

## 2

# Atmosphere

### 2.1 COMPOSITION OF THE ATMOSPHERE

The atmosphere has, broadly speaking, three categories of constituents—major, minor and trace. For pollution-free dry air at ground level, the components may be expressed as per cent by volume, as follows (within parentheses):

Major components:	Nitrogen (78.09)
	Oxygen (20.94)
	Water vapour (0.1–5)*
Minor components:	Argon ( $9.34 \times 10^{-1}$ )
	Carbon dioxide ( $3.25 \times 10^{-2}$ )*
Trace components:	Neon ( $1.82 \times 10^{-3}$ )
	Helium ( $5.24 \times 10^{-4}$ )
	Methane ( $2 \times 10^{-4}$ )
	Krypton ( $1.14 \times 10^{-4}$ )
	Nitrous oxide ( $2.5 \times 10^{-5}$ )
	Hydrogen ( $5 \times 10^{-5}$ )
	Xenon ( $8.7 \times 10^{-8}$ )
	Sulphur dioxide ( $2 \times 10^{-8}$ )
	Ozone (trace)
	Ammonia ( $1 \times 10^{-6}$ )
	Carbon monoxide ( $1.2 \times 10^{-5}$ )
	Nitrogen dioxide ( $1 \times 10^{-5}$ )
	Iodine (trace)*

The parameters of the atmosphere vary considerably with altitude. The density of the atmosphere shows a sharp decrease with increasing altitude. Pressure drops from 1 atmosphere at sea level to  $3 \times 10^{-7}$  atmosphere at 100 km above sea level, while temperature varies from –92 to 1200 °C. The total mass of the atmosphere is approximately  $5 \times 10^{15}$  tonnes, which is roughly 1 millionth of the earth's total mass.

### 2.2 ATMOSPHERIC STRUCTURE

The atmosphere may be broadly divided into four regions as shown in Table 2.1. It extends up to 500 km with temperatures varying from a minimum of –92 to a maximum of 1200 °C.

\*The corresponding values in parts per million (ppm) are obtained by multiplying the per cent volumes by  $10^4$ . Thus, nitrogen ( $78.09 \times 10^4$  ppm), oxygen ( $20.94 \times 10^4$  ppm), carbon dioxide (3.25 ppm), etc.

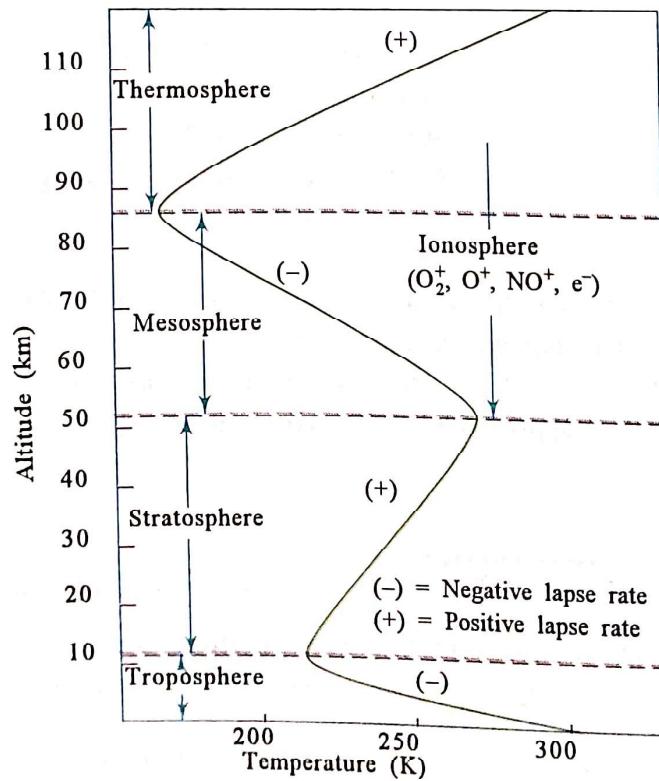
**Table 2.1** Major regions of the atmosphere

Region	Altitude range (km)	Temperature range ( $^{\circ}\text{C}$ )	Important chemical species
Troposphere	0–11	15 to $-56$	$\text{N}_2, \text{O}_2, \text{CO}_2, \text{H}_2\text{O}$
Stratosphere	11–50	$-56$ to $-2$	$\text{O}_3$
Mesosphere	50–85	$-2$ to $-92$	$\text{O}_2^+, \text{NO}^+$
Thermosphere	85–500	$-92$ to $1200$	$\text{O}_2^+, \text{O}^+, \text{NO}^+$

The *troposphere* contains 70% of the mass of the atmosphere. The upper limit of the troposphere may vary by kilometre or more, depending on factors such as temperature, nature of terrestrial surface, etc. Air is far from uniformity with respect to density and temperature. Density decreases exponentially with increasing altitude. In respect of composition, the troposphere is more or less homogeneous in the absence of air pollution, mainly due to the constant circulation of air masses in this region. The water content, however, varies due to the hydrological cycle. The troposphere is also a turbulent region due to the global energy flow arising from imbalances of heating and cooling rates between the equator and the poles.

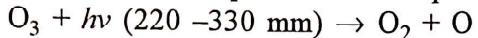
The temperature in the troposphere falls off uniformly with increasing altitude. The air near ground level is heated by radiation from the earth. The cold layer ( $-56^{\circ}\text{C}$ ) at the top of the troposphere is called the *tropopause*, which marks temperature inversion, i.e., transition from negative to positive lapse rates (slopes of temperature-altitude curve: Fig. 2.1).

The *stratosphere* is the quiescent layer having a positive lapse rate. The temperature increases with increase in altitude, with a maximum of  $-2^{\circ}\text{C}$  at the upper limit of the stratosphere. Ozone in this region absorbs ultraviolet radiation and raises the temperature causing a positive lapse rate (Fig. 2.1).



**Fig. 2.1** Major regions of the atmosphere, with temperature profile

It plays an important role in the stratosphere. It acts as a protective shield for life on earth from the injurious effects of the sun's ultraviolet rays and at the same time, supplies the heat source for partitioning the atmosphere into a quiescent stratosphere and turbulent troposphere.



Because of slow mixing in the stratosphere, the residence times of molecules or particles in this region are quite long. If the pollutants can somehow reach or are injected into the stratosphere, they pose long-term global hazards compared to their impact in the much-denser troposphere.

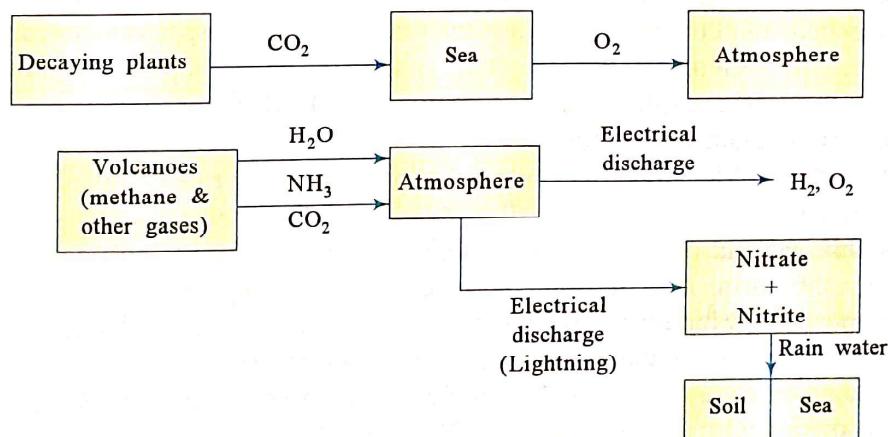
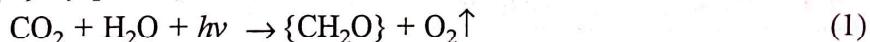
The *mesosphere* shows negative lapse rate, i.e., temperature falls with increasing altitude. This is due to low levels of ultraviolet-absorbing species, particularly ozone.

In the *thermosphere* immediately above the mesosphere, the temperature rises once again, giving a positive lapse rate (maximum temperature,  $1200^\circ\text{C}$ ). Here, the atmosphere gases, particularly oxygen and nitric oxide, split into atoms and also undergo ionization after absorption of solar radiation in the far-ultraviolet region.

### 2.3 EVOLUTION OF THE ATMOSPHERE

How did the earth's atmosphere originate? There are many views but it is commonly believed that the atmosphere was quite different from its present state, the changes being brought about by biological activity.

More than 3 billion years ago, volcanoes synthesised and emitted  $\text{CO}_2$ , water vapour and  $\text{NH}_3$  from methane and other gases deep in their cores. **The first primitive life molecules were formed in this chemically-reducing atmosphere.** Intense bombardment of the atmosphere by ultraviolet light, along with lightning and radiation from radionuclides, provided the required energy to initiate these chemical reactions which led to the production of relatively complicated molecules evolved from the rich chemical mixture in the sea. These life forms drew their energy from fermentation of organic matter arising from chemical and photochemical processes. Finally, they were capable of producing organic matter  $\{\text{CH}_2\text{O}\}$  by photosynthesis:



Thus, the stage was set for massive biochemical transformation which led to the generation of atmospheric  $\text{O}_2$ . The life forms might have been blue-green algae whose limy deposits have been

of energy in the infrared region from the earth; (b) conduction of energy through the interaction of atoms or molecules, and (c) convection of energy through massive air circulation. The latter two mechanisms are responsible for loss of heat from the earth's surface through transport to clouds, and consequent radiation from the clouds.

The average surface temperature of the earth is maintained around  $15^{\circ}\text{C}$  due to reabsorption of most of the outgoing infrared radiation ( $2\text{--}40\ \mu$ ) by water vapour ( $4\text{--}8\ \mu$ ), and to a lesser extent by carbon dioxide ( $12\text{--}16.3\ \mu$ ). The combined effect of water vapour and carbon dioxide leads to the *greenhouse effect*\* which is of great significance in governing the climate on earth. This will be discussed in the following section.

Increasing agricultural and industrial outputs can also upset the earth's radiation balance by changing the *albedo* (fraction of sunlight reflected and scattered back to the atmosphere). Deforestation and the consequent soil erosion increase the albedo. Furthermore, both agriculture and industry release large quantities of dust and fumes into the atmosphere. The effects of these human practices are small compared to the natural forces (wind, sea, spray, volcanoes, etc.) which contribute to a large extent to the particle loading of the atmosphere. These atmospheric particles have a cooling effect on the earth's surface through increased scattering of the sun's rays. Dark particles (deposited on soot) can absorb light whereas light particles reflect light. The former helps in the heating of the earth's atmosphere, while the latter removes heat. The effect of particles on climate can be understood by a detailed analysis of the sources of these particles and their overall loading in the atmosphere (Sec. 2.9).

## 2.5 PARTICLES, IONS AND RADICALS IN THE ATMOSPHERE

*Particles* are the important contents of the troposphere. They may vary in the number from several hundred per cubic centimetre in very pure air to more than  $10^5$  per cubic centimetre in highly polluted air. Their size is in the range of  $0.1\text{--}10\ \mu$ . The particulate mass level ranges from  $10\ \mu\text{g}/\text{m}^3$  in clean air to  $60\text{--}2000\ \mu\text{g}/\text{m}^3$  in the polluted air in urban areas.

Colloidal-size particles in the atmosphere are known as *aerosols*. Aerosols of natural origin with diameter less than  $0.2\ \mu$  are called *Aitken* particles. These particles originate from vegetation. Other particles of natural origin in the atmosphere are bacteria, fog, pollen grains and volcanic ash.

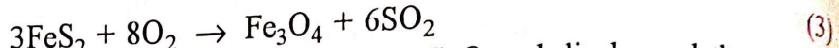
In USA, about 13.4 MT (metric tonnes) of primary particles are emitted per year, out of which about 5 MT are smaller than  $3\ \mu$ . The chemical nature and size of the particles are more important than the particulate matter load in the atmosphere. Particles in the size range  $0.1\text{--}1\ \mu$  exert several important effects.

- (a) They are responsible for electrical phenomena in the atmosphere, cloud and fog formation.
- (b) They play an important role in determining the heat balance of the earth's atmosphere through light reflection.
- (c) They serve as nuclei for the formation of ice crystals and water droplets.
- (d) They are involved in several chemical reactions in the atmosphere: (i) Neutralization reactions in water droplets; (ii) catalytic effects of small particles of metal oxides on oxidation reactions; (iii) photochemical oxidation reactions.

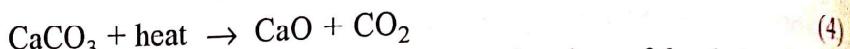
\* See Sec. 2, 7.

### Chemical Processes for Formation of Inorganic Particulate Matter

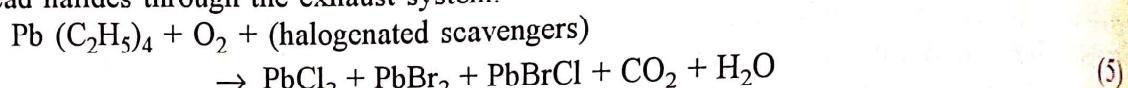
Metal oxides form a major group of inorganic particles in the atmosphere. They originate from the combustion of fuels. Thus, the particulate iron oxide originates in the combustion of pyrite-containing coal:



Part of the  $\text{CaCO}_3$  in the ash fraction of coal is converted to  $\text{CaO}$  and discharged through the stack:



Automobiles are sources of lead particles in the atmosphere. Combustion of leaded gasoline discharged lead halides through the exhaust system:



(The halogenated scavengers are dichloroethane and dibromoethane). In USA, more than  $2 \times 10^5$  tonnes of lead is dumped into the atmosphere every year. In recent years, however, this quantity is decreasing with the use of unleaded gasoline.

Aerosol mists arise from sulphuric acid, obtained by oxidation of sulphur dioxide which collects water vapour to form small liquid droplets:



In the presence of basic air pollutants such as ammonia or calcium oxide, salts are formed:

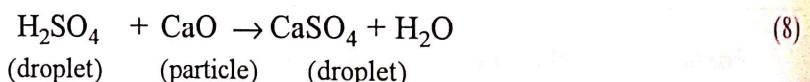
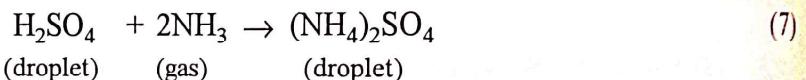
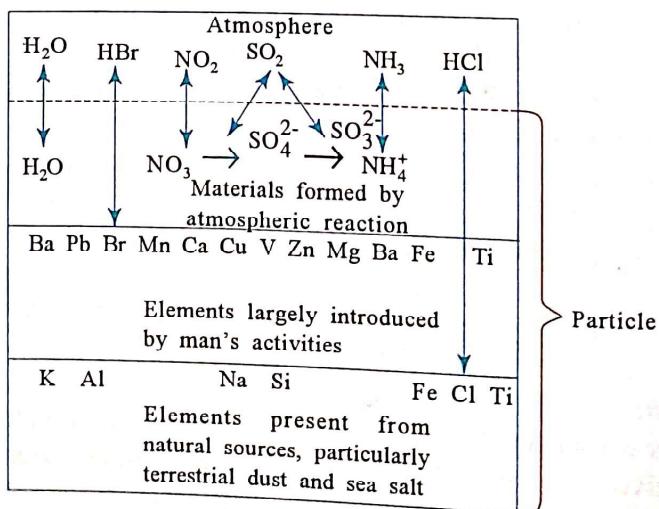


Figure 2.2 illustrates the components of inorganic particulate matter and their origins.



**Fig. 2.2** Some of the components of inorganic particulate matter and their origins (Reprinted by permission of Brooks/Cole Publishing Company, Monterey, California 93940 USA from *Environment Chemistry*, 3rd edn., S.E. Manahan, p. 369, 1979, Willard Grant Press, Statler Office Building, Boston, Massachusetts).

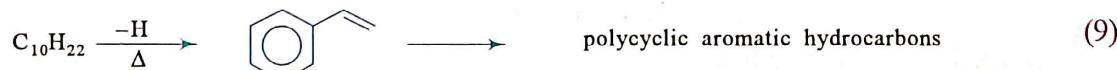
A typical analysis of particulate matter in the air in United States urban locations revealed the following composition ( $\mu\text{g}/\text{m}^3$ ): total suspended particulate matter (105),  $\text{NH}_4^+$  (1.3),  $\text{NO}_3^-$  (2.6),  $\text{SO}_4^{2-}$  (10.6), benzene-soluble organics (6.8), Sb (0.01), As (0.02), Cd (0.002), Cr (0.015), Cu (0.09), Fe (1.58), Pb (0.79), Mn (0.10), Ni (0.034), Sn (0.02), Ti (0.04), V (0.05) and Zn (0.67).\*

### Chemical Processes for Formation of Organic Particulate Matter

Organic particulate matter originates from a wide variety of sources, e.g., emissions from vegetation and automobiles, combustion of fuel, etc. Typical organic particulate matter, as obtained in the form of a benzene-extractable fraction from 200 air samples in USA showed an average formula,  $\text{C}_{32.4}\text{H}_{48}\text{O}_{3.8}\text{S}_{0.083}\text{halogen}_{0.065}\text{alkoxy}_{0.12}$ . Such particles are in the  $1-\mu$  size range and are potential health hazards.



Polycyclic (polynuclear) aromatic hydrocarbons (PAH) in organic particulate matter are known to have *carcinogenic effect*. Among these, benzo ( $\alpha$ ) pyrene is well known. PAH compounds commonly occur in urban atmospheres at about the  $20 \mu\text{g}/\text{m}^3$  level. They originate from the pyrolysis of higher paraffins present in fuels and plant material. High molecular weight paraffins are pyrolyzed to yield  $\text{C}_{10}\text{H}_{22}$  which undergoes further pyrolysis:



Most of the PAH compounds remain adsorbed on soot particles.

Soot is formed as a residue on combustion of fuel in power plants and automobiles. It accounts for 50% of the particulate load in urban areas. Chemically, it is highly condensed product of polynuclear aromatic hydrocarbons, consisting of several thousand interconnected crystallites, i.e., graphic platelets each having about 100 condensed aromatic rings. The hydrogen content of soot is 1–3% and oxygen content about 5–10% due to partial surface oxidation. Because of its large surface area, soot acts as a carrier for toxic organics, e.g., benzo ( $\alpha$ ) pyrene, and toxic trace metals, e.g., beryllium, cadmium, chromium, manganese, nickel, vanadium, etc.

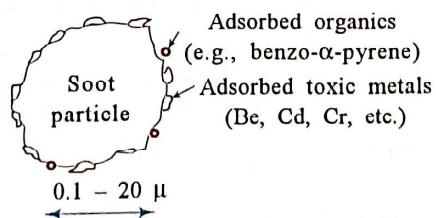


Fig. 2.3 Soot particle containing adsorbed toxic metals and organic carcinogens

\*Air Quality Data 1964-65, US Dept. of Health, Education and Welfare, Division of Air Pollution, Cincinnati, Ohio, 1966, pp. 1-2.

\*\*E. Sawicki, Arch. Environm. Health, 14, 46 (1967).

In general, atmospheric particles enter human bodies through the respiratory tract. Among these, small particles ( $0.1\text{--}1 \mu$  size) reach the lungs and are retained there, causing health hazards. The removal of particulate matter from gas streams is an important strategy for air pollution control, which will be discussed in a subsequent section (Ch. 10).

### Ions and Radicals

The ions dominate above the stratosphere in the region known as the *ionosphere*. Both positive ions ( $\text{O}_2^+$ ,  $\text{O}^+$ ,  $\text{NO}^+$ , etc.) and electrons exist at significant levels in the ionosphere. They persist for long periods without recombining to give neutral species due to rarefied conditions in the upper atmosphere.

Ultraviolet radiation is primarily responsible for the production of ions in the ionosphere. At night in the absence of ultraviolet light, the positive ions slowly recombine with free electrons to form the original neutral species. This process occurs rapidly in the lower regions of the ionosphere where the species exist in relatively high concentrations. The ions are strongly influenced by the earth's magnetic field, giving rise to the phenomenon of *Van Allen belts*. The latter consist of two belts of ionizing particles encircling the earth.

Besides ions, free radicals are generated by electromagnetic radiation. They consist of atoms or group of atoms with impaired electron, having half-lives of several minutes or more in the rarefied upper atmosphere. They are highly reactive. They take part in chain reactions in which one of the products of each reaction is a free radical. Finally, one of the free radicals in a chain is destroyed and the chain is terminated:



where RH = aliphatic hydrocarbon



Free radicals play an important role in photochemical smog formation.

## 2.6 CHEMICAL AND PHOTOCHEMICAL REACTIONS IN THE ATMOSPHERE

The study of chemical reactions in the atmosphere poses serious problems due to the very low concentrations involved, which makes the detection and analysis of reaction products extremely difficult. High altitude reactions at very low pressure can not be simulated in the laboratory.

Chemicals in the atmosphere participate in photochemical reactions by absorption of solar radiation. Such reactions occur even in the absence of chemical catalysts at much lower temperatures. These photochemical reactions play a key role in governing the ultimate fate of a chemical in the atmosphere.

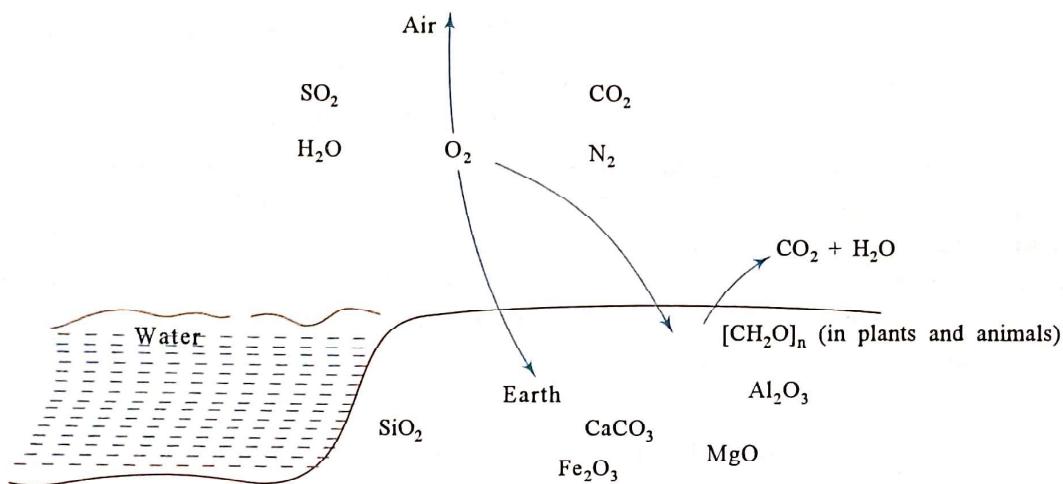
Some typical chemical and photochemical reactions will now be illustrated. It should be noted that the atmosphere is a *tremendously dynamic system with wide fluctuations of the parameters, viz. composition, temperature, humidity and intensity of sunlight*. Obviously, different processes will be observed under varying atmospheric conditions.

While  $\text{O}_2$  plays an important role in the troposphere,  $\text{O}_3$  plays a key role in the stratosphere.

### 2.6.1 Oxygen and Ozone Chemistry

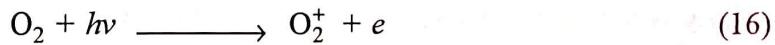
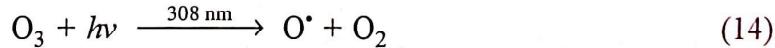
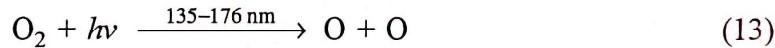
The chemical activity of oxygen plays an important role in the lower atmosphere. The stable forms of almost all the elements are oxides, as shown in Fig. 2.4. The atmosphere contains gases such as carbon dioxide and sulphur dioxide.

The oceans are full of the oxide of hydrogen, while the earth's crust contains mainly the solid oxides of silicon, carbon, calcium, magnesium, iron and aluminium.



**Fig. 2.4** Most elements are stable as oxides

In the upper atmosphere, the species of oxygen are  $\text{O}_2$ ,  $\text{O}$ ,  $\text{O}^\bullet$ ,  $\text{O}^+$ ,  $\text{O}_2^\bullet$  and  $\text{O}_3$ , i.e., molecules, atoms, ions, and excited atoms and molecules. Ultraviolet radiation causes photochemical dissociation, ionization, etc.



**Ozone**,  $\text{O}_3$  is the important species in the stratosphere, acting as a protective radiation shield for living organisms on earth. The *maximum ozone concentration is around 10 ppm in the stratosphere at an altitude of 25–30 km*.

Ozone is formed by a photochemical reaction, followed by a three-body reaction:



The third body ( $\text{M}$ ) absorbs the excess energy liberated by the above reaction and thereby stabilize the  $\text{O}_3$  molecule.

Ozone strongly absorbs ultraviolet light in the region 220–330 nm and thereby protects life on earth from severe radiation damage. Only a small fraction of the ultraviolet light reaches the lower atmosphere and the earth.

The mechanism of ozone removal is not well understood. It is believed that ozone is eliminated by reaction with atomic oxygen, reactive hydroxyl radicals and mainly by nitric oxide.



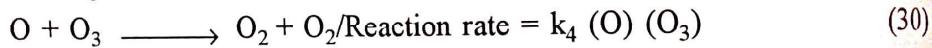
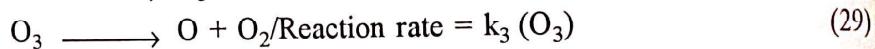
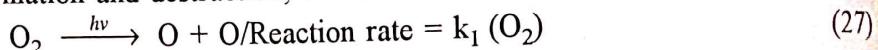


It may be noted that nitric oxide is produced in the stratosphere, below 30 km, by the reaction of nitrous oxide ( $\text{N}_2\text{O}$ ) with excited oxygen atoms, and above 30 km by ionizing radiation on nitrogen.



**Ozone distribution**— $\text{O}_3$  is highly unstable relative to  $\text{O}_2$ . At equilibrium,  $\text{O}_2/\text{O}_3$  ratio is  $10^{25}$  while it is  $3 \times 10^5$  at an altitude of 30 km where  $\text{O}_3$  concentration has its peak value. The actual  $\text{O}_3$  concentration is determined by the rate of its formation and rate of destruction. The rate of formation depends on the flux of ultra-violet solar radiation in the stratosphere. This solar flux being variable,  $\text{O}_3$  concentration is also subject to variations depending on the altitude.

Referring back to  $\text{O}_3$  formation and destruction, we have the reaction rates:



$$\text{At equilibrium: } k_2(\text{O})(\text{O}_2)(\text{M}) = k_3(\text{O}_3) + k_4(\text{O})(\text{O}_3) \quad (31)$$

The steady state  $(\text{O}_3)/(\text{O}_2)$  ratio

$$\frac{(\text{O}_3)}{(\text{O}_2)} = \left( \frac{k_1 k_2 (\text{M})}{k_3 k_4} \right)^{1/2} \quad (32)$$

This ratio is largely dependent on the altitude. The density of air and (M) concentration decrease with increasing altitude.  $k_1$  and  $k_3$  increase with increase in photon flux while  $k_2$  and  $k_4$  increase slightly with rise in temperature as the altitude increases in the stratosphere. It can be calculated that at an altitude of 30 km:

$$(\text{Air}) = 10^{17.7} \text{ mol/cm}^3$$

$$k_1 = 10^{-11}, k_2 = 10^{-32.7}, k_3 = 10^{-3} \text{ and } k_4 = 10^{-4}$$

$$(\text{O}_3)/(\text{O}_2) = 10^{-4}$$

The calculated value of  $\text{O}_3$  concentration differs from the observed value by a factor of two. Presumably there are some other mechanisms for  $\text{O}_3$  destruction.

On the average, ozone is more plentiful near the poles than at the equator and more abundant in winter than in summer. Despite its low concentration (10 ppm i.e.,  $10^{-5}$  per cent of atmosphere), the presence of ozone shield is important for the welfare of mankind. The maximum concentration of ozone is around an altitude of 25 km. in the stratosphere ( $5 \times 10^{12} \text{ mol. cm}^{-3}$ ).

## 2.6.2 Sulphur Dioxide

There are four possible routes along which sulphur dioxide may react:

- (a) photochemical reactions

- (b) photochemical and chemical reaction in the presence of nitrogen oxides and/or hydrocarbons
- (c) chemical processes in water droplets containing metal salts and ammonia
- (d) reaction on solid particles in the atmosphere

Sulphur dioxide absorbs solar radiation in the region 300–400 nm, particularly in the lower atmosphere, to produce electronically-excited states of  $\text{SO}_2$ .

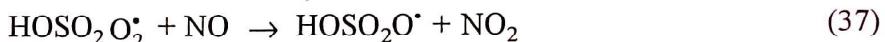


In natural sunlight, at the 5–30 ppm level of  $\text{SO}_2$  and relative humidity, 32–90%, the overall reaction is

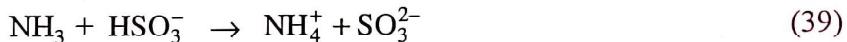


which is promoted by the presence of hydrocarbons and nitrogen oxides, key components of photochemical smog (Sec. 10.1.3).

The free radical  $\text{HO}^{\bullet}$  present in photochemical smog also contributes to the oxidation of  $\text{SO}_2$ , ending up as a sulphate.



In relatively humid atmosphere,  $\text{SO}_2$  is probably oxidized by reactions occurring inside water aerosol droplets, which proceed faster in the presence of ammonia and catalysts such as manganese (II), iron (II), nickel (II), copper (II), etc.



Solid particles such as *soot* provide heterogeneous phases for catalysing the oxidation of  $\text{SO}_2$ . Soot particles (Sec. 2.4) are common features of polluted atmospheres. There is an evidence of the presence of sulphate in soot particles from photoelectron spectroscopy.

Sulphur dioxide, one of the serious air pollutants (Sec. 10.1.4), is responsible for smog, resulting in several incidents of loss of human lives. It also contributes to acid rains (Sec. 10.1.5).

### 2.6.3 Nitrogen Oxides

The nitrogen oxides in the atmosphere are nitrous oxide,  $\text{N}_2\text{O}$ , nitric oxide,  $\text{NO}$ , and red-brown nitrogen dioxide  $\text{NO}_2$ .

Nitrous oxide originates from microbiological processes and occurs in unpolluted air at a level of about 0.25 ppm. In the lower atmosphere, it has practically no influence on chemical reaction, but at higher altitudes, it helps to deplete the ozone layer.



Nitric oxide and pungent red-brown nitrogen dioxide are important constituents of polluted air. These oxides, collectively designated  $\text{NO}_x$ , enter the atmosphere mainly from anthropogenic (man-made) sources, *i.e.*, combustion of fossil fuels in both stationary and mobile sources. The annual global input of  $\text{NO}_x$  is of the order of 86 million tonnes.

*Sources and sinks for  $\text{NO}_x$* —The bulk of  $\text{NO}_x$  on a global basis originates from microbial action (bacterial decay of organic matter) in the earth's surface, which yields  $\text{N}_2\text{O}$ . This  $\text{N}_2\text{O}$  is inert in the troposphere but it reacts with O atom in the stratosphere to form NO and then enters the  $\text{O}_3$  destruction cycle. This cycle is disrupted when  $\text{NO}_2$  reacts with  $\text{OH}^\cdot$  (radical) to give  $\text{HNO}_3$ .

At the next step NO reacts with  $\text{OH}^\cdot$  to produce  $\text{HNO}_2$ . These acids being soluble in water, are quickly rained out in the troposphere. The sources and sinks of  $\text{NO}_x$  are summarized below:

The overall process for the elimination of NO probably consists of its reaction with  $\text{O}_2$ ,  $\text{O}_3$  or O (in the presence of a third body, M) to yield  $\text{NO}_2$ :

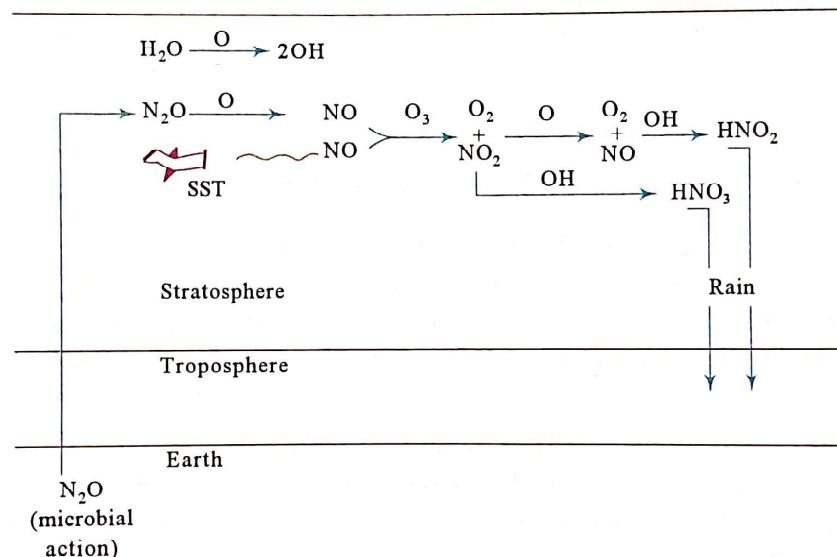
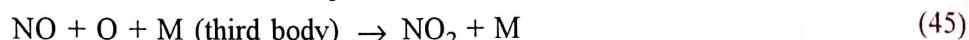
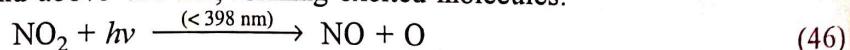


Fig. 2.5 Sources and sinks for  $\text{NO}_x$

Nitrogen dioxide is an important species in the atmosphere. It absorbs sunlight below 398 nm undergoing photodissociation, and above 430 nm, forming excited molecules.



The photodissociation of  $\text{NO}_2$  can yield a series of inorganic reactions, besides a number of reactions involving organic species:





Nitrogen dioxide finally ends up as  $\text{HNO}_3$ , nitrates or organic nitrogen compounds (under conditions of photochemical smog).



In the stratosphere,  $\text{NO}_2$  also reacts with the hydrogen radical,  $\text{HO}$  to form  $\text{HNO}_3$ .



It appears that  $\text{HNO}_3$  is the temporary sink for  $\text{NO}_2$  in the stratosphere. Nitric acid produced from  $\text{NO}_2$  is removed as acid rains. Alternatively, it reacts with bases (ammonia, particulate lime) to yield particulate nitrates.

Thus, the  $\text{NO}_x$  pool is consumed by conversion to  $\text{HNO}_3$  and  $\text{HNO}_2$  but balanced by the activation of  $\text{N}_2\text{O}$  from the earth below. The  $\text{O}_3$  chemistry is more complicated than that represented above and in the preceding section (oxygen and ozone chemistry). The movement of air masses within the stratosphere being slow, the reaction rates in many parts of the stratosphere are obviously slow. In order to have a correct picture of the distribution of gases in the stratosphere, it is necessary to have elaborate computer programmes.

Human activities also play a significant role in the matter of  $(\text{NO})_x$  load in the stratosphere. The supersonic aircrafts (SST) fly in the stratosphere because of low air resistance which helps in maintaining supersonic speed. But these discharge large quantities of  $(\text{NO})_x$  in their exhaust gases directly into the stratosphere. It is calculated that a fleet of 500 SSTs, flying 7 hours each day, will contribute annually the existing concentration of  $(\text{NO})_x$  in the stratosphere. The residence times of the gases in the stratosphere are of the order of a year or so. Hence, there is a possibility of doubling of the stratospheric concentration of  $(\text{NO})_x$  which in turn will tend to reduce  $\text{O}_3$  concentration by about 40%. Recently it has been found that the hydroxyl radical is very efficient in removing  $(\text{NO})_x$  from the stratosphere. All these considerations appear to confirm the observed depression in the calculated  $\text{O}_3$  concentration (2.7/Ozone distribution).

An additional factor regarding man-made  $(\text{NO})_x$  load in the stratosphere may be taken into account. Nuclear explosions produce large quantities of  $(\text{NO})_x$  which are injected directly into the stratosphere. The nuclear tests conducted by USA and USSR in the early 60s reduced  $\text{O}_3$  concentration by about 4% which may rise to 50%, if the bulk of the nuclear arsenals of USA and USSR are released. This will lead to extensive reduction in the  $\text{O}_3$  shield which in turn will spell disaster for mankind in terms of large scale damage to food production with increased exposure to ultraviolet radiation.

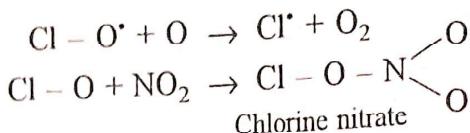
The estimated value of  $(\text{NO})_x$  in the stratosphere is  $3$  to  $5 \times 10^9$  molecules  $\text{cm}^{-3}$ . This fairly agrees with the calculations.

It may be noted that many sources and sinks for  $(\text{NO})_x$  in the troposphere remain to be identified. There is a large reserve of ambient  $\text{N}_2\text{O}$  concentrations (1300 MT approx.) with annual fluctuations indicating a residence time of about 10 years so that the production rate is 130 MT/year. The ocean waters are also supersaturated with  $\text{N}_2\text{O}$  which is released with a global production rate of 100 MT per year.

These figures are, however, tentative which show that lots of studies remain to be done on  $\text{N}_2\text{O}$  cycle.

**Chlorofluorocarbons (CFC)**—Apart from  $\text{NO}_x$ , chlorine also plays an effective role in removing  $\text{O}_3$  in the stratosphere.

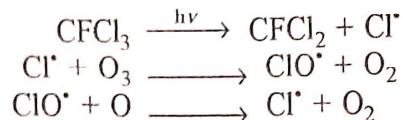




The sources and sinks for Cl are discussed.

### Sources

1. Chlorofluorocarbons (CFC) used as refrigerants and aerosol spray can propellants—they are inert in the troposphere but slowly diffuse into the stratosphere where they are subjected to ultraviolet radiation at about 200 nm generating Cl<sup>·</sup> free radical. The latter immediately reacts with O<sub>3</sub>.

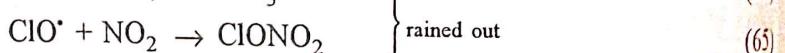
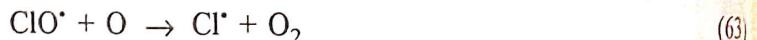


In a cyclic reaction, each ClO<sup>·</sup> can initiate a series of chemical reactions which lead to destruction of upto 100,000 molecules of O<sub>3</sub> without being destroyed itself in the process.

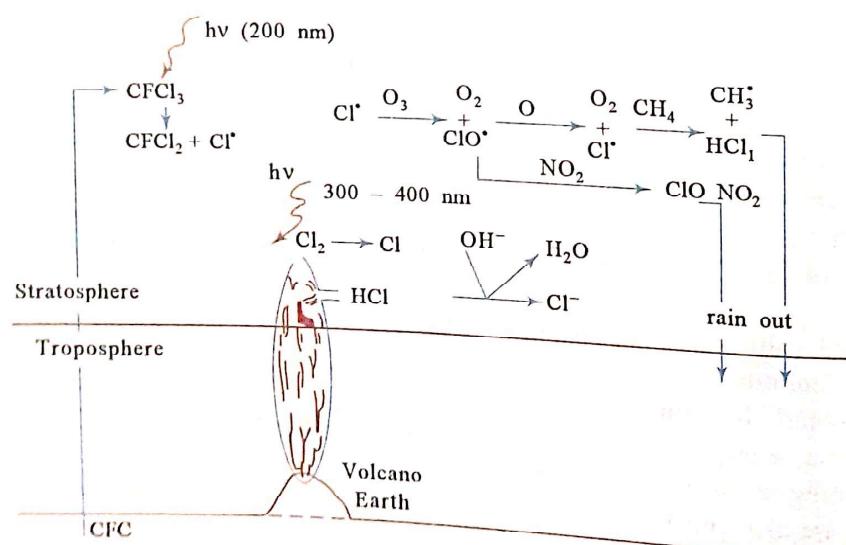
The use of CFCs was being phased out by the end of 20th century (Montreal Protocol 1987; London Conference 1990: see Sec. 2.8 Ozone Hole).

2. Volcanoes inject Cl<sub>2</sub> and HCl directly into the stratosphere. Cl<sub>2</sub> on exposure to UV radiation (300–400 nm) forms Cl<sup>·</sup> while HCl reacts with OH<sup>·</sup> to give Cl<sup>·</sup>.

### Sinks:



By reaction with CH<sub>4</sub>, Cl<sup>·</sup> is trapped as HCl which is rained out in the troposphere.



**Fig. 2.6** Chlorine reactions in the stratosphere

The reaction of  $\text{ClO}^*$  with  $\text{NO}_2$  to form a stable product, chlorine nitrate is significant since it reduces the catalytic cycles of Cl and  $\text{NO}_x$  for  $\text{O}_3$  destruction thereby lowering the overall  $\text{O}_3$  depletion rates.

#### 2.6.4 Organic Compounds

Hydrocarbons and other organic compounds in the atmosphere are susceptible to oxidation through a series of steps of chemical and photochemical reactions. As a result, many *noxious* secondary pollutant products and intermediates are produced, which belong to the category of photochemical smog (Sec. 10.1.3):



Organic compounds in the atmosphere readily enter into reactions with  $\text{O}_3$ ,  $\text{NO}_3^-$ , and free radicals such as  $\text{HOO}^*$ ,  $\text{HO}^*$ , etc.



(propylene)

Free radicals are generated from photochemical reactions as well as several chemical reactions.



Metal oxides and charcoal in particulate matter catalyse the oxidation of hydrocarbons.

Organic compounds in the atmosphere play an important role in photochemical smog formation (Sec. 10.1.3).

### 2.7 CLIMATE CHANGE—NATURAL AND MAN-MADE

#### The Earth's Mechanisms and Global Climate

A new concept of the planet earth has emerged during the past decades as a result of research using satellites to monitor ocean currents, examining tree rings and fossilised pollen for evidence of past climate and simulating the world's future climate on computers. There are indications that the earth is a complex interdependent system in which oceans, atmosphere and life affect one another and help shape the face of the planet.

The world's worst ecological disaster made human life possible. About three billion years ago, the tiny organisms which flourished in the earth's primordial oceans dumped huge amount of toxic waste into their environment. Eventually it killed them along with much of the other living forms on the planet. That deadly substance was oxygen, which sustains the present living species including man. The art of simple bacteria to remake the entire atmosphere is one of the recent discoveries about the earth.

The recent discoveries about the earth's mechanism for its stability and controlling the global climate are:

- (i) Plant and animal life have saved the earth from a fate similar to Venus's "runaway" greenhouse effect.

Pteropod, a tiny marine snail, holds the key to marine life in the Southern oceans. It supports as food source to an entire community of marine organisms — fish, seals, penguins, whales. However, pteropods make their shells from minerals found in sea water only where pH is around 7.0. Acidic sea/ocean water reduces shell formation and hinders reproduction so that pteropod snails find it difficult to survive and the food chain of marine organisms gets disrupted.

[*Independent, London, 26.03.2008*]

## 2.9 OZONE HOLE (MAKING A HOLE IN THE SKY)

When *chlorofluorocarbons (CFCs)* were first introduced in the 30s (*i.e.*, some 75 years ago), they were hailed as miracle chemicals because of their non-toxic, non-inflammable and stable nature. They were used as coolants in refrigerators and air-conditioners, in blowing plastic foams and in spray cans and in cleaning computer circuits. But during the last decade, they were found to be responsible for ozone depletion in the stratosphere.

In September 1980, scientists reported a large hole in the ozone layer over Antarctica where ozone level dropped by 30 per cent. CFC was the prime suspect for causing ozone depletion. It was established that *one molecule of CFC is capable of destroying one lakh  $O_3$  molecules in the stratosphere*.

Subsequently, a similar hole was discovered over the thickly-populated northern hemisphere. This stirred the citizens of north Europe and USA, the potential victims of skin cancer, into action. A study by NASA scientists (National Aeronautics and Space Administration, USA) revealed that the amount of ozone over the northern hemisphere decreased by 3 per cent between 1969 and 1986. Each 1 per cent reduction in  $O_3$  may cause as much as 6 per cent increase in skin cancer cases annually from exposure to UV radiation. The overall reduction in the  $O_3$  layer is now estimated to be about 8 per cent.

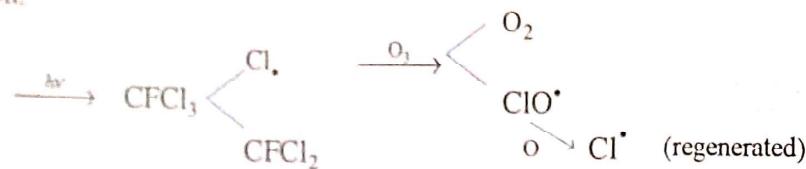
An international agreement made in 1987 at a conference in Montreal and signed by 34 countries (*Montreal Protocol*) called for a freeze on use of CFC and a reduction of upto 50 per cent by the end of 20th century. Because *CFCs persist as long as a century* before they finally breakdown, these efforts may not be enough to hold  $O_3$  destruction in check. A recent study by the Environmental Protection Agency concluded that an 85 per cent reduction would be necessary just to prevent the CFC levels in the atmosphere from growing further. The companies producing CFCs are now working on the production of chemical substitutes for CFCs.

Since the Montreal Protocol, the ozone layer has been found to disappear at a faster rate than expected. In June 1992, Japanese scientists announced that they had found that the ozone hole was 13 times wider in 1991 than it had been in 1981. In June 1990 at London Conference the developed countries agreed to 100 per cent ban of CFCs by 2000 A.D. instead of 50 per cent as per Montreal Protocol, with a 10-year time-lag for the developing countries. The London amendment to the Montreal Protocol was ratified in May 1992 and came into effect on August 10, 1992.

A team of 100 scientists is engaged in European Arctic stratosphere ozone experiment at the strange base in Sweden. During winter of 1991 to 92, they used 39 balloons with payloads upto 500 kg and 800 ozone probes. Their findings revealed that ozone layer was reduced by 15–20 per cent. Furthermore, chlorine was found in the atmosphere in active form. The volcanic eruptions of *Mt. Pinatubo* in the Philippines in 1991 are responsible for much of this disruption.

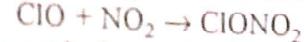
### More About Ozone Hole

[B. Lacoste—"Our Planet", UNEP Magazine, Vol. 4, NO. 4, 4-7 (1992).] As mentioned above, the major culprit in ozone depletion consists of CFC compounds, commonly known as "freons". The extreme chemical stability and non-toxicity of CFCs enable them to persist for years in the atmosphere and to enter the stratosphere. In the stratosphere, CFCs are subjected to photochemical dissociation by intense UV radiation.

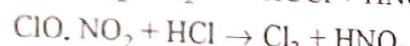
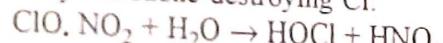


The net result is regeneration of  $\text{Cl}\cdot$  radical which sustains the chain reaction. It is known that one  $\text{Cl}$  atom/radical can destroy one lakh  $\text{O}_3$  molecules. CFCs have lifetimes of the order of 100 years.

The Antarctic ozone hole appears during Antarctic's late winter and early spring of severely-depleted ozone (upto 50%) over the polar region. The reasons why this occurs are related to the normal effect of  $\text{NO}_2$  in limiting  $\text{Cl}$ -atom-catalysed destruction of ozone by combining with  $\text{ClO}$ :



But these  $\text{NO}_x$  gases in Antarctica are removed along with water by freezing in polar stratospheric clouds at temperature below  $-70^\circ\text{C}$  as  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ . Furthermore, chlorine species can be liberated from  $\text{ClO} \cdot \text{NO}_2$  and other chlorine compounds such as  $\text{HCl}$  by reactions in the cloud ice, followed by photodissociation to yield ozone-destroying  $\text{Cl}\cdot$



The destruction of  $\text{O}_3$  by  $\text{Cl}$  involves an intermediate  $\text{ClO}\cdot$ , which should be observed if  $\text{Cl}$  is the cause of  $\text{O}_3$  depletion. Satellite measurements have confirmed the presence of  $\text{ClO}$  (radical) in both the Arctic and Antarctic atmospheres during periods of severe  $\text{O}_3$  depletion.

[J.W. Waters, L. Froidevaux, W.G. Read *et al.*—Nature, 362: 597-602 1993]

**CFC substitutes**—The frequently used CFCs are CFC-11 ( $\text{CFCl}_3$ ) and CFC-12 ( $\text{CF}_2\text{Cl}_2$ ). As a safeguard against ozone depletion, the recommended CFC substitutes are hydrohaloalkanes, compounds containing at least one H-atom—HCFCs (hydrochlorofluorocarbons) or HFCs (hydrofluorocarbons). Typical such compounds are HCFC-22 ( $\text{CHClF}_2$ ), HCFC-142 ( $\text{CH}_3\text{CClF}_2$ ); HFC-134a ( $\text{CH}_2\text{FCF}_3$ ) and HFC-152a ( $\text{CH}_3\text{CHF}_2$ ). Each of such molecules has an H—C bond, susceptible to attack by  $\text{HO}\cdot$  in the troposphere thereby eliminating the compound with its potential to produce  $\text{O}_3$ —depleting  $\text{Cl}$  atom tropospheric lifetime so that the compound is destroyed before migrating to the stratosphere.

### Current Status Report

The hole in the ozone layer is now three times larger than USA—the largest it has ever been. An ozone hole layer larger than 11 million square miles has been detected. Atmospheric variations from year to year combine with man-made gases to determine the hole's size.

Further circular winds, known as *vortices*, trap air, giving chemicals the chance to react with ozone. Chlorine compounds, used in refrigerants, aerosol sprays, solvents, foam-blown agents and bromine compounds used in fire-fighting etc. cause most ozone depletion. The temperature over Antarctica also contributes significantly to each year's hole.

For most of the year, the stratosphere over Antarctica has fairly high concentration of ozone. The ozone formed over the tropics levels along with CFC to polar regions via atmospheric motion. This traps the ozone over the south pole for several months except winter. It is within this vortex the ozone loss was first detected in 1980 (about 30% loss was reported). The major damage due to ozone hole occurs during winter when tiny ice particles are formed in polar stratosphere. These particles act as catalyst to enhance, directly or indirectly, the conversion of chlorine into its ozone destroying form, chlorine monoxide,  $\text{ClO}^\cdot$  (radical). The mechanism of ozone depletion is shown in the preceding sub-section.

The reactions are particularly intense within stratosphere clouds over Antarctica in the winter over southern hemisphere. Reactions which occur on the surfaces of ice particles within the clouds release chlorine and bromine from CFC and halogens in active form that accumulate through winter (May–August). When the sun rises in the spring, the clouds break up to release active chlorine and bromine which rapidly destroy ozone. Thus ozone hole appears during Antarctica spring.

## 2.10 HUMAN ACTIVITIES AND METEOROLOGY

The age-old proverb "Everybody talks about weather but nobody does anything about it" is not valid in this century. Our activities have some impact on the climate, although we may not be aware of it.

Meteorology, the science of atmospheric phenomena, involves the study of physical parameters such as temperature, wind, moisture and movement of air masses in the atmosphere. It is, however, affected by the chemical properties of the atmosphere and the chemical reactions going on in it.

The pattern of air circulation governs the dispersal of air pollutants. In this context, *temperature inversion* has an important role. It happens when a warm air mass is above a cold air mass, resulting in air stagnation and trapping of air pollutants in localised areas. This occurs when warm air blows over a mountain range and flows over cool air on the other side of the range. Such a phenomenon is observed in Denver, Colorado, USA, on the east of the Rocky mountains.

**Table 2.4** Worldwide addition of particulate matter of the atmosphere from human and natural sources (C. Junge, Chemical and Engineering News, August 16, 1971, p. 40; Cited Manahan, *Environmental Chemistry*, 3rd, edn., Willard Grant Press Boston 1983, Ch. 11)

Material	Natural	Annual production (million tonnes)	
		Man-made	
Total particles	773–2200	185–415	
Dust and smoke	—	—	
Soil, volcanic ash, sea	—	—	
Salt forest fires	438–1100	—	
Sulphate particles	130–200	130–200	
Nitrates	30–35	140–700	
Hydrocarbons	15–20	75–200	