3 + SiF_4 \tag{11.9.2}$

Another gaseous fluorine compound, sulfur hexafluoride, SF₆, occurs in the atmosphere at levels of about 0.3 parts per trillion. It is extremely unreactive with an atmospheric lifetime estimated at 3200 years,⁶ and is used as an atmospheric tracer. It does not absorb ultraviolet light in either the troposphere or stratosphere, and is probably destroyed above 60 km by reactions beginning with its capture of free electrons. Current atmospheric levels of SF₆ are significantly higher than the estimated background level of 0.04 ppt in 1953 when commercial production of it began. The compound is very useful in specialized applications including gasinsulated electrical equipment and inert blanketing/degassing of molten aluminum and magnesium. Increasing uses of sulfur hexafluoride have caused concern because it is the most powerful greenhouse gas known, with a global warming potential (per molecule added to the atmosphere) about 23,900 times that of carbon dioxide.

Chlorine and Hydrogen Chloride

Chlorine gas, Cl_2 , does not occur as an air pollutant on a large scale but can be quite damaging on a local scale. Chlorine was the first poisonous gas deployed in World War I. It is widely used as a manufacturing chemical in the plastics industry, for example, as well as for water treatment and as a bleach. Therefore, possibilities for its release exist in a number of locations. Chlorine is quite toxic and is a mucousmembrane irritant. It is very reactive and a powerful oxidizing agent. Chlorine dissolves in atmospheric water droplets, yielding hydrochloric acid and hypochlorous acid, an oxidizing agent:

$$H_2O + Cl_2 = H^+ + Cl^- + HOCl$$
 (11.9.3)

Spills of chlorine gas have caused fatalities among exposed persons. For example, the rupture of a derailed chlorine tank car at Youngstown, Florida, on February 25, 1978, resulted in the deaths of 8 people who inhaled the deadly gas, and a total of 89 people were injured.

Hydrogen chloride, HCl, is emitted from a number of sources. Incineration of chlorinated plastics, such as polyvinylchloride, releases HCl as a combustion product.

CI H H H CI H H H CI H

$$\cdots \cdots \stackrel{l}{\leftarrow} \stackrel{l}{\leftarrow}$$

Some compounds released to the atmosphere as air pollutants hydrolyze to form HCl. One such incident occurred on April 26, 1974, when a storage tank containing 750,000 gallons of liquid silicon tetrachloride, $SiCl_4$, began to leak in South Chicago, Illinois. This compound reacted with water in the atmosphere to form a choking fog of hydrochloric acid droplets:

$$\operatorname{SiCl}_{4} + 2\operatorname{H}_{2}\operatorname{O} \qquad \operatorname{SiO}_{2} + 4\operatorname{HCl} \tag{11.9.4}$$

Many people became ill from inhaling the vapor.

In February, 1981, in Stroudsburg, Pennsylvania, a wrecked truck dumped 12 tons of powdered aluminum chloride during a rainstorm. This compound produces HCl gas when wet,

$$AlCl_{3} + 3H_{2}O \qquad Al(OH)_{3} + 3HCl \qquad (11.9.5)$$

and more than 1200 residents had to be evacuated from their homes because of the fumes generated.

11.10. HYDROGEN SULFIDE, CARBONYL SULFIDE, AND CARBON DISULFIDE

Hydrogen sulfide is produced by microbial processes including the decay of sulfur compounds and bacterial reduction of sulfate (see Chapter 6). Hydrogen sulfide is also released from geothermal steam, from wood pulping, and from a number of miscellaneous natural and anthropogenic sources. Because it is so readily oxidized, most atmospheric hydrogen sulfide is rapidly converted to SO_2 . The organic homologs of hydrogen sulfide, the mercaptans, enter the atmosphere from decaying organic matter and have particularly objectionable odors.

Hydrogen sulfide pollution from artificial sources is not as much of an overall air pollution problem as sulfur dioxide pollution. However, there have been several acute incidents of hydrogen sulfide emissions resulting in damage to human health and even fatalities. The most notorious such incident occurred in Poza Rica, Mexico, in 1950. Accidental release of hydrogen sulfide from a plant used for the recovery of sulfur from natural gas caused the deaths of 22 people and the hospitalization of more than 300. The symptoms of poisoning included irritation of the respiratory tract and damage to the central nervous system. Unlike sulfur dioxide, which appears to affect older people and those with respiratory weaknesses, there was little evidence of correlation between the observed hydrogen sulfide poisoning and the ages or physical conditions of the victims.

In a tragic incident that occurred in February 1975, hydrogen sulfide gas leaking from an experimental secondary-recovery oil well near Denver City, Texas, killed

nine people trying to flee the lethal fumes. A process was being tried in which carbon dioxide, rather than water, was injected under high pressure to recover petroleum. Leakage from the well released deadly hydrogen sulfide present in the oil-bearing formation. Efforts to tap very deep natural gas formations have increased the hazard from hydrogen sulfide. A pocket of H_2S was struck at 15,000 feet while drilling such a well near Athens, Texas, in 1978. Leakage of hydrogen sulfide on May 12, 1978, forced the evacuation of 50 families. As an emergency measure in such cases, the gas may be ignited, although that releases large quantities of pollutant SO₂ to the atmosphere.

Hydrogen sulfide at levels well above ambient concentrations destroys immature plant tissue. This type of plant injury is readily distinguished from that due to other phytotoxins. More sensitive species are killed by continuous exposure to around 3000 ppb H_2S , whereas other species exhibit reduced growth, leaf lesions, and defoliation.

Damage to certain kinds of materials is a very expensive effect of hydrogen sulfide pollution. Paints containing lead pigments, $2PbCO_3 \cdot Pb(OH)_2$ (no longer used), are particularly susceptible to darkening by H_2S . Darkening results from exposure over several hours to as little as 50 ppb H_2S . The lead sulfide originally produced by reaction of the lead pigment with hydrogen sulfide eventually may be converted to white lead sulfate by atmospheric oxygen after removal of the source of H_2S , thus partially reversing the damage.

A black layer of copper sulfide forms on copper metal exposed to H_2S . Eventually, this layer is replaced by a green coating of basic copper sulfate, $CuSO_4 \cdot 3Cu(OH)_2$. The green "patina," as it is called, is very resistant to further corrosion. Such layers of corrosion can seriously impair the function of copper contacts on electrical equipment. Hydrogen sulfide also forms a black sulfide coating on silver.

Carbonyl sulfide, COS, is now recognized as a component of the atmosphere at a tropospheric concentration of approximately 500 parts per trillion by volume, corresponding to a global burden of about 2.4 million tons. It is, therefore, a significant sulfur species in the atmosphere. It is possible that the HO[•] radical-initiated oxidation of COS and carbon disulfide (CS₂) would yield 8-12 million tons as S in atmospheric sulfur dioxide per year. Though this is a small yield compared to pollution sources, the HO[•]-initiated process could account for much of the SO₂ burden in the remote troposphere.

Both COS and CS_2 are oxidized in the atmosphere by reactions initiated by the hydroxyl radical. The initial reactions are

 $HO^{\bullet} + COS \qquad CO_2 + HS^{\bullet} \tag{11.10.1}$

$$HO^{\bullet} + CS_2 \qquad COS + HS^{\bullet} \qquad (11.10.2)$$

These reactions with hydroxyl radical initiate oxidation processes that occur through a series of atmospheric chemical reactions. The sulfur-containing products that are initially formed as shown by Reactions 11.10.1 and 11.10.2 undergo further reactions to sulfur dioxide and, eventually, to sulfate species.

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QUESTIONS AND PROBLEMS

- 1. Why is it that "highest levels of carbon monoxide tend to occur in congested urban areas at times when the maximum number of people are exposed?"
- 2. Which unstable, reactive species is responsible for the removal of CO from the atmosphere?
- 3. Which of the following fluxes in the atmospheric sulfur cycle is smallest: (a) sulfur species washed out in rainfall over land, (b) sulfates entering the atmosphere as "sea salt," (c) sulfur species entering the atmosphere from volcanoes, (d) sulfur species entering the atmosphere from fossil fuels, (e) hydrogen sulfide entering the atmosphere from biological processes in coastal areas and on land?
- 4. Of the following agents, the one that would not favor conversion of sulfur dioxide to sulfate species in the atmosphere is: (a) ammonia, (b) water, (c) contaminant reducing agents, (d) ions of transition metals such as manganese, (e) sunlight.
- 5. Of the stack gas scrubber processes discussed in this chapter, which is the least effficient for the removal of SO_2 ?
- 6. The air inside a garage was found to contain 10 ppm CO by volume at standard temperature and pressure (STP). What is the concentration of CO in mg/L and in ppm by mass?
- 7. How many metric tons of 5%–S coal would be needed to yield the H₂SO₄ required to produce a 3.00–cm rainfall of pH 2.00 over a 100 km² area?
- 8. In what major respect is NO₂ a more significant species than SO₂ in terms of participation in atmospheric chemical reactions?
- 9. Assume that an incorrectly adjusted lawn mower is operated in a garage such that the combustion reaction in the engine is

 $C_8H_{18} + \frac{17}{2}O_2 = 8CO + 9H_2O_2$

If the dimensions of the garage are $5 \times 3 \times 3$ meters, how many grams of gasoline must be burned to raise the level of CO in the air to 1000 ppm by volume at STP?

- 10. A 12.0-L sample of waste air from a smelter process was collected at 25° C and 1.00 atm pressure, and the sulfur dioxide was removed. After SO₂ removal, the volume of the air sample was 11.50 L. What was the percentage by weight of SO₂ in the original sample?
- 11. What is the oxidant in the Claus reaction?
- 12. Carbon monoxide is present at a level of 10 ppm by volume in an air sample taken at 15°C and 1.00 atm pressure. At what temperature (at 1.00 atm pressure) would the sample also contain 10 mg/m³ of CO?
- 13. How many metric tons of coal containing an average of 2% S are required to produce the SO_2 emitted by fossil fuel combustion shown in Figure 11.1? (Note that the values given in the figure are in terms of elemental sulfur, S.) How many metric tons of SO_2 are emitted?
- 14. Assume that the wet limestone process requires 1 metric ton of $CaCO_3$ to remove 90% of the sulfur from 4 metric tons of coal containing 2% S. Assume that the sulfur product is $CaSO_4$. Calculate the percentage of the limestone converted to calcium sulfate.
- 15. Referring to the two preceding problems, calculate the number of metric tons of $CaCO_3$ required each year to remove 90% of the sulfur from 1 billion metric tons of coal (approximate annual U.S. consumption), assuming an average of 2% sulfur in the coal.
- 16. If a power plant burning 10,000 metric tons of coal per day with 10% excess air emits stack gas containing 100 ppm by volume of NO, what is the daily output of NO? Assume the coal is pure carbon.
- 17. How many cubic kilometers of air at 25° C and 1 atm pressure would be contaminated to a level of 0.5 ppm NO_X from the power plant discussed in the preceding question?