10.1: More Than Just Air to Breathe

A Sea of Gas

We live and breathe in the **atmosphere**, a sea of gas consisting primarily of elemental O_2 and N_2. The fundamental properties of gases determine the properties of the atmosphere. Recall that gases consist of molecules and (in the case of noble gases) atoms with large amounts of space between them. The gas molecules are in constant, rapid motion, which causes gases to exert pressure. The motion of gas molecules becomes more rapid with increasing temperature. This motion also means that gas molecules move by a process called **diffusion**. The relationships among the amount of gas in moles, its volume, temperature, and pressure can be calculated by the gas laws discussed in Section 10.2.

Whereas seawater in the ocean has a well-defined volume and a distinct surface, the same cannot be said for the mass of gases comprising the atmosphere. Although most of the atmosphere is within a few kilometers of Earth's surface, there is no distinct point at higher altitude where the atmosphere ends. Instead, air becomes progressively thinner with increasing altitude. This is noticeable to humans who have traveled to higher altitudes on mountains where the thinner air makes breathing more difficult. Indeed, climbers who scale the highest mountain peaks commonly carry oxygen to aid breathing.

Atmospheric Composition

What is air? At our level, it is a mixture of gases of uniform composition, except for water vapor, which composes 1-3% of the atmosphere by volume, and some of the trace gases, such as pollutant sulfur dioxide. On a dry basis, air is 78.1% (by volume) nitrogen, 21.0% oxygen, 0.9% argon, and 0.04% carbon dioxide. Normally, air is 1–3% water vapor by volume. Trace gases at levels below 0.002% in air include ammonia, carbon monoxide, helium, hydrogen, krypton, methane, neon, nitrogen dioxide, nitrous oxide, ozone, sulfur dioxide, and xenon.

By a wide margin, oxygen and nitrogen are the most abundant gases in the atmosphere. Because of the extremely high stability and low reactivity of the N_2 molecule, the chemistry of atmospheric elemental nitrogen is singularly unexciting, although nitrogen molecules are the most common "third bodies" that absorb excess energy from atmospheric chemical reactions, preventing the products of addition reactions in the atmosphere from falling apart. Oxides of nitrogen actively participate in atmospheric chemical reactions. Elemental nitrogen is an important commercial gas extracted from the atmosphere by nitrogen-fixing bacteria and in the industrial synthesis of ammonia.

Oxygen is a reactive species in the atmosphere that reacts to produce oxidation products from oxidizable gases in the atmosphere. Two such species that are particularly important are sulfur dioxide gas, SO_2, and pollutant hydrocarbons. Molecular O_2 does not react with these substances directly but only indirectly through the action of reactive intermediates, especially **hydroxyl radical**, HO•.

A crucially important atmospheric chemical phenomenon involving oxygen is the formation of stratospheric ozone, O_3. The formation of this gas in the stratosphere is discussed in Section2.13 and shown by Reactions 2.13.1 and 2.13.2.

Oxygen in the atmosphere is consumed in the burning of hydrocarbons and other carbon-containing fuels. It is also consumed when oxidizable minerals undergo chemical weathering, such a

$$4\,\mathrm{FeO} + \mathrm{O_2} \rightarrow 2\,\mathrm{Fe_2O_3} \tag{10.1.1}$$

All of the oxygen in the atmosphere was originally placed there by photosynthesis shown by

$$\mathrm{CO_2} + \mathrm{H_2O} + h\nu \rightarrow (\mathrm{CH_2O}) + \mathrm{O_2} \tag{10.1.2}$$

where $\{CH_2O\}$ is a generic formula representing biomass

Unlike molecular oxygen, which can undergo direct photodissociation in the stratosphere, the very stable N_2 molecule does not encounter ultraviolet radiation sufficiently energetic to cause its photodissociation at altitudes below 100 km. However, nitrogen dioxide, NO_2, readily undergoes photodissociation in the troposphere.

$$\mathrm{NO_2} + h\nu \rightarrow \mathrm{NO} + \mathrm{O} \tag{10.1.3}$$

to generate highly reactive O atoms. These in turn can attack hydrocarbons in the atmosphere, leading to the formation of photochemical smog discussed later in this chapter.