10.10: Miscellaneous Gases in the Atmosphere

There are several inorganic gases other than oxides that can be significant atmospheric he most common of these is ammonia, NH_3. In addition to industrial pollution, such as from heating coal to make coke for steel making, ammonia can be added to the atmosphere by bacterial sources, from sewage treatment, and from the decay of animal wastes. Accidental releases can occur from liquid anhydrous ammonia used as an agricultural nitrogen fertilizer.

Ammonia is strongly attracted to water, so it is normally present in the atmosphere in water droplets. It is the only significant gaseous base in the atmosphere, so that it reacts with atmospheric acids to produce corrosive ammonium salts as shown by the following reactions:

$$\mathrm{NH_3 + N_2SO_4 \rightarrow NH_4HSO_4} \tag{10.10.1}$$

$$\mathrm{NH_3 + HNO_3 \rightarrow NH_4NO_3} \tag{10.10.2}$$

Gaseous chlorine, fluorine, and volatile fluorides are uncommon air pollutants, but very serious where they occur. Elemental chlorine, Cl_2, is widely produced and distributed as a water disinfectant, bleach, and industrial chemical. It is very reactive and so toxic that it was the first poisonous gas used as a military poison in World War I. Most toxic exposures of chlorine occur as the result of transportation accidents leading to its release.

Hydrogen chloride, HCl, can get into the atmosphere from accidental releases of the gas, from reaction with atmospheric water of reactive chlorine-containing chemicals, of which one of the most common is $SiCl_4$,

$$\mathrm{SiCl_4 + 2\,H_2O \rightarrow 2\,SiO_2 + 4\,HCl} \tag{10.10.3}$$

and from the combustion of chlorine-containing polyvinylchloride (PVC) plastic. The strong affinity of HCl gas for water means that it exists as droplets of hydrochloric acid in the atmosphere. Atmospheric HCl is very irritating to mucous membrane tissue and damaging to corrodable materials.

Elemental fluorine (F_2) and hydrogen fluoride are both highly toxic. Fortunately, occurrences of these gases in the atmosphere are very rare. Gaseous silicon tetrafluoride, SiF_4, can be released during steel making and some metal smelting processes when fluorspar (CaF_2) reacts with sand (SiO_2)

$$\mathrm{2\,CaF_2 + 3\,SiO_2 \rightarrow 2\,CaSiO_3 + SiF_4} \tag{10.10.4}$$

Sulfur hexafluoride, SF_6, is an astoundingly unreactive gaseous compound used to blanket and degas molten aluminum and magnesium and in gas-insulated electrical equipment. It lasts essentially forever in the atmosphere. As noted in Section 10.6, the greatest concern with its release is that it is a powerful greenhouse warming gas with an effect per molecule about 24,000 times that of carbon dioxide.

Hydrogen sulfide, H_2S, enters the atmosphere from a number of natural sources including geothermal sources, the microbial decay of organic sulfur compounds and the microbial conversion of sulfate, SO_4^{2-}, to H_2S when sulfate acts as an oxidizing agent in the absence of O2. Wood pulping processes can release hydrogen sulfide. Hydrogen sulfide may occur as a contaminant of petroleum and natural gas, and these sources are the most common source of poisoning by H_2S, which has about the same toxicity as hydrogen cyanide. A tragic incident of hydrogen sulfide poisoning occurred in Poza Rica, Mexico, in 1950 as the result of a process to recover H_2S from natural gas. Incredibly, the hydrogen sulfide byproduct was burned in a flare to produce sulfur dioxide. The flare became extinguished at night so that toxic hydrogen sulfide spread throughout the vicinity, killing 22 people and hospitalizing over 300. A 2003 blowout in a natural gas field in southwestern China released hydrogen sulfide that killed almost 200 people in the surrounding area. As an emergency measure the escaping gas was set on fire producing sulfur dioxide, SO_2, still a toxic material, but much less deadly than hydrogen sulfide. Atmospheric H_2S is phytotoxic, destroying immature plant tissue and reducing plant growth. It also affects some kinds of materials, forming a black coating of copper sulfide, CuS, on copper roofing. This coating weathers to a rather attractive green layer (patina) of basic copper sulfate, $CuSO_4$•$3Cu(OH)_2$, which protects the copper from further attack. Hydrogen sulfide in the atmosphere becomes oxidized to SO_2. This process is especially rapid under oxidizing atmospheric conditions such as those in which photochemical smog is formed.

Carbonyl sulfide, COS, is another inorganic sulfur gas that can be detected in the atmosphere, though it is usually at very low levels. A related compound, carbon disulfide, CS_2, also occurs in the atmosphere