

*Breath of Life! and Kiss of Death!*

Air is taken for granted. We can neither see it nor smell it, and tend to ignore it. But without it we would not be able to live. Not only we, humans, but also the majority of living organisms on this Earth depend on it. Only a small number of organisms can live without it, or rather they will be killed by air. These organisms are called “anaerobic,” whereas we are “aerobic.” When we say “air” in these sentences, we mean “oxygen.” Air is a mixture of nitrogen ( $N_2$ , about 78%) and oxygen ( $O_2$ , about 21%) plus minor components such as argon (Ar), carbon dioxide ( $CO_2$ ), and water vapor ( $H_2O$ ).

Of the two main components, nitrogen is relatively inert, but oxygen is reactive. Oxygen burns many substances; combustion is a chemical reaction in which oxygen binds with other chemicals. This reaction releases a lot of heat (energy). You will see and feel that in a fire. Oxygen can burn our body, but it requires certain conditions for oxygen to do so, and those conditions do not prevail ordinarily. That is why we are OK (not burned) in the presence of a lot of oxygen. However, oxygen does a lot of other kinds of damage to our body, the chemical basis of which is the same as combustion. As a matter of fact, oxygen can be regarded as toxic to organisms. Probably, this comes as a surprise to you. We talk about this issue later.

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## 2.1 Where Did “Air” Come From?

Where have they (nitrogen and oxygen) come from? Nitrogen, being nonreactive, has remained more or less unchanged in the atmosphere throughout the history of the Earth. It does not mean that no change has occurred to nitrogen. Some reactions have taken place and do take place with nitrogen. Nitrogen, for example, can react with oxygen in the atmosphere under, say, lightning conditions. As a result, some nitrogen oxides ( $NO$ ,  $NO_2$ , etc.) form. More importantly, nitrogen is fixed as

ammonia by a number of microorganisms; the reaction is:  $\text{N}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 2\text{NH}_3$ . Ammonia ( $\text{NH}_3$ ) is utilized by organisms, and it eventually turns back to nitrogen ( $\text{N}_2$ ) or nitrate ( $\text{NO}_3^-$ ). Nitrate is also used by organisms. However, the quantity that undergoes these reactions is miniscule compared with the entire nitrogen ( $\text{N}_2$ ) present in the atmosphere, which is  $4 \times 10^{18}$  kg. The amount of nitrogen biologically fixed is estimated to be  $2 \times 10^{11}$  kg/year.

Oxygen, all of it, on the other hand, has come from an entirely different route. By the way, the oxygen in the air exists as dioxygen ( $\text{O}_2$ ) molecules, but we often use simply oxygen to mean dioxygen. The current prevailing idea about the ancient Earth asserts that no significant free oxygen ( $\text{O}_2$ ) was present in the earlier atmosphere. A main reason for this thinking is that oxygen, being reactive, would have reacted with a number of compounds available at the time of formation of the Earth, and thus, would not have remained as free molecule long in the atmosphere, even if there were free oxygen at the beginning. If so, then where has the free “oxygen” come from and why would not “oxygen” be consumed and hence disappear? On the present Earth, we, animals and others, are consumers of oxygen, and who are the producers? Yes, green plants and a lot other minute organisms, phytoplankton (algae), are the producers. They produce carbohydrates using carbon dioxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ), with the aid of sunlight; that is, they carry out photosynthesis. The reaction can be written essentially as  $6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6$  (carbohydrate) +  $6\text{O}_2$ . Reactions involved in photosynthesis are very complicated, and of multiple steps, but oxygen comes from the decomposition of water. So plants produce oxygen, which animals consume, and a steady state has been established. And so, the current 21% figure (oxygen in the air) seems to be more or less constant (see also Chap. 3).

There is no other good way of making free oxygen in nature. An alternative is a direct decomposition of water by sunlight. It does occur, but it is not very significant. Photosynthesis then must have been the only significant means to create the free oxygen in the atmosphere throughout the history of the Earth. So when did photosynthesis start or rather when did the first photosynthetic organisms emerge? By the way, there are other types of photosynthesis where water is not decomposed; for example, some photosynthetic bacteria use hydrogen sulfide ( $\text{H}_2\text{S}$ ) instead of water. Hence, what we are interested in is “water-decomposing” photosynthetic organisms. The earliest such organisms are believed to be similar to the contemporary cyanobacteria (often called bluegreen algae). When they emerged has not been determined unequivocally, but many people believe that it was sometime around 2.7–3 billion years ago. By the way, the Earth is 4.6 billion years old, and the earliest organisms are believed to have emerged around 3.5–3.8 billion years ago.

Cyanobacteria kept proliferating and releasing an increasing amount of oxygen ever since about 3 billion or so years ago. However, the oxygen content in the atmosphere stayed quite low for a long time, up until about 2.2 billion years ago (a current hypothesis says so). There were a vast amount of oxygen-consuming materials (oxygen sink) in the ocean; the most important was iron. The result was the formation of a vast amount of iron ores, known as “banded iron formation.” The main iron ore in Minnesota, for example, is of this type. (This issue is discussed further in Chap. 14).

The oxygen content of the atmosphere started to go up about 2.2 billion years ago, perhaps, because the consumable iron in the ocean had been exhausted about that time. Up until then, the majority of organisms were living without oxygen, that is, “anaerobic,” including most of cyanobacteria. They could not live in the presence of oxygen, because they were made of compounds that readily react with oxygen and thus would be destroyed when exposed to oxygen. So the increase of oxygen in the air was a grave pollution threat for the majority of the organisms then living, and most of them did actually perish. Some organisms found ways to defend themselves against this terror, and they and their descendants including us have survived to this day.

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## 2.2 Biological Functions of Oxygen

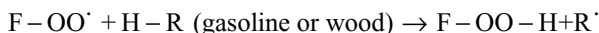
An oxygen atom binds fairly strongly with other atoms, and as a result, an oxidation of a compound by oxygen tends to produce stable end products. Hence, such an oxidation reaction will release a lot of energy (heat) and is a preferred reaction, that is, thermodynamically preferred. For example, the oxidation of methane ( $\text{CH}_4$ ) will produce very stable compounds, carbon dioxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ), and will release energy of 890 kJ/mol (or 13,300 kcal/l kg). Methane is the major component of the natural gas; hence, this heat is what we use for cooking and house heating. Likewise, we burn our food with oxygen in our body to extract energy for our lives (see Chap. 3). This is the positive side of oxygen.

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## 2.3 Toxicity of Oxygen

Oxygen ( $\text{O}_2$ ), more precisely dioxygen, is a rather abnormal molecule, as mentioned in Chap. 19. The majority of stable molecules including  $\text{H}_2$  (hydrogen molecule), proteins, carbohydrates, and DNAs have even numbers of electrons, and all of the electrons in these molecules are paired up. [Just a brief review: An electron is like a tiny magnet, which can be positioned in two ways. In one position the north (of the magnet) is up, and in the other the north is down. In ordinary molecules, electrons combine in such a way that an electron of the north up pairs up with another of the north down. As a result, the magnetic effects of electrons are canceled in such a molecule. This situation is called “diamagnetic” (not magnetic)]. On the other hand,  $\text{O}_2$  has two unpaired electrons in its most stable form (the ground state). It can be expressed as  $\cdot\text{O}=\text{O}\cdot$ , where the dot represents a single electron. A molecular entity with unpaired electron(s) behaves “paramagnetically” (like a magnet), and is also called a “free radical.” In general, a free radical is very reactive and tends to acquire an electron to pair up. However, dioxygen has two unpaired electrons (and hence called “biradical”), and it is relatively nonreactive toward ordinary compounds with no unpaired electrons. For example, when hydrogen ( $\text{H}_2$ ) is mixed with  $\text{O}_2$ , the reaction to form water ( $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ ) should occur potentially, but it doesn’t, at least not at an appreciable rate (see Chap. 19). That is why dioxygen would not readily react with us, animals and plants, though oxygen potentially can burn us.

But if you produce a free radical (with a single unpaired electron), oxygen immediately reacts with it. When you strike a match, for example, you are producing a small amount of such free radicals. Once free radicals form, they react with oxygen, and this reaction results in the formation of free radicals. Let us see that in the form of chemical equations:



then  $R^{\cdot}$  will carry on similar reactions.

In the first step, the odd electron on  $F^{\cdot}$  pairs up with one of the unpaired electrons on the oxygen. In the second step, the free radical  $FOO^{\cdot}$  abstracts a hydrogen atom from another molecule. This kind of reaction can automatically produce reactive entities (free radical in this case), and hence it will continue, once started. Besides, the reaction with oxygen produces a lot of heat, and the temperature will rise, accelerating the reaction; thus combustion takes place. The chemical equations given above represent only a few important reactions involved in combustion. The whole process of combustion is very complicated. Because the cell membrane is made of essentially the same type of compounds as gasoline (called hydrocarbons), as we see in Fig. 1.5 (Sect. 1.2), that is  $RH$  in the above equations, the cell membranes will be attacked by oxygen once a free radical is somehow produced. A result of such a reaction is the formation of  $ROOH$  entities (they are called hydroperoxides). Hydroperoxides further decompose resulting in damages in the structural integrity of cell membranes. This is considered to contribute to the aging processes of cells.

Oxygen, that is, dioxygen can obtain one more electron:  $O_2 + e$  (electron)  $\rightarrow OO_2^{\cdot-}$  ( $O_2^{\cdot-}$ ). The resulting entity has now a single unpaired electron, and it is called “superoxide” (free radical). This is much more reactive than oxygen (dioxygen) itself. For example, it can abstract a hydrogen atom as in the second step of the equation shown above. Therefore, superoxide is much more damaging than the ordinary oxygen. Superoxide forms as a byproduct in several enzymatic reactions involving oxygen and is intentionally produced in some immunological cells to attack and kill the invading bacteria.

A hydroperoxide  $ROOH$  (e.g.,  $CH_3OOH$ ) will be one of the first products of free radical chain reaction of  $O_2$  or  $O_2^{\cdot-}$  with hydrocarbons. A hydroperoxide is reactive and will react in the following manner with iron ( $Fe(II)$ ), for example:  $ROOH + Fe(II) \rightarrow RO^{\cdot} + OH^- + Fe(III)$ . A similar reaction can happen with hydrogen peroxide  $HOOH + Fe(II) \rightarrow HO^{\cdot} + OH^- + Fe(III)$ . The free radicals formed in these reactions,  $RO^{\cdot}$  and  $HO^{\cdot}$  are extremely reactive and damaging to cells and tissues. These reactions of oxygen, superoxide, hydroperoxide, hydroxy radical ( $HO^{\cdot}$ ), or alkoxy radical ( $RO^{\cdot}$ ) are the reasons for the toxicity of oxygen. The reactive oxygen-free radicals (such as  $HO^{\cdot}$ ) are considered to be involved in damaging DNAs as well, and the damage may lead to mutation and hence, a cancerous state.

A special kind of iron compound is contained in a number of proteins and enzymes involved in respiration. The iron compound takes the form of either  $Fe_2S_2$

or  $\text{Fe}_4\text{S}_4$  (called “iron–sulfur cluster” – see Chap. 6). The iron in some of these clusters can readily be oxidized by oxygen, and the protein or the enzyme that contains it then loses its biological activity. This is another source of oxygen toxicity. Some organisms take advantage of this fact, and use such an iron–sulfur cluster as a monitoring device for the presence of oxygen.

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## 2.4 Biological Strategies Against Oxygen Toxicity: Antioxidants, Etc.

As expounded above, the rise of the oxygen content of the atmosphere starting around 2.2 billion years ago created a panic among the then-living organisms. Many of them did not survive. The rise was not abrupt, and hence the organisms had chances to evolve to develop the defense mechanisms against this toxicity.

One of the most basic ways to do this is to consume oxygen in the cell all the time so that the free oxygen level in the cell may be maintained at a very low level. Some organisms invented the “aerobic respiration.” The energy that is potentially available in foodstuff was not fully utilized in the “anaerobic” organisms. In other words, carbohydrates are only partially oxidized in the anaerobic metabolism (it is called “fermentation” or glycolysis). Most of the energy inherent in carbohydrates is unused or wasted. You can further oxidize the products of fermentation, but that requires oxygen. This is what some organisms devised. They succeeded in developing ways and means to oxidize them further using oxygen and extracting much more energy from the same amount of food, and simultaneously keeping the intracellular oxygen level very low. This is the aerobic respiration (see Chap. 3).

Of course, this may not be sufficient to counter the toxic effects of various types of oxygen-derived entities. Therefore, organisms have developed various means to destroy some very toxic oxygen entities, superoxide and hydroperoxide (and hydrogen peroxide). They have not developed very effective specific means to combat very reactive  $\text{HO}^\cdot$  or  $\text{RO}^\cdot$  radicals.

Hydrogen peroxide ( $\text{HOOH}$ ) forms as a product of certain enzymatic reactions and is a stronger oxidizing agent than oxygen ( $\text{O}_2$ ) itself. It can be decomposed by an enzyme called catalase:  $2\text{HOOH} \rightarrow \text{O}_2 + 2\text{H}_2\text{O}$ . You might have seen the action of catalase yourself. When you cut your hand, sometimes your mother applied a solution that contained hydrogen peroxide to the cut. It hurts but is supposed to disinfect. You might have observed that bubbles formed on the applied spot. The blood on the cut contains catalase, and that decomposes the hydrogen peroxide and forms oxygen gas that forms bubbles. This oxygen is slightly different from the oxygen in the air and has a stronger reactivity (thus, called “active oxygen”) and hence is supposed to kill bacteria. Anyway, catalase is widely distributed in your body, as well as among different organisms. Catalase has iron in it, which acts as the catalyst for decomposing hydrogen peroxide.

In recent years, another group of enzymes has been discovered that quickly decomposes hydrogen peroxide. It is called peroxiredoxin and is found both in

humans and bacteria. In this enzyme, the catalytic element that decomposes hydrogen peroxide is sulfur, the sulphydryl group of cysteine amino acid.

Hydroperoxides (ROOH) can be decomposed by enzymes called peroxidases. Most of peroxidases are dependent on iron as catalyst, but a few of them use manganese. A very interesting peroxidase, called glutathione peroxidase, uses selenium as its catalytic element. Selenium is one of the most toxic elements, but a very small quantity of it is required by almost all organisms. It is used for glutathione peroxide as well as a few other enzymes. This enzyme is much more efficient in destroying certain types of hydroperoxides than the other more common iron-dependent peroxidases.

A more toxic superoxide free radical  $O_2^-$  is taken care of by enzymes called superoxide dismutases. They catalyze this reaction:  $2O_2^- + 2H^+ \rightarrow O_2 + H_2O_2$ . That is, it converts superoxide into less toxic hydrogen peroxide and oxygen.

The derivatives of oxygen such as superoxide and hydroxyl radical are damaging to cells, and hence they are often called “active oxygen.” Another type of active oxygen is the so-called singlet oxygen. At the beginning, we talked about the fact that  $O_2$  (dioxygen) has two unpaired electrons. That is, the most stable form of dioxygen. However, these two electrons can pair up, and the  $O_2$  molecule in such a situation is called “singlet oxygen.” The energy of singlet oxygen is higher than the regular dioxygen. This means that the singlet (di)oxygen is less stable than the regular dioxygen. Such an oxygen molecule can form, for example, as a result of radiation of ultraviolet ray on the regular oxygen. The singlet oxygen has different reactivities from that of regular oxygen and sometimes leads to damage of DNA and other cell components. Hence, the singlet oxygen is often considered to be one of the active oxygen (species).

Some naturally occurring compounds act as scavenger or quencher for these (bad) active oxygen species. These compounds are often called “antioxidants.” Vitamin C, E, and K react readily with the free radical entities, superoxide and hydroxyl radical, and make them nonradical, nonreactive compounds. These are called scavengers. Red wine has been recognized to be good for health. Some of the chemicals (particularly, polyphenols) contained in red wine are believed to act as free radical scavenger. Vitamin A and its relative carrotene (the orange pigment of carrot) are known to convert the singlet oxygen to the regular form. This process is a kind of quenching.

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## 2.5 Air Pollution

The oxygen in the air is in fact quite toxic as mentioned in the previous sections. But it is not considered to be a pollutant, as it is essential as well to the living organisms. Any extraneous compound that is put into the atmosphere can be potentially a pollutant. Three different kinds of pollutant can be recognized. One kind affects the physiology of plants and animals and causes ill effects on their health. Acid rain-causing and smog-causing compounds are such examples. The second kind is to increase the greenhouse effect of the atmosphere. Carbon dioxide is one of the important

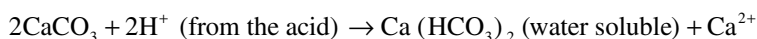
greenhouse effect enhancing gases, but it does not cause any significant physiological harm to living things at the current ambient level. It must be noted, though, that at a high level carbon dioxide can suffocate people, as some people in Cameroon were killed by an explosive release of a large amount of carbon dioxide from a lake. Carbon dioxide is not the only greenhouse enhancing gas; almost any organic compounds as well as water vapor can act as a greenhouse gas. The third kind causes depletion of ozone in the stratosphere.

### 2.5.1 Acid Rain and Smog

Modern human living produces a lot of different chemicals. For example, we need electricity for our living. How do we produce electricity? Most of electricity comes from power generation stations, though a significant amount is obtained from hydro-electric generators in some countries. In the power generation station, coal or petroleum is burned to produce heat that produces steam that drives the electric generator. Coal is chemically mostly carbon, and petroleum is made of mainly carbon and hydrogen. Therefore, the burning of coal or petroleum should produce only carbon dioxide and water. Carbon dioxide may contribute to the greenhouse effect but is not toxic to organisms.

The problem is that the fossil fuels contain small quantities of sulfur and nitrogen compounds (and others). After all, they have arisen from living organisms that were made of carbon, hydrogen, nitrogen, oxygen, and smaller quantities of phosphorus and sulfur (plus many microelements – see Chap. 6). Therefore, all fossil fuels contain small quantities of sulfur and nitrogen, though the actual content varies widely depending on the location of the source.

When coal or petroleum is burned, sulfur dioxide and some nitrogen oxide will be produced. Sulfur dioxide ( $\text{SO}_2$ ) can react with oxygen in the air under a certain condition and forms sulfur trioxide ( $\text{SO}_3$ ). Sulfur trioxide then reacts with water in the air or rain and turns into sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and the reaction is:  $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ . This is a simplified picture of how acid rain occurs. Sulfuric acid is one of the most corrosive acids and affects the physiology of plants and animals, if inhaled, and corrodes buildings and statues made of marble, concrete, or metal. Sulfur dioxide itself forms sulfurous acid ( $\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$ ). Sulfurous acid is also corrosive but less so than sulfuric acid. Nitrogen oxide can also form acid when it reacts with water. And, this acid also contributes to making acid rain. Why a strong acid like sulfuric acid is corrosive is illustrated by its effect on a marble statue. Chemically, it is due to reactions such as:



That is, the marble will be washed away by acidic rain.

The internal combustion engine in our car burns gasoline fuel. Gasoline is a mixture of hydrocarbons that are made of elements carbon and hydrogen. So when

gasoline is burned, carbon dioxide and water will form as the end products, neither of which is toxic. A little of gasoline, unburned or partially burned, may be spewed out from the exhaust pipe. The car uses air for the combustion. Air consists of nitrogen and oxygen. Oxygen is used to burn gasoline. No problem! Nitrogen, though quite unreactive as mentioned earlier, can react with oxygen at high temperatures in the engine. This reaction will produce nitrogen oxide(s). Nitrogen oxide may consist of several different chemical species:  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$ , but mostly “NO.” These compounds will form acids, when bound with water.

Hydrocarbons or their partially burned compounds will rise to the higher level in the atmosphere and so will nitrogen oxides. At higher level under the strong effect of sunlight (particularly, ultraviolet portion of sunlight), hydrocarbons (or partially burned compounds) react with a reactive chemical species OH (you recall this is called “hydroxyl radical”) in the atmosphere. This reactive species forms under the effect of sunlight. Some of the compounds that form in these reactions are aldehydes. (Aldehyde has a chemical formula  $\text{RCHO}$  in general; R can be H,  $\text{CH}_3$ , or others.) Some of them are toxic themselves. “NO” reacts with OH radical (or O radical) and turns into  $\text{NO}_2$  (nitrogen dioxide). NO can also turn into  $\text{NO}_2$  by just reacting with  $\text{O}_2$ .  $\text{NO}_2$  is colored yellow to brown. This is the cause of the brown haze in the smog. Smog is usually caused by the effect of sunlight, and so it is more properly called “photochemical smog.”  $\text{NO}_2$  and an intermediate in the hydrocarbon’s reaction then react and form peroxyacetyl nitrate (PAN) (chemical formula is  $\text{CH}_3\text{COONO}_2$ ). PAN and aldehydes are the eye- and throat-irritating components of the smog. In the lower level of atmosphere, the reactive species OH reacts with oxygen (dioxygen) and forms ozone ( $\text{O}_3$ ). Ozone is also toxic and has a pungent smell. All these chemical species that form under the strong sunlight contribute to the smog.

## 2.5.2 Greenhouse Effect

Global warming is a topic talked about every day and everywhere these days. It may be contributing to the increase in the formation of tornadoes and other severe weather phenomena. Carbon dioxide ( $\text{CO}_2$ ) is blamed mainly for its cause, though there are other causes natural and anthropological. Carbon dioxide comes from a number of sources. We, living organisms, burn our foodstuff (in physiological sense) and turn the organic compounds in the food into water and carbon dioxide, which we exhale. We cannot help but to release carbon dioxide. The quantity of carbon dioxide released by all living organisms is significant, but carbon dioxide is also consumed by another type of organisms, that is, plants. Plants use carbon dioxide and convert it to carbohydrate (food) through photosynthesis (see Chap. 3). Release and consumption of carbon dioxide seems to have been well balanced before the civilization of mankind started to release a lot of carbon dioxide into the atmosphere. We burn fossil fuel to energize most of things: automobile, production of electricity, and so forth. This will produce carbon dioxide (and water). As a result, the content of carbon dioxide in the atmosphere is rising. Why does this cause the global warming? It is because carbon dioxide is a greenhouse gas.



What is the greenhouse effect? This is more of a physics question, but relevant here. So we will talk about it a little. A greenhouse lets sunlight in. Sunlight is mostly light of wavelength of visible range and just outside of visible range. The light shone on any material excites the motions of atoms and molecules in the material; this will show up as temperature rises. That material reradiates energy as heat or rather light in the infrared range. The night vision camera or eyeglasses detect infrared radiation coming from an object. The infrared radiation is dependent on the temperature of the object. So a living human body will show up clearly in the night vision camera, though it is dark. [Let us review the wavelength of different types of light (electromagnetic wave). A light of wavelength range of 200–350 nm (nm=nanometer= $10^{-9}$  m) is called ultraviolet; the visible range (i.e., light the human eyes can detect) is 350–800 nm; the range from about 1,000 nm (1 mm=micrometer) to 50 mm or so is called “infrared.”]

Scientists have derived an equation that relates the wavelength of radiation to the temperature of the radiating body. This is known as the blackbody radiation equation. Using this equation, we can calculate how radiation from a body will distribute in terms of wavelength. For example, the surface temperature of our sun is about 6,000 K (K=Kelvin is degrees in Celsius plus 273). The radiation from this body (Sun) can be estimated to be centered around 480 nm or so (this is in the visible range). This agrees with the observation of sunlight. The radiation from a body whose surface temperature is 15–25°C (60–77°F) centers around 10  $\mu$ m, which is in the middle of infrared range.

Now let's get back to the greenhouse effect. The material inside a greenhouse becomes heated by sunlight that gets in. Suppose that the temperature becomes 25°C; then the inside surface of the greenhouse radiates infrared light centering around 10  $\mu$ m. Now the crux of the matter is that the glass (or plastic) window of the greenhouse can let visible sunlight through, but that the glass absorbs the infrared light, that is, would not let it through. The glass then radiates infrared light, most likely about the half of it to the outside and the rest to the inside. So, only about half of the heat generated inside can escape to the outside. Hence, there is a further heat up inside the greenhouse. Heat can also escape through the glass by heat conduction, which is dependent on the temperature difference between inside and outside.

On the Earth, the atmosphere functions as the glass of greenhouse. Sunlight comes through the atmosphere. A number of compounds in the atmosphere absorb some portions (particularly, in the ultraviolet region) of sunlight, but a substantial portion of it reaches the surface of the Earth. We live on that light. It also heats the Earth. Now the Earth's surface radiates back infrared light. And because the surface temperature is somewhere around 15°C on the average, the infrared radiation centers around 10  $\mu$ m. A portion of it then escapes into the space, and a steady state has been established between the incoming energy flux and the outgoing energy flux. Hence the surface temperature has been more or less constant overall.

Atmosphere contains carbon dioxide and other compounds as minor components. Carbon dioxide absorbs infrared light. The major components of the air, nitrogen and oxygen, do not absorb infrared light. So, the infrared light radiated

from the Earth's surface is absorbed by carbon dioxide. Carbon dioxide will reradiate the heat about half into the outer space and about half is radiated back onto the Earth's surface. As the concentration of carbon dioxide in the atmosphere increases, the heat trapped inside the atmosphere will then increase and heat up the Earth's surface. This is the mechanism of greenhouse effect of carbon dioxide, though quite simplified, and is considered by many to be the major cause of the current global warming.

Carbon dioxide is not the only greenhouse gas. As can be inferred from the description above, any compound that absorbs the appropriate portion of infrared range will act as greenhouse gas. Methane, the major component of natural gas, is one such example. Methane comes from microorganisms (methane bacteria), and also cows and other animals produce methane in their digestive systems. Some people even think that methane may be the major cause of greenhouse effect. Some chlorofluoro carbons that are discussed below in connection with the ozone depletion are also effective greenhouse gases. No matter what, carbon dioxide is believed to be the most important greenhouse gas, as we human beings burn fossil fuels as well as any material containing carbon (wood, for example) as an energy source, and that inevitably produces carbon dioxide. It might be pointed out that the temperature of the surface of Venus is about 430°C, partially due to the predominant presence (about 90%) of carbon dioxide in its atmosphere.

### 2.5.3 Ozone Depletion

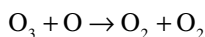
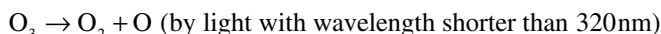
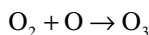
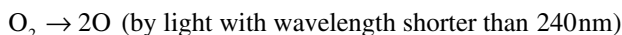
In the previous section we talked about how sunlight is partially blocked by the Earth's atmosphere. What blocks the sunlight? A number of minor components in the atmosphere absorb light in the ultraviolet region. Examples include some of the organic compounds such as aldehyde(s) and benzene, and inorganic compounds such as  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{NO}_2$ . The most important of all such compounds is ozone ( $\text{O}_3$ ); that is, it is made of three oxygen atoms. The composition tells you that it will form when  $\text{O}_2$  (dixxygen, the form found in the air) reacts with  $\text{O}$  (oxygen atom). How ozone is produced and decomposed is a crucial issue.

In order to understand this matter, we need to introduce the concept of the energy of light. Light is a wave and hence is characterized by its wavelength  $\lambda$  or frequency  $\nu$ . The energy of a light with frequency  $\nu$  is given by  $h\nu$ , where  $h$  is Planck's constant (a universal physical constant). As wavelength  $l$  and frequency  $\nu$  are related by an equation  $c = \lambda\nu$ , the energy of a light is related to its wavelength in the form of  $hc/\lambda$ , where  $c$  is the speed of light. This says that a light of a shorter wavelength has a larger energy than that of a longer wavelength. Hence, ultraviolet light (shorter than 320 nm; nm = nanometer = one billionth of meter =  $10^{-9}$  m) has larger energy and is more damaging than visible light (320–800 nm).

Now, the sunlight consists of lights of varying wavelength centered about 480 nm as mentioned earlier. It contains light with shorter wavelength than that as

well as light with longer wavelength. When it hits the upper layer of the Earth's atmosphere, it cleaves the bond of  $O_2$  (dioxygen, i.e., the regular oxygen molecule in the air). This bond is difficult to split, as it requires a lot of energy. So it occurs only when dioxygen absorbs light with wavelength shorter than 240 nm (way into the ultraviolet range). As a result, dioxygen splits into two oxygen atoms, and simultaneously the sunlight shorter than 240 nm will be consumed or stopped there and would not reach the lower part of the atmosphere. The oxygen atom produced then reacts with dioxygen and forms ozone ( $O_3$ ). The O–O bond in an ozone molecule is more easily split than that in a dioxygen molecule. So the decomposition of ozone occurs with light of longer wavelength and is known to occur with light of 320 nm or shorter. This means that light of wavelength shorter than 320 nm (i.e., ultraviolet light) will be consumed to decompose ozone, and not significant amount of ultraviolet light reaches the Earth's surface. So ozone layer will act as a filter of ultraviolet light.

The reactions involved in these processes are:

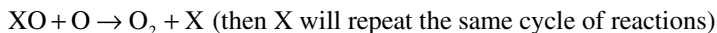
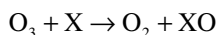


These reactions constantly generate and decompose ozone, and a steady-state ozone layer has been established in the upper level of atmosphere. The maximum level of ozone occurs at about 18–20 km above the Earth's surface. This layer protects all living organisms from being exposed to the dangerous ultraviolet light. As a matter of fact, the creation of the ozone layer is believed to have made possible the emergence of terrestrial (land) organisms.

A satellite Nimbus has on board a spectrometer to measure ozone level in the atmosphere. Data from the satellite showed that the ozone level above the Antarctic continent during the winter season started to decrease noticeably from about 1980. It developed further to form almost a hole (no significant ozone there); hence, this phenomenon is known as "ozone hole." There is a sign that the range of ozone hole is further spreading. Even in the Northern Hemisphere, a region of low ozone level has developed over the Arctic ocean and the Northern Siberia. Is the decrease of ozone level occurring only above the Polar regions? No, it is spreading to the southern mid-latitude. A decrease of ozone in the upper atmosphere means that an increased amount of ultraviolet will reach the Earth's surface.

The critical question is what is causing the decrease of ozone level in the atmosphere. Scientists, particularly atmospheric chemists, tried to figure out this problem for the last 2 decades, by lab works and computer modeling (i.e., simulating what might be happening in the atmosphere), and measuring the levels of various chemical species in the atmosphere. The consensus of these investigations is that ozone is

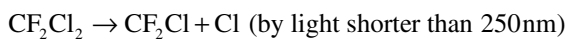
being decomposed chemically by free radical species. As mentioned somewhere else, a free radical is a chemical species with an unpaired electron. A free radical X reacts with ozone ( $O_3$ ) in the following way:



X can be almost any free radical species including NO and OH, but chlorine (and bromine) has been recognized to be the major culprit.

Where does “chlorine” come from? It is believed to come from chlorofluorocarbons (CFCs; a collective name for chloro/fluoro derivatives of hydrocarbons). CFCs have been manufactured since the 1930s. CFC-12 (chemically  $CF_2Cl_2$ , dichloro difluoro methane) was introduced originally as refrigerant. CFC-12 is non-toxic and nonflammable, making the refrigerator safe enough. Other CFCs have also been used for refrigerators, as an expanding agent for foams, propellants for aerosol sprays (CFC-11,  $CFCl_3$ ), and cleaning agents for microelectronic components (chiefly CFC-113,  $CF_2ClCF_2Cl$ ). CFCs in the troposphere were about 50 parts per trillion (ppt) by volume in 1971 and had risen to about 270 ppt by 1993.

CFC-11 and -12 are not reactive in the troposphere; they go up to the stratosphere where they are susceptible to a slow decomposition by ultraviolet light (shorter than 250 nm):



The chlorine atom (Cl) thus produced then reacts with ozone, destroying it. (C–F bonds would not be split easily by the ultraviolet light.) Other CFCs behave similarly. The problem with CFCs is that they are quite inert compounds and are slow to decompose to form Cl and hence they persist in the stratosphere. Their lifetimes have been estimated to range up to 100 years.

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