

**Studies in Environmental Science 11**

# **ATMOSPHERIC CHEMISTRY**

**Fundamental Aspects**

by

## **E. Mészáros**



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# **Atmospheric Chemistry**

## **Fundamental Aspects**

by

**E. Mészáros**

**Institute for Atmospheric Physics  
Budapest, Hungary**



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**“Hurt not the earth, neither  
the sea, nor the trees.”**

**(Revelation 7:3)**

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## Preface

The first version of this book was published in the Hungarian language in 1977. The aim of that edition was to make the elements of air chemistry known to meteorologists, biologists, geochemists and chemists. Until the publication of this book, air chemistry was practically unknown by the Hungarian scientific community except for a very limited group of people. The writer thus wished to summarize its main results and problems in a *short* and coherent way for those scientists and students who are not familiar with this branch of atmospheric science.

It was a pleasant surprise for the author when the Publishing House of the Hungarian Academy of Sciences in Budapest and Elsevier Scientific Publishing Company in Amsterdam decided to publish this book jointly in English. Like the original Hungarian version the present English publication is recommended to those readers who wish to become acquainted relatively easily and quickly from *one book* with the basic results and concepts on the atmospheric part of the biogeochemical cycle of different constituents. The purpose is thus to summarize, without details, our present knowledge of the concentration, sources and sinks of atmospheric gases and aerosol particles, as well as their physical and chemical transformation in the lower atmosphere (troposphere and stratosphere). Since the chemical composition of the Earth's atmosphere is discussed in relation to atmospheric equilibrium and climate, the content of the book is closely related to environmental sciences.

Since the preparation of the Hungarian manuscript was finished (beginning of 1975), new, important results have been published in the literature on various problems of air chemistry. For this reason many parts of the original text have been rewritten and enlarged to some extent. Taking into account the great number of publications in this rapidly growing field, the author had to make some selection in the themes and references. Such a selection is strongly subjective. It is hoped, however, that the author's aim to compile the basic elements of air chemistry in a compact way has at least been achieved to a satisfactory degree.

The English version was reviewed and corrected by Dr. J. P. Lodge (Boulder, Colorado, U.S.A.) who helped the writer to update the manuscript; his kind and invaluable help is gratefully acknowledged. The author is also indebted to Mrs. M. Antal and Mrs. A. Szép (both from Institute for Atmospheric Physics, Budapest, Hungary) who typed the text and prepared the figures, respectively.

*E. Mészáros*

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## **1. Introduction. Composition and structure of the Earth's atmosphere**

### **1.1 Composition of the air**

The Earth's atmosphere is a reservoir of several gases. The gas molecules in this reservoir are continuously exchanged because of the interaction of different sources and sinks. The average time spent in the atmosphere by the molecules of a given gas is called average residence time, or simply *residence time*. The atmospheric cycle of a material can also be characterized by the *turn-over time* ( $\tau$ ) which can be, in the case of equilibrium ( $F = R$ ), defined as follows:

$$\tau = \frac{M}{F} = \frac{M}{R} \quad [1.1]$$

where  $M$  is the quantity of the material in the atmospheric reservoir, while  $F$  and  $R$  are its formation (source strength) and removal (sink) rates, respectively. Since it can be demonstrated that under equilibrium conditions the residence time is equal to the turn-over time (Bolin and Rodhe, 1973), only the more common residence time is used in the following.

The concept of the residence time gives a good basis for classifying the atmospheric gases. Thus on the basis of the differences in residence time Junge (1963) proposed the following classification:

- (1) highly variable gases with a residence time of several days or weeks (generally less than 1 year);
- (2) variable gases with a residence time of the order of years, and
- (3) quasi-permanent gases the residence time of which is much longer (generally longer than  $10^3$  years).

It is to be noted that the relative and absolute quantities of the present quasi-permanent gases were variable during geological times. This means that their concentration can only be considered loosely as permanent if we study the atmospheric phenomena on a time scale short compared to the age of the Earth. Even at the present time only the noble gases (except helium) are strictly permanent

since they have practically no sources and sinks. In this sense we cannot speak about their atmospheric cycles.

The residence time of atmospheric gases has a very important characteristic: the longer the residence time of a given constituent the smaller the variability of its concentration in time and space. This rule based on atmospheric observations was recently verified theoretically (Junge, 1974).

Table 1 gives the concentration and residence time of atmospheric gases on the basis of the data of different authors. In the table the concentrations of quasi-permanent and variable gases are expressed partly in parts per hundred (percent by volume) and partly in parts per million (ppm). In the case of some highly variable gases the concentrations are also expressed in  $\mu\text{g}/\text{m}^3$  STP because these units are widely used in atmospheric chemical measurements. (For the conversion of ppm concentrations into  $\mu\text{g}/\text{m}^3$  values see Table 4, p. 30).

Table 1

Composition of unpolluted air near the Earth's surface and residence time ( $\tau$ ) of different gases in the atmosphere. In the case of permanent gases the data were taken from Gluekauf (1951) and Junge (1963 and 1974). Concerning data sources for other gases the reader is referred to the corresponding section of the book

Gas	Formula	% by volume	ppm <sup>1</sup>	$\mu\text{gm}^{-3}$ STP <sup>2</sup>	$\tau$
<i>Quasi-permanent (permanent)</i>					
Oxygen*					
Oxygen*	O <sub>2</sub>	20.946			$5 \times 10^3$ yr
Nitrogen*	N <sub>2</sub>	78.084			$\sim 10^6$ yr
Argon*	Ar	0.934			
Neon	Ne		18.18		
Helium	He		5.24		$10^7$ yr
Krypton	Kr		1.14		
Xenon	Xe		0.087		
<i>Variable</i>					
Carbon dioxide	CO <sub>2</sub>		~330		5–6 yr
Methane	CH <sub>4</sub>		1.3–1.6		4–7 yr
Hydrogen	H <sub>2</sub>		~0.5		6–8 yr
Nitrous oxide	N <sub>2</sub> O		0.25–0.35		$\sim 25$ yr
Ozone	O <sub>3</sub>		$(1–5) \times 10^{-2}$		$\sim 2$ yr
<i>Highly variable</i>					
Water	H <sub>2</sub> O		$(0.4–400) \times 10^2$		10 days
Carbon monoxide	CO		0.05–0.25		0.2–0.5 yr
Nitrogen dioxide	NO <sub>2</sub>		$\sim (0.1–5) \times 10^{-3}$	0.2–10	8–10 day
Ammonia	NH <sub>3</sub>		$\sim (0.1–10) \times 10^{-3}$	0.1–10	~5 day
Sulfur dioxide	SO <sub>2</sub>		$\sim (0.03–30) \times 10^{-3}$	0.1–10	~2 day
Hydrogen sulfide	H <sub>2</sub> S		$\sim (<0.006–0.6) \times 10^{-3}$	$<0.01–1$	$\sim 0.5$ day
Organic carbon <sup>3</sup>				5–50	~2 day

Note: <sup>1</sup> ppm: parts per million; 1 ppm =  $10^{-6}$  % by volume; <sup>2</sup>  $\mu\text{g} = 10^{-6}$  g; STP: Standard temperature and pressure;

<sup>3</sup> excluding CH<sub>4</sub> and halocarbons.

The main constituents are designated by an asterisk

It should be mentioned that in the atmospheric reservoir gases other than those listed in Table 1 can be found. For the sake of simplicity the atmospheric cycle of these gases will not be presented. However, the effect of different halogen compounds, including anthropogenic chlorofluorocarbons, on the stability of atmospheric ozone layer will be discussed, in relation to the ozone budget.

The atmospheric gases can also be classified on the basis of their relative quantity. The gaseous components with concentrations larger than or equal to about 1% are called *main constituents* (oxygen, nitrogen and argon), while gases of smaller concentration constitute the category of *trace gases*. It should be noted that the air also contains minute suspended liquid and solid particles of different composition. Thus the atmosphere is a dispersed system called an *aerosol*. The quantity of these air-borne particles is very small compared to the mass of the air (see Chapter 4). For this reason the trace gases and aerosol particles have a common name: *trace constituents*.

The aim of this book is, first of all, to present the atmospheric cycle of the trace constituents. We will discuss in more detail the trace substances (Chapter 3) with relatively short residence time (<10 yr). The study of these compounds is particularly interesting since their sources and sinks as well as their concentrations are very variable in space and time. They undergo several physical and chemical transformations in the atmosphere. Among these transformations the processes leading to the formation of aerosol particles have unique importance. The aerosol particles control the optical properties of the air, the formation of clouds and precipitation and, together with some gases, the radiation and heat balance of the Earth-atmosphere system. Because of their importance the physical and chemical characteristics of aerosol particles will be summarized in a separate chapter (see Chapter 4).

A very significant peculiarity of the atmosphere is that so-called self-cleaning processes take place within the air. Due to these processes even those trace constituents which have no other chemical or biological sinks are relatively quickly removed from the air. Hence these removal mechanisms are of great importance for the control of the atmospheric pathways of some trace gases and aerosol particles (see Chapter 5).

The study of trace constituents is also very important in order to estimate the effect of the activity of mankind on their atmospheric concentration levels. Taking into account their relatively low concentrations, an anthropogenic modification of their level is much easier than in the case of the main constituents. These alterations in the atmospheric composition raise the possibility of inadvertent climate modification since, as we shall see (see Chapter 6), there is a well determined relation between the composition of the atmosphere and the Earth's climate.

However, the problems connected with trace constituents cannot be evaluated fully without knowledge of the chemistry and budget of the main components and without a discussion of the formation of the present "permanent" chemical composition. For this reason, Chapter 2 is devoted to a brief presentation of the

evolution of the Earth's atmosphere during geological times. The evolution and composition of our atmosphere will be discussed in connection with the composition of the atmospheres of other inner planets (Mars, Venus), which consist mainly of carbon dioxide. Therefore, a discussion of the variations of this gas in the Earth's atmosphere will also be presented in this chapter.

## 1.2 Structure of the atmosphere

One can see from Table 1 that in the Earth's atmosphere molecular nitrogen has the greatest relative concentration near the Earth's surface. The effective molecular weight of air is thus rather close to that of this constituent (the two values are 28.973 and 28.022, respectively). However, the composition of the air and consequently its molecular weight are constant only in the lower 80–100 km layer of the atmosphere which is termed the *homosphere*. Above this layer the so-called *heterosphere* can be found in which the molecular weight is a function of the altitude. The constant chemical composition in the homosphere is controlled by atmospheric mixing, while in the heterosphere the variations in the composition are due to the photodissociation of air molecules produced by solar radiation and to their sheer mass differences in the gravitational field. These effects lower the molecular weight of the air. In the heterosphere, on the other hand, the concentration of the free electrons and positive ions is rather high (the electron density has a maximum near 300 km) which justifies the name ionosphere which is frequently applied in atmospheric physics to this layer.

In all atmospheric layers the density and the pressure of the air decrease with increasing altitude. Under normal conditions near the Earth's surface when the temperature and pressure are 0 °C and 1013.25 mb, respectively, the air density is equal to  $1.2923 \times 10^{-3}$  g/cm<sup>3</sup>.<sup>1</sup> Around 100 km the density is about 10<sup>6</sup> times smaller.

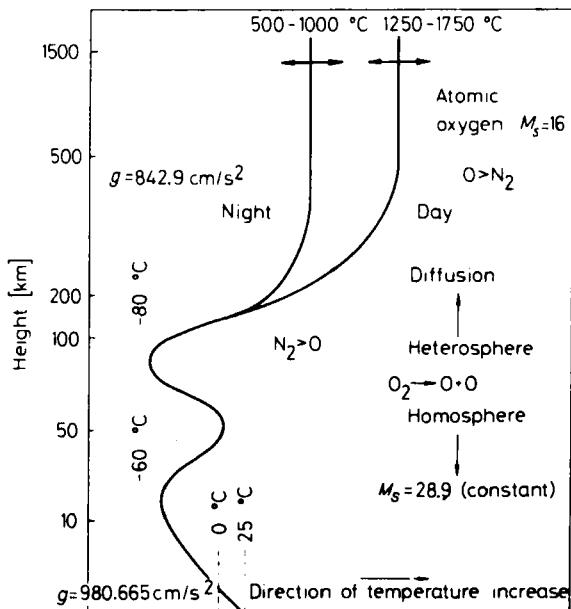
According to the character of the thermal structure, the homosphere is divided into three further layers. The lowest one is termed the *troposphere*. The altitude of the troposphere is approximately 18 km above the equator and 8 km above the poles. In this layer the temperature generally decreases with increasing altitude<sup>2</sup> (Fig. 1). The average temperature gradient is equal to 6.5 °C/km.

The troposphere receives the thermal energy from the Earth's surface which absorbs the Sun's radiation. Because of the heating of the air by the infrared radiation emitted by the surface, intensive vertical (convective) motions can be generated. This convection transports heat, water vapour and other trace constituents of surface origin to the higher levels of the troposphere. In such an

<sup>1</sup> The number of molecules in 1 cm<sup>3</sup> of air is  $2.687 \times 10^{19}$  under these conditions.

<sup>2</sup> On occasion there are thin layers in the troposphere in which the temperature is constant or increases with height. These are called isothermal and inversion layers, respectively.

updraft the air cools down leading to the condensation of the water vapour. Thus, the formation of clouds and precipitation, and, generally speaking, the atmospheric cycle of the water, essentially takes place in the troposphere. Since during the formation of clouds and precipitation a large part of the atmospheric aerosol particles and soluble gases is ad- and absorbed by the cloud and precipitation



**Fig. 1**

The structure of the atmosphere according to Nicolet (1964). The plotted curve gives the temperature profile, while  $M_3$  and  $g$  are the molecular weight and the gravitational constant, respectively. (By courtesy of Publishing House Mir)

elements (wet removal), the cycle of the water significantly controls the tropospheric pathway of many other trace constituents. In the troposphere the speed of the horizontal motions generally increases with increasing altitude. Both the horizontal and vertical motions have a turbulent character which promotes the mixing of atmospheric constituents as well as the dry removal of aerosol particles and such gaseous components as are adsorbed by the soil and vegetation (see Chapter 5). The top of the troposphere is called the tropopause. Between the high and low tropopauses of equatorial and polar regions there is frequently a tropopause gap which is a very important factor in the control of the vertical exchange.

The second layer in the homosphere is termed the *stratosphere*. In this part of the atmosphere the temperature generally increases with altitude due to the interaction of the short wave solar radiation and different oxygen molecules ( $O_2$ ,  $O_3$ ). Thus the

tropopause is defined as the point at which temperature stops decreasing with increasing altitude and begins to increase. This thermal pattern hinders the formation of strong convective currents. If we disregard the relatively slow diffusion processes, the bottom of the stratosphere is closed by the tropopause, except in the regions of tropopause gaps.

On the other hand, the effect of the wet removal can be practically neglected here.<sup>3</sup> It is thus understandable that the residence time of trace constituents is greater in the stratosphere than in the troposphere. Above the tropopause the horizontal wind speed first decreases then increases with height. Consequently, a secondary maximum in the wind speed can be observed in this atmospheric layer. The increase of the temperature ends approximately at an altitude of 50 km (stratopause), where the temperature is around 0 °C (see Fig. 1). Above this level, in the *mesosphere*, the temperature again decreases (third layer in the homosphere). For this reason the stratopause can be considered as an active heat-supplying surface similar to the Earth's surface. In this atmospheric region the distribution of the temperature makes possible the convection which, in favourable cases, results in a formation of so-called noctilucent clouds at an altitude of about 80 km (mesopause) where the temperature is only around -80 °C. This is the coldest level of our atmosphere.

Above the mesosphere a rather hot atmospheric layer can be found, the *thermosphere*. Since its chemical composition changes with altitude, this thermal layer is the same as the heterosphere, where air molecules (mainly O<sub>2</sub>) dissociate under the effect of absorbed external radiation.

In this book *air chemistry* is defined as a branch of atmospheric science dealing with the atmospheric part of the biogeochemical cycle of different constituents. In other words this means that we will deal mainly with the atmospheric pathways of those components that are involved in the mass flow between the atmosphere and biosphere, as well as in chemical interactions between the air and the other media of our environment (soils, oceans etc.). It follows from this definition that, on the one hand, our discussion will be restricted to the troposphere and the stratosphere<sup>4</sup> and, on the other hand, the photochemistry of the upper layers, the subject matter of the *aeronomy* (e.g. Nicolet, 1964), will be omitted. This separation of the (photo) chemistry of the lower (troposphere and stratosphere) and upper atmosphere makes it possible to give a more compact treatment of our problem, including the global anthropogenic effects due to the increase of air pollution.

<sup>3</sup> In the case of tall thunder clouds which penetrate into the lower part of the stratosphere there is a possibility for stratospheric wet removal.

<sup>4</sup> As in Junge's classical book (Junge, 1963).

## **2. Formation and evolution of the Earth's atmosphere. Chemistry of main constituents**

### **2.1 Statement of the problem**

It can clearly be seen from Table 1 that the Earth's atmosphere consists mainly of nitrogen and oxygen. However, this composition, which makes the present life on our planet possible, cannot be considered "normal" in the solar system. Thus, even the nearest planets like Mars and Venus have a very different atmospheric composition.

The results of space research, especially the results obtained by the Soviet Venera and the American Mariner space-crafts, make it possible to estimate numerically these differences in the composition. Table 2 contains data on the global composition of the atmosphere of Venus, Earth and Mars according to Lovelock and Margulis (1974). The values given in the table are expressed in millibars partial pressure of the gas considered. It follows from the table that the pressure on the surface of Venus is high while it is low in the case of the Martian atmosphere. However, on both planets the atmosphere consists essentially of carbon dioxide, and oxygen is either missing or its pressure is very low. On the other hand, the Earth's atmosphere is composed of nitrogen and oxygen and the quantity of  $\text{CO}_2$  is virtually negligible. In the fourth column of the table are values obtained by interpolation on the basis of the astronomical data of the Earth (e.g. distance from the Sun) and of the composition of the atmospheres of Venus and Mars. This interpolated atmosphere is called the estimated equilibrium atmosphere (Lovelock and Margulis, 1974). One can see that the real  $\text{CO}_2$  partial pressure is a thousand times smaller while the real  $\text{O}_2$  pressure is nearly a thousand times greater than these values obtained by interpolation between Mars and Venus.

Another peculiarity of the Earth's atmosphere is the relatively high nitrogen pressure. Considering the physicochemical conditions on our planet, this fact is contradictory to chemical equilibrium considerations. Thus under our conditions (temperature, oxygen pressure, pH in ocean waters etc.) the stable state of nitrogen would be in nitrate compounds dissolved in ocean waters (Sillén, 1966).

It follows from this discussion that our atmosphere has many peculiar characteristics, on the one hand relative to the Venus and Mars or, on the other hand, considering it separately in the Earth-atmosphere system. The question therefore arises: how did this anomalous gas cover of the Earth form and what

**Table 2**

Composition of atmosphere of Venus, Earth and Mars according to Lovelock and Margulis (1974)

Gas	Venus	Earth	Mars	Earth (equi- librium)	Earth (real/ equi- librium)
CO <sub>2</sub>	90 000	0.3	5	300	$1.0 \times 10^{-3}$
N <sub>2</sub>	1 000	780	0.05	30	$2.6 \times 10$
O <sub>2</sub>	0	210	0.1	0.3	$7.0 \times 10^2$

*Note:* The estimated equilibrium composition of the Earth's atmosphere is also given. Values are the partial pressures in mb

mechanism controls this strange gas mixture? Briefly, the biosphere played an important part in the formation and evolution of the atmosphere of our planet, and it is a major determining factor in the control of the present composition.

The formation of life on Earth is explained by the special characteristics of this planet. Among others, one can mention the distance between the Sun and the Earth,<sup>1</sup> the dimension of the Earth and also, in relation with the parameters mentioned, the composition of the primeval atmosphere. After its formation the biosphere became an active partner in the control of environmental conditions; that is, linkage was formed between the biosphere and the other media of the Earth.

Because of this active role, some authors (e.g. Lovelock and Margulis, 1974) refer directly to the homeostasis of the atmosphere. This homeostasis (that is, the capacity for control) was established and is regulated by the biosphere. Furthermore the atmosphere can be regarded as a contrivance in which each gas has its own function, it is considered a part of the biosphere.

The aim of this chapter is to discuss in some detail the formation and evolution of this anomalous atmosphere. The factors which governed the atmospheric composition during the formation of Earth and during geologic time will be presented briefly. Attention will be devoted to the formation of the present oxygen level and, generally speaking, to problems related to the interactions between the atmosphere and the biosphere.

## 2.2 Dissipation of cosmic gases from the Earth's atmosphere

The protoplanet forming the Earth was probably a disperse system containing materials in three phases (Szádeczky-Kardoss, 1968). Particles with greater density and dimension were found in the central part of the system. At a greater radial

<sup>1</sup> According to Rasool and De Bergh (1970) if the Earth were only 6% nearer to the Sun, the atmosphere of our planet would be very similar to that of Venus.

distance from the centre the aerosol became more and more dilute until finally it became pure gaseous phase.

In space, including the solar system, the abundance of the elements decreases with increasing atomic weight. The second column of Table 3 gives the cosmic abundance of the elements expressed relative to silicon as  $10^4$  (Urey, 1952). The last two columns of this table contain the stable compounds of the elements for a pressure of  $10^{-3}$  atm and for two different temperatures. On the basis of these data it can be assumed that the gas phase of the protoplanet consisted mainly of  $\text{H}_2$  and He with lesser amounts of  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{H}_2\text{S}$ . In the case of the inner planets the development of the gravitation field and the temperature (due to the radioactive heating and solar radiation) promoted the dissipation of the cosmic gases, which means that these planets lost their original gaseous materials rather quickly. According to model calculations (e.g. Szádeczky-Kardoss, 1968) the mass of the Earth before dissipation was at least 190 times greater than the present value. The duration of this dissipation is estimated by Kuiper to be around  $10^8$  years (see in Szádeczky-Kardoss, 1968). It is possible, however, that this time was even longer since, in the original system, the dissipation was somewhat hindered by the presence of dispersed particles.

It seems evident that the degree of dissipation was small in the case of the outer giant planets. This explains the fact that the atmosphere of these planets is composed of the above mentioned substances. Thus, according to Öpik (see Cadle, 1966),

Table 3

Cosmic and terrestrial abundance of elements and their stable compounds under different conditions of temperature and pressure (Urey, 1952). The values of the dissipation losses are also given

Element	Cosmic abundance (Si = $10^4$ )	Present Earth (gram atom $\text{cm}^{-2}$ )	Loss <sup>1</sup>	Stable components ( $P = 10^{-3}$ atm) <sup>2</sup>	
				$T = 298$ K	$1200$ K
H	$3.5 \times 10^8$	$3.0 \times 10^4$	$9.4 \times 10^{-4}$	$\text{H}_2, \text{CH}_4,$ $\text{NH}_3, \text{H}_2\text{O}$	$\text{H}_2, \text{H}_2\text{O},$ $\text{H}_2\text{S}$
He	$3.5 \times 10^7$	$1.7 \times 10^{-4}$	$5.0 \times 10^{-11}$	He	He
C	$8.0 \times 10^4$	$3.5 \times 10^2$	$4.7 \times 10^{-2}$	$\text{CH}_4$	$\text{C}, \text{Fe}_3\text{C}$
N	$1.6 \times 10^5$	$5.4 \times 10^{-1}$	$3.7 \times 10^{-3}$	$\text{NH}_3, \text{NH}_4^+$	$\text{N}_2$
O	$2.2 \times 10^5$ ( $1.75 \times 10^5$ as $\text{H}_2\text{O}$ )	$1.5 \times 10^4$	1.0	$\text{H}_2\text{O}$	$\text{H}_2\text{O}$
Ne	$(9.0 \times 10^3 -$ $- 2.4 \times 10^5)$	$6.5 \times 10^{-4}$	$1.6 \times 10^{-7}$	Ne	Ne
Si	$1.0 \times 10^4$			$\text{SiO}_2$	$\text{SiO}_2$
S	$3.5 \times 10^3$	$1.5 \times 10$	$4.5 \times 10^{-2}$	FeS	$\text{H}_2\text{S}$
Fe	$1.8 \times 10^4$			$\text{FeS}, \text{Fe}_3\text{O}_4$ $\text{Fe}_2\text{SiO}_4$	Fe

Note: <sup>1</sup> Relative to oxygen; <sup>2</sup> For  $P = 1$  atm and  $T = 298$  K the stable compounds are the same as for  $P = 10^{-3}$  atm and  $T = 298$  K.

99.5% of the Jupiter's atmosphere consists of hydrogen and helium, while the clouds of the planet probably consist of ammonia crystals.

In the case of the inner planets, there was no dissipation of those gaseous compounds that either condensed on (depending on temperature and pressure conditions) or chemically reacted with the solid and liquid phases. Under the conditions of the proto-Earth water accumulated, an event of major importance. It was this accumulation that made the formation of the biosphere possible, the evolution of which led to the appearance of a thinking species, man.

It can be seen from Table 3 that the dissipation of noble gases was particularly intense. This is reasonable, since these gases did not react with the solid or liquid materials forming the planet Earth. On the other hand the loss in the case of hydrogen was relatively small, a significant portion of this element remained in a condensing compound (water).

The process of dissipation can be well demonstrated by the so-called deficiency factor of rare gases. This factor gives the ratio between terrestrial and solar abundances. The deficiency factors of rare gases in meteorites and in the atmosphere as a function of the atomic weight are plotted in Fig. 2 (Suess, 1966). One can see that

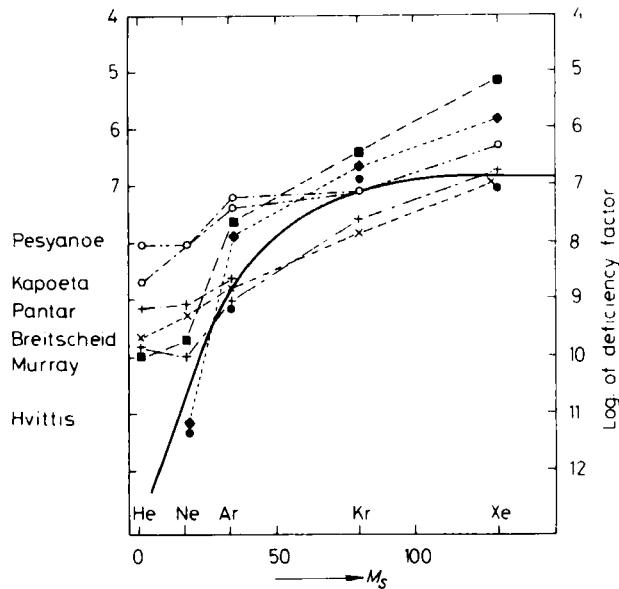


Fig. 2

The deficiency factor of rare gases on the Earth (solid line) and in some meteorites according to Suess (1966), where  $M_s$  is the molecular weight (By courtesy of *Tellus*)

even the quantity of xenon with an atomic weight of 130 decreased by a factor of  $10^7$ . It can also be seen that the abundance of argon on the protoplanet must have been some hundred millionsfold greater than in the present atmosphere. Thus the present quantity of atmospheric argon is only a small residue of this huge mass.

### 2.3 "Secondary" constituents

After the dissipation of cosmic gases (approximately  $4 \times 10^9$  years ago) several gaseous materials were liberated from the solid Earth. The substances formed in this way are termed secondary constituents. These atmospheric components were due either to volcanic, desorption and thermal processes or to chemical reactions.

At an early age the iron in the upper part of the mantle was in a reduced state (as evidenced by very old iron minerals; see Junge, 1966). The presence of reduced iron means that the gases and vapours given off by the solid mantle were also reduced; otherwise they would have oxidized the iron. Probably, the secondary atmosphere consisted mainly of methane, ammonia and water vapour.<sup>2</sup>

With the decrease of the abundance of hydrogen, the composition of the volatile materials approached that of the present time. This means that they were in a more oxidized state than was the case earlier— $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{H}_2\text{O}$ . The temperature at the Earth's surface was around  $-10$  to  $-15^\circ\text{C}$  (Rasool and De Bergh, 1970), considering the Sun–Earth distance and the surface albedo. With the increase in the quantity of secondary constituents, the atmosphere also became a controlling factor of the temperature, since  $\text{CO}_2$  and water vapour absorb the infrared radiation emitted by the Earth's surface to a significant degree. Hence the temperature began to rise. When its value reached  $0^\circ\text{C}$  and the vapour pressure of water reached 6.1 mb condensation processes took place leading to the accumulation of ocean waters.

At this time in the Earth's history the carbon dioxide abundance was higher than its present value since this gas accumulated in the absence of a biosphere. Rutten (1966) speculated that the atmospheric  $\text{CO}_2$  level was 10 times PAL (present atmospheric level) about  $3 \times 10^9$  years ago. On the other hand the presence of  $\text{H}_2\text{O}$  in the atmosphere led, by photochemical dissociation, to the formation of free radicals and molecular oxygen. An estimate of the importance of these reactions is necessary to give some idea of the oxygen level in pre-biospheric times. The photodissociation of water vapour can be represented as follows (Suess, 1966):



Two atomic oxygens formed in this way can combine to yield molecular oxygen:



where M is a neutral third body. It was demonstrated by Nicolet and Bates (1950) that the photolysis of water is induced by solar radiation with wavelengths shorter than  $0,195 \mu\text{m}$ . Since oxygen strongly absorbs the short-wave radiation in the same

<sup>2</sup> The laboratory experiments of Miller (1953) proved Oparin's hypothesis, according to which the organic compounds necessary for the formation of life were produced in a reducing atmosphere.

range, photochemical reactions [2.1] and [2.2] are "shadowed" by the end-product of the process. The equilibrium  $O_2$  concentration formed in this way is calculated to be  $10^{-3}$  PAL (Berkner and Marshall, 1965 and 1967). Walker (1978) recently argued that this equilibrium value is even smaller if the recombination of the products of photolysis is also taken into account.

Thus it should be stated: in spite of the fact that some free oxygen could be formed in the pre-biologic atmosphere by the photodissociation of water vapour, its present level cannot be explained by this process alone.

Among the secondary gaseous constituents,  $CO_2$  reacted with silicates in the solid Earth (see later), while an important part of the  $H_2O$  condensed. However, the inert  $N_2$ , which comprises only 1% of volcanic gases, accumulated in the atmosphere (Rasool and de Bergh, 1970) and became the major component of the gaseous envelope of our planet. It can be seen from Table 2 that the abundance of nitrogen in the Earth's atmosphere is approximately equal to that found in the gaseous covering of Venus. This fact can be explained by the similar size of the two planets since similar size suggests a similar volcanic activity in the past. If this explanation is correct the relatively smaller  $N_2$  abundance of the Martian atmosphere connotes lesser volcanic activity on this smaller planet.

#### **2.4 Relation between atmospheric nitrogen and the biosphere**

Rasool and De Bergh (1970) mention that nitrogen was accumulated in the atmosphere because of volcanic activity. On the other hand Lovelock (1972) and Lovelock and Margulis (1974) speculate that without the biosphere the Earth's atmosphere would be as depleted in nitrogen as the atmosphere of Mars. According to these authors the nitrogen abundance in the Earth's atmosphere is about  $10^{10}$  times larger than its equilibrium value under our conditions. Lovelock and Margulis (1974) also think that our atmosphere would lose its nitrogen content rather quickly if the biosphere came to an end on the Earth. Thus, under the effect of external radiation and electric discharges  $N_2$  would oxidize rather rapidly. The nitrogen oxides would dissolve in ocean waters to give nitrate ions. Because of these processes, both  $N_2$  and  $O_2$  would be quickly removed from our atmosphere and this latter would consist only of argon and carbon dioxide. Lovelock and Margulis (1974) mention that this phenomenon is ineffective on Venus since the atmosphere does not contain oxygen, there are no oceans and the temperature is much higher than in the Earth's atmosphere.

Sillén (1966) assumes that it is not impossible that some marine biological process rapidly transforms the nitrate ions to  $N_2$ . This phenomenon would use the oxygen of nitrate ions for some oxidation process in spite of the presence of  $O_2$ . However, he also states, that such organisms have not been discovered. This means that the explanation of the anomalous high nitrogen content of our atmosphere remains an open question. Nevertheless we cannot exclude the possibility that this high

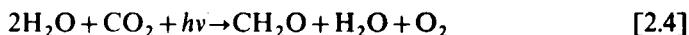
atmospheric N<sub>2</sub> level is somehow due to the presence of the biosphere. In other words this means that the atmosphere as a part of the biosphere (Lovelock and Margulis, 1974) is in a disequilibrium which is a characteristic state for living systems.

It follows from this discussion that in this field there are many problems to solve. It is indisputable, however, that the atmospheric cycle of N<sub>2</sub> is regulated by the biosphere. The atmospheric N<sub>2</sub> is utilized by certain bacteria in the soils and aquatic systems by transforming it into nitrogen compounds which are useful for the biosphere. From dead plants and animals the nitrogen returns in the soil and into ocean waters where the denitrifying bacteria liberate it in gaseous molecular form into the atmosphere. The strength of this biological N<sub>2</sub> source is estimated to be around  $10^9 \text{ t yr}^{-1}$  (Lovelock and Margulis, 1974). The total nitrogen content in the atmosphere is  $3.9 \times 10^{15} \text{ t}$ , as can easily be calculated from the mass of the atmosphere ( $5.15 \times 10^{15} \text{ t}$ ). Thus, formula [1.1] yields a value of  $3.9 \times 10^6$  years for the residence time of this component.

This biologically governed cycle is now in some measure disturbed by the activity of mankind. According to Söderlund and Svensson (1976) the total abiological nitrogen fixation was  $0.055 \times 10^9 \text{ t yr}^{-1}$  in 1970 and its value is increasing at approximately 4% per year. This anthropogenic N<sub>2</sub> fixation is due partly to the production of nitrogenous fertilizers and partly to the combustion of fossil fuels. These latter authors estimate about  $0.3 \times 10^9 \text{ t yr}^{-1}$  for the total value (biological + abiological) of N<sub>2</sub> fixation which is about one-third of the rate of fixed nitrogen production given by Lovelock and Margulis (1974). In any case it can be concluded that the abiological nitrogen fixation seems to be small compared to the total nitrogen quantity in the atmosphere. However, anthropogenic production tends to be localized, and to produce high concentrations where it occurs. Hence, it may have effects on biological nitrogen sinks larger than its average global value would suggest. Much more research is needed to determine the consequence of this anthropogenic modification.

## 2.5 Increase of the oxygen level during geological times

There is considerable documentation in the literature to show that the major part of the increase in the oxygen level during geological time was due to the photosynthetic activity of the biosphere, which can be summarized as follows:



A part of the biosphere, specifically plants, uses water and carbon dioxide according to this equation to synthesize organic materials under the influence of solar radiation of appropriate wavelengths. An important peculiarity of this reaction is that the O<sub>2</sub> on the right-hand side of [2.4] comes from the oxygen of the water.

The increase of the atmospheric oxygen level will be discussed in the following on the basis of the coherent model of Berkner and Marshall (1965 and 1967) in spite of the fact that some conclusions of these authors are not generally accepted. Thus, according to Fisher (1972) the increase of the oxygen level began earlier than in the model mentioned. This idea is supported by the calculations of Schidlowski (1978) who determined the photosynthetic oxygen quantity on the basis of the abundance of organic carbon formed by reaction [2.4].

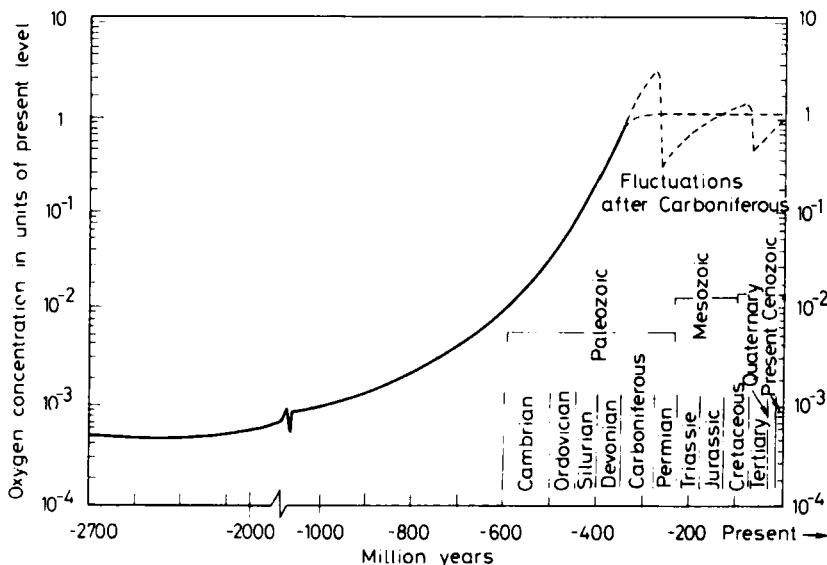
It has already been mentioned that life came into being in a reducing environment. The constituents of the reducing atmosphere (e.g. methane, ammonia) were absorbed in waters to produce a solution in which organic compounds were formed under the effect of electric discharges and short-wave radiations (Miller, 1953). The first anaerobic organisms originated from these compounds (e.g. Bernal, 1967).

According to Berkner and Marshall (1965 and 1967) the oxygen content of the Earth's atmosphere about  $3 \times 10^9$  years ago was very small:  $10^{-3}$  PAL (see Section 2.3). It followed from this low oxygen level that the ozone concentration also had to be negligible. Furthermore, the altitude of the maximum ozone formation depends upon the oxygen concentration: it decreases with decreasing oxygen partial pressure. For this reason the small amount of  $O_3$  became concentrated in these early times in layers near the Earth's surface. Life was formed at such depths in the liquid water that, on the one hand, the lethal UV radiation was absorbed, but, on the other hand, the radiation with wavelengths greater than  $0.29 \mu m$  still penetrated. Berkner and Marshall (1965 and 1967) estimate this depth to be about 10 m. The convection which occurred in the water transported the organic materials, produced as a result of UV radiation near the water surface, to this level. However, this convection was not so intensive as to carry the primitive organisms to the surface.

The first organisms were primitive algae and bacteria. The lack of fossils from this early age suggests that, until the Paleozoic era, organisms had no hard parts which would have been preserved in solid crust. As a result of the development of photosynthetic life around the beginning of the Cambrian (600 millions years ago) the atmospheric oxygen level reached 0.01 PAL, which made the conversion from fermentation to respiration possible for some organisms. At the same time, life could be spread even in surface waters. The oxygen concentration of 0.01 PAL is called the first critical level.

In the Cambrian period life began to develop very quickly. For this reason the oxygen concentration increased rather rapidly. Thus, in the late Silurian (420 millions years ago) the oxygen level was as high as 0.1 PAL (Fig. 3) which is termed the second critical level. With the increase of the oxygen concentration the quantity of ozone in the atmosphere increased, together with an increase in the altitude of maximum ozone production. This latter, in the late Silurian period reached 20 km level, which made the spread of life onto dry land possible. At the same time the thermal structure of the atmosphere was drastically changed, which resulted in the appearance of the stratosphere. It was shown previously that our atmosphere has an

anomalous composition. This anomalous composition involves a rather strange temperature profile, which is caused by the presence of free oxygen and ozone. Berkner and Marshall speculated that the stratosphere was built up several hundred million years ago. However, according to the more recent study of Ratner and



**Fig. 3**

Variation of the oxygen level in the Earth's atmosphere during geological time (Berkner and Marshall, 1967). (By courtesy of Academic Press)

Walker (1972) it is not excluded that the biologically protective ozone shield was formed at this altitude at an earlier time.

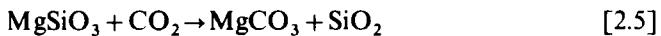
After the late Silurian era the rate of oxygen production further increased. It is probable that in the Carboniferous period the rapid increase of the oxygen level resulted in a higher concentration than the present one. After this age the oxygen level varied (see Fig. 3) as a function of the photosynthetic oxygen production and of the oxidation of decaying organic materials.<sup>3</sup> Finally, as a result of different processes a constant atmospheric oxygen level came into being. In the present quasi-equilibrium state, the  $O_2$  production is estimated to be  $7 \times 10^{13}$  molecules  $cm^{-2} s^{-1}$  (Berkner and Marshall, 1967) and the atmospheric residence time of this species is around one thousand years.

<sup>3</sup> While photosynthesis makes free  $O_2$ , decay consumes it. Net  $O_2$  is produced by the mechanism proposed by Berkner and Marshall (1967) only if fixed carbon is buried. If not, for the explanation of the  $O_2$  content of the atmosphere by the presence of the biosphere some other biological process is necessary as discussed by Lovelock and Lodge (1972).

An important task in air chemistry research is to study the effect of the activity of mankind on this quasi-permanent oxygen concentration. Industrial and other combustion processes, together with damage to photosynthetic plants, can modify this quasi-stable level. According to Davitaya (1971) the relative decrease of O<sub>2</sub> during the past fifty years, calculated on the basis of the quantity of fossil fuels used, should have been 0.02 %. Very precise measurements of the O<sub>2</sub> content of the atmosphere, however, did not reveal any change in the time interval mentioned (Machta and Hughes, 1970). This difference between calculations and measurements can only be explained if we suppose that the atmosphere has some self-regulation capacity which eliminates even such small changes. It also goes without saying that the lack of anthropogenic effects at present does not mean that in the future we may neglect this problem. The survey of the oxygen concentration in the atmosphere must be involved in global monitoring programs aimed at determining anthropogenic changes in the composition of our atmospheric environment.

## 2.6 Variations of CO<sub>2</sub> level

One can see from Table 2 that the so-called equilibrium CO<sub>2</sub> level in the Earth's atmosphere would be higher than the present concentration. It can also be seen that Venus has a much greater CO<sub>2</sub> partial pressure than the terrestrial value. The difference between the two neighbouring planets can first of all be explained by the difference in their distance from the Sun which produced different initial temperatures. In the case of the Earth the temperature was less than 300 °C. Under these conditions gaseous CO<sub>2</sub> formed carbonate minerals by the following type of reaction (Urey, 1952):



which decreased the CO<sub>2</sub> level in the atmosphere to an important degree. Thus, the great majority of terrestrial CO<sub>2</sub> accumulated in the solid Earth as limestone and dolomite, while a huge amount of CO<sub>2</sub> on the Venus remained in the gaseous phase.

The second, but probably less important, factor in the decrease of CO<sub>2</sub> level of our atmosphere was the biospheric activity since plants used (and use) CO<sub>2</sub> to form organic carbon compounds (see reaction [2.4]). In any case this factor could only operate after the first had decreased the temperature below 100 °C. It seems likely that according to this process CO<sub>2</sub> and O<sub>2</sub> levels varied inversely in the biospheric era (Rutten, 1966) of the Earth's history. Thus, the variations in Fig. 3 representing the increase of O<sub>2</sub> levels during geological times also give an idea about the changes in atmospheric CO<sub>2</sub> concentration.

Finally, the CO<sub>2</sub> sources (respiration, decay of plants and humus) and sinks (photosynthesis of plants) became quasi-balanced. In establishing this natural equilibrium state the hydrosphere also played an important role. Before the

industrial revolution of the 19th century, the CO<sub>2</sub> production of the biosphere was around  $480 \times 10^9$  t yr<sup>-1</sup> (Butcher and Charlson, 1972), while the total amount of CO<sub>2</sub> burden was estimated to be  $2250 \times 10^9$  t (Bolin, 1977a). According to equation [1.1] these figures yield a rounded-off value of 5 years for the residence time.

The concentration of CO<sub>2</sub> in the air in the lowest layers of the troposphere shows expected diurnal and yearly variations (Junge, 1963). For example, photosynthesis can occur only in the presence of solar radiation. For this reason, in clean (non-

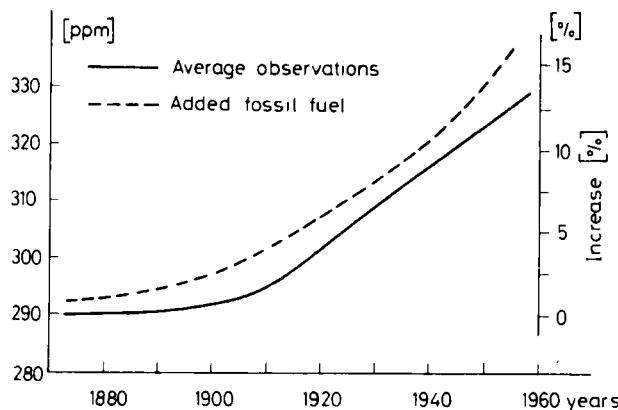


Fig. 4

Variation of the CO<sub>2</sub> level in the atmosphere between 1880 and 1960 according to Junge (1963). (By courtesy of Academic Press and the author)

polluted) air the daylight concentrations are generally smaller than those measured during the night. The amplitude of this diurnal variations obviously decreases with increasing height. Furthermore, in accordance with the annual variation in plant metabolism, maximum CO<sub>2</sub> concentrations can be observed in the Northern Hemisphere at the beginning of the vegetation period (early spring). Correspondingly, the CO<sub>2</sub> concentration shows a yearly minimum during the autumn. These yearly variations become less pronounced with increasing altitude above ground level in the troposphere and they became negligible above the tropopause (Bischof and Bolin, 1966). In contrast, in the Southern Hemisphere, the amplitude of yearly variations is small even in the surface air. This results from the world-wide distribution of land biota. More exactly this means that forests are concentrated in this hemisphere in the tropics where the yearly changes in the intensity of solar radiation and in vegetation can practically be neglected.

The most important peculiarity of the variation of CO<sub>2</sub> level is its present gradual increase which apparently began at the end of the last century (Fig. 4). Thus, the concentration of carbon dioxide increased from the pre-industrial value of less than 300 ppm to 327 ppm in 1975 (Bolin, 1977a). Accordingly the present total atmospheric CO<sub>2</sub> mass is estimated to be  $2,500 \times 10^9$  t, about 11 % greater than its

value before the industrial revolution. In other words this means that the delicate balance of CO<sub>2</sub> among different parts of the biosphere is already disturbed by the activity of men (see Chapter 6). All CO<sub>2</sub> sources, including human activity, at present yield around  $500 \times 10^9$  t yr<sup>-1</sup>.

It should be mentioned that only about the half of anthropogenic CO<sub>2</sub> remained airborne in the past decades.<sup>4</sup> However, this does not necessarily mean that the fraction of man-made CO<sub>2</sub> stored in the atmosphere will always be the same in the future. For this reason it is essential to determine from past variations the factors governing the fate of anthropogenic carbon dioxide. It is also essential to include these factors in so-called reservoir or box models<sup>5</sup> to calculate, on the one hand, the fraction absorbed by oceans and, on the other hand, the part of the emission used by the land biota. Since the uptake of carbon dioxide by ocean waters is governed by more or less known physical and chemical laws the response of land plants to the increase of CO<sub>2</sub> level, which is much more complicated, can be estimated by difference between total CO<sub>2</sub> input and oceanic absorption (e.g. Keeling, 1973).

We have to emphasize that the correct prediction of the future CO<sub>2</sub> concentrations is one of most important tasks of atmospheric science at present. This is explained by the fact that the CO<sub>2</sub> content of our atmosphere regulates, among other things, the radiation balance of the Earth-atmosphere system by absorbing infrared radiation emitted by the surface. Thus, we cannot exclude the possibility that the increase of the carbon dioxide concentration may cause inadvertent climatic variations in the future (see Chapter 6).

<sup>4</sup> This can be estimated by comparing the value calculated from fossil fuel combustion to the increase of total atmospheric CO<sub>2</sub> burden.

<sup>5</sup> The reservoirs which must be taken into account are: the atmosphere, the oceans and the land biota. It is useful to divide both the ocean and land biota into two further reservoirs: surface ocean and deep ocean as well as short-lived and long-lived land biota (Keeling, 1973).

### **3. Atmospheric cycle of trace constituents**

#### **3.1 Introduction**

The concentration of trace substances in the atmosphere is very variable in space and time and their residence time (see Table 1) is only some years, weeks or even less. The only exceptions are the noble or rare gases which, with the exception of helium and radon, have no sources and sinks so that we cannot speak of atmospheric cycles in this case. For this reason they are considered permanent constituents and will be omitted from further consideration.

The problems related to the water cycle will also not be considered in spite of the fact that, taking into account its quantity and atmospheric effects, water is one of the most important trace materials. This omission is explained by a historical precedent. The study of the atmospheric cycle of the water as well as the measurement of its concentration were included in the past in the program of other branches of atmospheric science. Thus, the formation of clouds and precipitation, the subject of the cloud physics (e.g. Mason, 1957, Fletcher, 1962), will only be discussed in relation with the wet removal of aerosol particles and water-soluble gases.

Furthermore it seems appropriate not to discuss radioactive materials here, but to leave them to a separate volume. The atmospheric fate of radioactive aerosols and gases is similar in some respects to that of other trace substances (e.g. dry and wet removal). However, the presentation of their formation and decay would render the present volume too diffuse. Thus, results gained by radioactive tracers will only be mentioned in Chapter 5 dealing with the removal processes. Concerning atmospheric radioactivity, the reader is referred to other textbooks (Junge, 1963; Cadle, 1966; Israël and Israël, 1973).

It should be mentioned in this introduction that atmospheric concentrations of trace constituents are sometimes given by the authors in different units. For this reason we have to discuss this problem in some detail. In Table 1 the concentration of trace gases is expressed either in ppm or in  $\mu\text{g}/\text{m}^3$  STP. The ppm is a so-called volume mixing ratio<sup>1</sup> which is equal to unity if the concentration of a certain gas in the air is  $1 \text{ cm}^3 \text{ m}^{-3}$ .

<sup>1</sup> The more exact abbreviation is ppmv (v: volume). In this book for the sake of simplicity we always use ppm for ppmv.

In the case of smaller concentrations pphm (parts per hundred million) and ppb (parts per billion; where billion =  $10^9$ ) can also be used. Another possibility to express the atmospheric level of trace gases and aerosol particles is the "mass concentration", which gives the mass of a substance per unit volume of air. The dimension of the mass concentration is  $\text{g cm}^{-3}$  or more frequently  $\mu\text{g m}^{-3}$ . This quantity is a function of the temperature and pressure since the air volume in the denominator depends upon these physical parameters. Thus, it is reasonable to express its values in  $\mu\text{g m}^{-3}$  STP (standard temperature and pressure). In this book we will use concentrations expressed mainly in ppm and in  $\mu\text{g m}^{-3}$  STP. Table 4

Table 4

Conversion factors for concentrations expressed in  $\mu\text{g m}^{-3}$  STP and ppm for different trace gases (Junge, 1963)

Gas	Conversion factor ( $\gamma$ )	
	$1 \text{ ppm} = / \mu\text{g m}^{-3}$	$1 \mu\text{g m}^{-3} = / \times 10^{-4} \text{ ppm}$
H <sub>2</sub>	89	112.00
He	178	56.20
CH <sub>4</sub>	712	14.05
CO	1259	8.10
O <sub>3</sub>	2140	4.67
N <sub>2</sub> O	1960	5.10
NO <sub>2</sub>	2050	4.88
NH <sub>3</sub>	760	13.15
SO <sub>2</sub>	2850	3.51
H <sub>2</sub> S	1520	6.58

gives the numerical factors to recalculate one into the other in case of different gases. It goes without saying that pphm and ppb values can easily be calculated from concentrations expressed in ppm.

In some references the concentration of a trace material is given in mass mixing ratio. The dimension of this concentration is  $\text{g g}^{-1}$ ,  $\text{g kg}^{-1}$  or  $\mu\text{g kg}^{-1}$ , where  $1 \mu\text{g} = 10^{-6} \text{ g}$ . By taking into account the air density, these figures can easily be converted to mass concentrations. Concerning this dimension, it is to be noted that  $\text{mg kg}^{-1}$  values can also be called ppmm (m: mass), which is widely used in precipitation chemistry studies (see Chapter 5) since for water  $1 \text{ kg} \approx 1 \text{ litre}$ .

It may be helpful for the reader that an indication is given here of the organization of the remainder of this book. In this chapter we will discuss the atmospheric cycle of all trace constituents including the particulate matter formed by transformation of gaseous compounds (organic vapours, gaseous nitrogen and sulfur compounds) by chemical and physical processes in the air. Later we shall present separately (see Chapter 4), in a coherent way, the physical and chemical properties, as well as the behaviour of atmospheric aerosol particles. Furthermore, in addition to chemical reactions in the air and to biological sinks discussed in this chapter, the so-called dry and wet removal processes also play an important part in the control of the

atmospheric fate of some constituents (especially those nitrogen and sulfur compounds soluble in water). Although these sink terms will also be given in relation to the cycle of nitrogen and sulfur compounds, the reader is referred to Chapter 5 for further details.

Finally, it should be emphasized that in the present volume we do not deal with the local air pollution<sup>2</sup> of cities and industrialized areas. This is done by textbooks on air pollution meteorology. Great attention will be devoted, however, to global air pollution, which denotes the anthropogenic modification of the atmospheric composition on a much larger scale. Generally, this will be done by the consideration of a single lumped anthropogenic source which can be compared to the strength of natural sources. This procedure makes possible to discuss in some detail the global atmospheric equilibrium of different trace materials.

### 3.2 Hydrogen and helium

#### 3.2.1 Hydrogen

The first acceptable hydrogen analyses in the atmosphere were carried out by Schuftan in Germany (see Junge, 1963). According to his data, taken in 1923, the concentration of hydrogen in the air is  $0.5 \pm 0.10$  ppm. Subsequently, many hydrogen measurements were made in polluted atmospheres. In really clean environments, the first samplings for hydrogen analysis were done by Bainbridge (see Schmidt, 1974) in remote areas of the Pacific Ocean. Later, air samples were taken over territories of the U.S.A. by means of an aircraft (Ehhalt and Heidt, 1973). In these programs individual air samples were analyzed. Thus, the number of data is rather limited. Hydrogen measurement in the atmosphere was facilitated by a refinement of the mercuric oxide method for carbon monoxide, which makes continuous monitoring possible.

This method was widely used in recent years by Schmidt (1974). He carried out measurements in the air near the surface as well as in the upper troposphere and lower stratosphere. His results obtained near ground level can be divided into three categories:

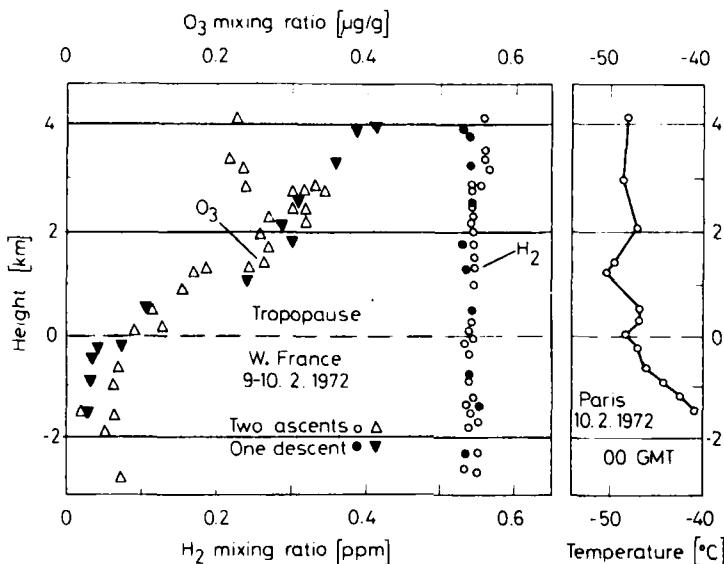
- (1) polluted atmosphere (Mainz, FRG);
- (2) Atlantic Ocean, Northern Hemisphere;
- (3) Atlantic Ocean, Southern Hemisphere.

One of most interesting features of his results is the fact that the hydrogen concentration in polluted air is higher than in clean air. The atmospheric hydrogen level is lowest in the clean air of the Southern Hemisphere. The mean concentration values for the categories mentioned are 0.800 ppm, 0.575 ppm and 0.550 ppm, respectively. The more recent data of Schmidt (1978) confirm essentially these

<sup>2</sup> This means that the concentrations given are generally so-called background concentrations.

concentrations. He reports that the average mixing ratio is 0.576 ppm in the Northern and 0.552 ppm in the Southern Hemisphere. The troposphere was found to be rather well mixed vertically and horizontally in both hemispheres. According to Schmidt's aircraft measurements carried out over France the  $H_2$  volume mixing ratio in the air does not change in passing from the upper troposphere to the lower stratosphere. Figure 5 gives his results obtained during two flights around the tropopause. In Fig. 5 the temperature profile and the vertical variation of the ozone concentration are also plotted. This last was determined simultaneously with the  $H_2$  measurement. It can be seen that the ozone concentration increases while the  $H_2$  level remains constant with increasing height.

Finally, it should be noted that Schmidt (1974) also measured the hydrogen concentration of ocean waters. He found that the  $H_2$  content of ocean waters is generally three times higher than the equilibrium value calculated on the basis of atmospheric measurements.



**Fig. 5**

The vertical profile of hydrogen and ozone in the vicinity of the tropopause according to Schmidt (1974).  
(By courtesy of *Tellus*)

Taking into account the above findings Schmidt (1974) hypothesized four  $H_2$  sources :

- (a) human activity;
- (b) surface of oceans;
- (c) soil surface;
- (d) photochemical formation in the troposphere.

The anthropogenic H<sub>2</sub> is emitted into the air in automotive exhaust gases, which contain H<sub>2</sub> in the range of 1–5 % by volume. The nature of the oceanic source is not entirely clear but it is probably due to microbiological activity. However, the supersaturation of ocean waters unambiguously indicates hydrogen gas formation there. The emission from soils is caused by the fermentation of bacteria.

From the point of view of air chemistry the photochemical H<sub>2</sub> formation is the most interesting source. Although this formation process is possible by the direct photolysis of water molecules (see reaction [2.2]), it is generally accepted that methane plays an important part in the reaction chain. The atmospheric methane (see Section 3.4) first reacts with OH radicals. These very reactive electrically uncharged atomic groups, called free radicals, can be formed partly by the photolysis of water (see later) and partly by the following process<sup>3</sup> (Warneck, 1974):



where the asterisk denotes that the oxygen atom is in excited state (see Subsection 3.4.2). The excited atomic oxygen comes from the destruction of ozone (see later). By the interaction of OH radicals and CH<sub>4</sub>, formaldehyde is formed, which dissociates under the influence of solar radiation with wavelengths of 0.30–0.36 μm (Calvert *et al.*, 1972):



According to Schmidt (1974) there are two important H<sub>2</sub> sinks:

- (a) chemical destruction in the troposphere;
- (b) soil.

The chemical destruction in the troposphere is also promoted by the presence of OH radicals which react with hydrogen in the following way:



The product of this reaction is partly water vapour and partly another chemically active free radical (H). The interaction of processes [3.2] and [3.3] results in an equilibrium H<sub>2</sub> concentration.

The numerical values of source and sink terms are given in Table 5 (Schmidt, 1974). It should be mentioned that the table does not contain the global soil source strength. It is speculated that its lower limit is around 0.1 × 10<sup>6</sup> t yr<sup>-1</sup>. Considering that the sum of known global source terms is about 66 % of the H<sub>2</sub> sinks, soil sources

<sup>3</sup> In polluted atmosphere free radicals are formed by other reaction steps, too (Haagen-Smit and Wayne, 1976).

must be about  $12.5 \times 10^6 \text{ t yr}^{-1}$  in order to balance sources and sinks. Further research is needed, however, to validate the numerical values given in Table 5.

On the basis of the H<sub>2</sub> measurements discussed above it can be calculated that the atmospheric reservoir contains  $204 \times 10^6 \text{ t}$  of hydrogen. More than the half of this quantity can be found in the atmosphere over the Northern Hemisphere. Dividing this figure by the global source or sink strengths, we obtain for values of between about 6 and 8 years for the atmospheric residence time.

**Table 5**

Sources and sinks of atmospheric H<sub>2</sub> expressed in  $10^6 \text{ t}$ .  
The data are combined from two tables of Schmidt  
(1974)

	Northern Hemisphere		Southern Hemisphere	
	Sources	Sinks	Sources	Sinks
Anthropogenic	11.0		2.0	
Oceans	1.6		2.4	
Photochemical	3.7	2.8	3.3	2.7
Soils	?	20.7	?	10.3
Sum	16.3	23.5	7.7	13.0

Note:  $10^6 \text{ t} = 10^{12} \text{ g} = 1 \text{ Tg}$  (teragram).

It follows from the above discussion that the strength of soil sources is probably smaller than that of sinks in the soil. We may also conclude that an important part of the atmospheric hydrogen (around 50 %) is provided by anthropogenic activity. It seems to be meaningful in this way to consider H<sub>2</sub> as a future global pollutant. This concept is further supported if the results of the first H<sub>2</sub> measurements (Schuftan) are compared to Schmidt's concentrations. This comparison suggests that the atmospheric hydrogen level has gradually increased in past decades. This fact is particularly important since H<sub>2</sub> takes part, as we have seen, in the formation and destruction of free radicals which participate in the control of the atmospheric cycle of many trace constituents (see later).

It is well known that protons from the Sun are continuously reaching the Earth's atmosphere. However, this external source does not increase the atmospheric hydrogen level since hydrogen atoms are also continuously leaving the upper atmosphere. It is to be noted that Lovelock and Lodge (1972) speculate that a significant part of the escaping H<sub>2</sub> comes from CH<sub>4</sub> since according to the results of recent measurements the methane quantity reaching the stratosphere from the troposphere is about three times greater than that of H<sub>2</sub>O. Thus, the photolysis of CH<sub>4</sub> produces six times more hydrogen than the photodissociation of water vapour. In this way methane plays an important role in the control of the removal of H<sub>2</sub> from the lower levels of the atmosphere.

Finally, it can be mentioned (Junge, 1963) that the deuterium content of the atmospheric hydrogen molecules is approximately 5 % of that found in ocean waters, where the D/H ratio is  $3.1 \times 10^{-4}$ . On the other hand the abundance of tritium in the atmosphere is about  $10^3$  times greater than the value in the hydrosphere ( $\sim 10^{-18}$ ).

### 3.2.2 Helium

The results of helium analyses carried out in the atmosphere were reviewed by Glueckauf (1951) who stated that the concentration of helium is a constant value:  $5.239 \pm 0.002$  ppm. These measurements also demonstrated that the  ${}^3\text{He}/{}^4\text{He}$  isotope ratio in the air is  $1.2 \times 10^{-6}$ , which means that only the formation of  ${}^4\text{He}$  is of interest from the point of view of air chemistry.

Atmospheric  ${}^4\text{He}$  is a product of radioactive processes taking place in the Earth's crust. About 98 % of the helium is produced by the decay of two radioactive isotopes:  ${}^{238}\text{U}$  and  ${}^{232}\text{Th}$ . The rate of  ${}^4\text{He}$  formation can be estimated from the lithospheric quantity of these isotopes and the escape rate of the helium formed. We can assume that helium formed in the Earth's mantle cannot escape into the air. Then only  ${}^4\text{He}$  produced in the crust reaches the atmosphere. This quantity is estimated to be  $7 \times 10^6 \text{ m}^3 \text{ STP per year}$  (Junge, 1963).

Since there appears to be no He sinks in the soil or in the lower levels of the atmosphere, it is more than probable that this noble gas escapes from the upper atmosphere into outer space. It follows from the constant atmospheric level that this sink balances the effect of the sources. When the total atmospheric helium mass is taken into account, as well as the above formation mechanism, the residence time of He is estimated to be approximately  $10^7$  years.

## 3.3 Carbon compounds

### 3.3.1 Methane

The presence of methane in the atmosphere was discovered by Migeotte (1948), who identified this trace gas on the basis of absorption bands found in the infrared spectrum of the solar radiation. These first optical measurements gave an atmospheric concentration of 2 ppm. According to more recent analyses carried out by gas chromatography, the methane concentration in the lower troposphere varies between 1.3–1.6 ppm (Ehhalt, 1974). The average mixing ratios of methane in the troposphere for Northern and Southern Hemispheres were found in 1972 to be 1.41 and 1.30 ppm, respectively (Ehhalt and Schmidt, 1978). It thus follows from these data that methane concentrations are somewhat smaller over the Southern than over the Northern Hemisphere. Furthermore, the average results also show that zonal and vertical concentration changes are negligible in spite of the fact that  $\text{CH}_4$

level may fluctuate in individual profiles. In the troposphere the amplitude of annual variations is also very small. (There is some indication of a concentration maximum during the autumn.) The lack of annual variations can be explained either by the interaction of several sources, or by the similar variation of source and sink strengths during the year.

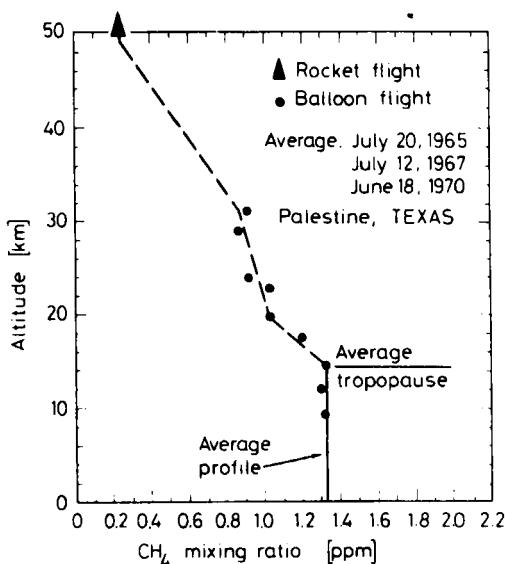


Fig. 6

The vertical profile of methane according to Ehhalt (1974). (By courtesy of *Tellus*)

An interesting feature of the vertical profile of CH<sub>4</sub> is the concentration decrease above the tropopause, which was first demonstrated by the measurements of Bainbridge and Heidt (1966) who made aircraft and balloon flights. This finding was later confirmed by the balloon observations of Ehhalt (1974) and the rocket measurements of Ehhalt *et al.* (1972). The result of these authors are plotted in Fig. 6. It can be seen that the methane level in the troposphere does not change with height. However, above the tropopause the volume mixing ratio decreases with increasing altitude. The initial decrease is rather rapid then, above a certain level, it becomes slower. On the basis of available data, the total atmospheric methane mass is calculated to be  $4000 \times 10^6$  t.

The origin of atmospheric methane can be estimated by determining its <sup>14</sup>C isotope abundance. This abundance should be the same as the <sup>14</sup>C content of living plants, if methane is of biological origin or is provided by recently dead organisms. CH<sub>4</sub> from fossil fuels or volcanic activity is practically free of radiocarbon, since fuel deposits are very old and their <sup>14</sup>C content has already decayed. Measurement of

the radiocarbon in atmospheric samples demonstrated that at least 80 % of CH<sub>4</sub> comes from organic materials of recent origin (Ehhalt, 1974). The remaining 20 % is termed "dead" methane, and is partly due to human activity.

**Table 6**  
Global strength of biological methane sources according to Ehhalt (1974)

Source	Annual production $10^6 \text{ t yr}^{-1}$
Enteric fermentation of animals	101–220
Paddy fields, swamps, marshes	410–540
Fresh water, lakes	1.25–25
Upland fields	10
Forests	0.4
Tundra	1.3–13
Oceans	
(a) open	4–6.7
(b) shelf	0.7–14
Total	529–825

The strength of different biological *methane sources* was estimated by Ehhalt (1974) and by Ehhalt and Schmidt (1978). Data in Table 6 are taken from one of Ehhalt's compilations. It can be seen from these estimates that the majority of CH<sub>4</sub> comes from swamps and marshes as well as from paddy fields; that is from an anoxic environment. In this environment, containing much organic matter, anaerobic bacteria produce a huge quantity of CH<sub>4</sub>. Furthermore, the enteric fermentation of animals is also a very important methane source. Finally, one can see from the table that from the biosphere (500–800) × 10<sup>6</sup> t CH<sub>4</sub> is liberated into the air. The strength of known "dead" methane sources (e.g. mining, industrial losses) is estimated to be between 15 × 10<sup>6</sup> and 50 × 10<sup>6</sup> t yr<sup>-1</sup> which is less than the 20 % of the contribution of biogenic sources indicated by radiocarbon analyses. Although the exact explanation of this discrepancy is not clear it appears that the impact of mankind on the atmospheric methane cycle can be neglected at present. This is further evidenced by the fact that no concentration increases were recorded during the last twenty years.

The rate of atmospheric CH<sub>4</sub> formation was also recently estimated by Lukshin *et al.* (1978) who carried out aircraft samplings over the European part of Soviet Union to measure the vertical profiles of CH<sub>4</sub> and radon during the spring of 1975. From the results of these measurements, they calculated the vertical diffusion flux of methane liberated at the surface. The chemical destruction of CH<sub>4</sub> (see later) in the troposphere was also taken into consideration. These authors found that the strength of global methane sources generalized on the basis of the CH<sub>4</sub> flux calculated is about one order of magnitude greater than the total value given by

Ehhalt (1974). It follows from this difference that, while the residence time from Ehhalt's results is 4–7 years, it is only 0.4 year from the estimate of Lukshin *et al.* (1978), by using the same figure for the amount of atmospheric CH<sub>4</sub> burden ( $4000 \times 10^6$  t). It is to be noted, however, that the number of flights in Lukshin's investigation was very limited. Clearly, more research is needed in this field.

Our knowledge of the sinks of atmospheric methane can be summarized as follows. Model experiments made under laboratory conditions show that the CH<sub>4</sub> uptake of soil is not important (Ehhalt, 1974). This means that soil microorganisms do not oxidize CH<sub>4</sub>. This also means that we have to look for methane sinks in the atmosphere.

The only atmospheric chemical process that provides an adequate sink is the reaction between CH<sub>4</sub> and OH (Ehhalt and Schmidt, 1978):



The reaction rate (see Subsection 3.4.1) of this process is  $5.5 \times 10^{-12} \exp(-1900/T)$  [cm<sup>3</sup>/molecules], where  $T$  is the absolute temperature.

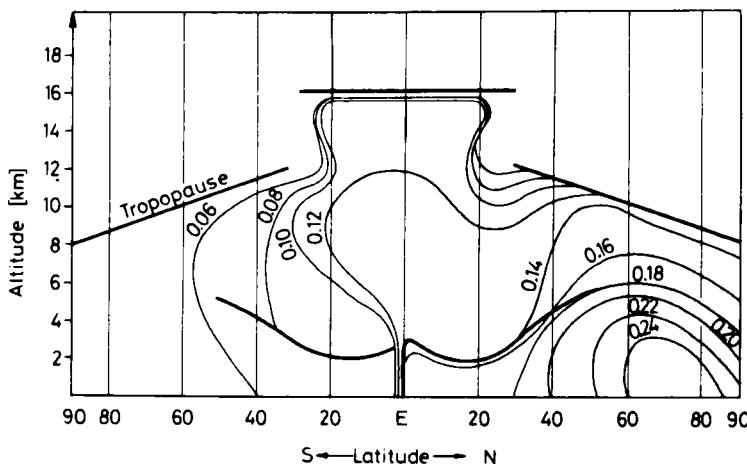
According to Levy (1971) the average concentration of OH radicals is  $2.5 \times 10^6$  cm<sup>-3</sup> in the troposphere. This calculated value is essentially confirmed by recent atmospheric measurements (e.g. Perner *et al.*, 1976). On the basis of the above figures a global tropospheric CH<sub>4</sub> destruction rate of  $900 \times 10^6$  t yr<sup>-1</sup> can be estimated, which is comparable to the total source strength given above. If this figure is correct the majority of CH<sub>4</sub> is destroyed in the troposphere. Thus, Ehhalt and Schmidt (1978) speculate that about 85–90 % of the methane is removed from the air in the troposphere; the remainder is destroyed in the stratosphere by the same process.

As mentioned in Section 3.2, reaction [3.4] is the first step of a reaction chain which ends in the formation of carbon monoxide and hydrogen. This means that the methane cycle in the atmosphere is connected with those of the substances mentioned. Furthermore, since CH<sub>4</sub> plays an important part in the control of the stratospheric budget of hydrogen compounds including water (formed by the oxidation of the hydrogen of CH<sub>4</sub>) and free radicals, the methane cycle is also of importance for chemical processes in the stratosphere.

It was also mentioned in Section 3.2 that tropospheric H<sub>2</sub> formed by the above process reacts with OH to form water. The CO formed from the carbon atoms of methane is transformed into CO<sub>2</sub> by appropriate chemical processes (see Subsection 3.3.2). Both water and carbon dioxide are used by the plants during their photosynthetic activity. Thus, a major part of hydrogen and carbon of CH<sub>4</sub> returns to the plants, thus closing the atmospheric methane cycle.

### 3.3.2 Carbon monoxide

Like  $\text{CH}_4$ , carbon monoxide was first optically identified in the atmosphere by Migeotte (1949). It was believed at that time that atmospheric CO was wholly due to anthropogenic sources. However, more recent studies show that carbon monoxide is emitted into the air by many other sources. Furthermore, it became clear that the atmospheric cycle of this trace gas is much more complicated than was thought at the time of its discovery.



**Fig. 7**

Volume mixing ratio (ppm) of carbone monoxide in the troposphere (Seiler, 1974). (By courtesy of Tellus)

Investigation of the cycle of CO in the air was stimulated by the development of a continuous chemical monitoring technique (Seiler and Junge, 1970). This method, based on the destruction of mercuric oxide by CO, was widely used by Seiler (1974) to determine the carbon monoxide concentration in the air as a function of geographical location and altitude. His results are summarized in Fig. 7. It can be seen that in surface air maximum concentrations are found in the Northern Hemisphere ( $> 0.2$  ppm). Data also show that at the latitudes where the CO level has a maximum the variations of concentration are also rather significant. In the vicinity of the equator, in the intertropical convergence zone<sup>4</sup>, the volume mixing ratios are between 0.10 and 0.16 ppm. The concentration begins to increase in the Northern Hemisphere just north of the convergence zone.

The concentration of CO in the upper troposphere also varies in agreement with the latitudinal changes observed in surface air. However, the magnitude of upper air

\* Zone where the southeast trade winds of the Southern Hemisphere meet the northeast trade winds of the Northern Hemisphere. This "convergence" at the surface is the result of continual rising of air at the point of meeting.

variations is small compared with fluctuations in the lower troposphere. In the Northern Hemisphere the concentration decreases with increasing tropospheric altitudes. These vertical variations become insignificant in the Southern Hemisphere. Finally, Seiler's measurements show that above the tropopause the concentration decreases rapidly in the first 1 km layer, then it remains practically constant in the stratosphere (0.05 ppm).

According to Seiler (1974) and Seiler *et al.* (1978) the atmospheric carbon dioxide is mostly produced by the following sources (see Table 7):

- (a) anthropogenic sources;
- (b) emission of CO from the ocean;
- (c) burning of bushes and forests;
- (d) oxidation of non-methane hydrocarbons;
- (e) direct production by plants;
- (f) oxidation of methane.

Robinson and Moser (1971) speculate that the majority of anthropogenic CO (64 %) is emitted into the air by automobile exhausts mainly over the Northern Hemisphere. Seiler (1974) reports a slightly higher figure (70–80 %). The strength of global anthropogenic source was estimated by Robinson and Moser (1971) on the basis of data from 1966. They concluded that the total emission is  $285 \times 10^6 \text{ t yr}^{-1}$ . According to Jaffe (see Seiler, 1974), who used data relative to 1971, the rate of anthropogenic CO formation is equal to  $460 \times 10^6 \text{ t yr}^{-1}$ . Seiler (1974) believes that even this latter value can be considered as a lower limit. He argues that the authors underestimated the effect of domestic heating. Furthermore, they did not take into consideration emissions from some industrial processes. Finally, the above emission rates were estimated mainly on the basis of data from USA, where the emissions are rather severely controlled. For these reasons Seiler gives a global value of  $640 \times 10^6 \text{ t yr}^{-1}$ .

According to the results of measurements carried out in the ocean (Seiler, 1974) the carbon monoxide concentration in near surface marine layers is  $5 \times 10^{-5} \text{ ml l}^{-1}$  on an average. This water concentration would be in equilibrium with a surface air CO level of 2.5 ppm. However, the carbon monoxide concentration in air over the ocean surface is between 0.04 ppm and 0.20 ppm, which means that the ocean water is supersaturated with CO. It follows from these data that the ocean is a CO source, the global strength of which is about six times less than the total anthropogenic emission (Table 7).

It is believed that CO formation caused by natural burning is also small as compared to the production rate of man-made atmospheric carbon monoxide. The same is probably true in case of the oxidation of terpenoid hydrocarbons emitted by vegetation (see Subsection 3.3.3). However, as Wilks (1959) pointed out green plants can directly emit carbon monoxide due to the photodecomposition of pigments and

Table 7

Estimated annual production rates and sinks of atmospheric CO according to Seiler (1974) and Seiler *et al.* (1978)

	N. Hemisphere	S. Hemisphere	Total
<i>Sources [10<sup>6</sup> t yr<sup>-1</sup>]</i>			
Anthropogenic	540	100	640
Oceans	40	60	100
Bush- and forest fires	40	20	60
Oxidation of hydrocarbons	40	20	60
CH <sub>4</sub> oxidation			1500–4000 (?)
Direct production by plants			50–100
<i>Sinks [10<sup>6</sup> t yr<sup>-1</sup>]</i>			
Soil uptake	300	150	
Oxidation			1940–5000 (?)
in the troposphere	90	20	
in the stratosphere			110

chlorophyl. According to recent laboratory experiments of Seiler *et al.* (1978) this source provides carbon monoxide in an amount similar to that of the above sources, except for human activity.

Unfortunately rather different opinions can be found in the literature concerning the rate of CO formation by the oxidation of methane in the atmosphere. Thus, according to Seiler (1974) the global strength of this source is between  $1500 \times 10^6$  t  $\text{yr}^{-1}$  and  $4000 \times 10^6$  t  $\text{yr}^{-1}$ . However, Warneck (1974) gives a figure of  $300 \times 10^6$  t  $\text{yr}^{-1}$ , based in part on a calculation of the removal of OH radicals from the air by aerosol particles. On the other hand, Lukshin *et al.* (1978) argue that the quantity of CO formed yearly by this process in the atmosphere is about one order of magnitude greater than Seiler's estimate. Finally, Ehhalt and Schmidt (1978) propose a figure similar to that given by Seiler (1974). Because of this latter agreement the present author uses a value of about  $(1000–1500) \times 10^6$  t  $\text{yr}^{-1}$  for this term (see later Fig. 8). This discussion makes it clear that the sources of carbon monoxide are not well defined numerically. Efforts are needed in the future to obtain more realistic figures. This is particularly important if we want to estimate correctly the man-made contribution to the atmospheric budget of carbon compounds.

At present it appears that there are two major carbon monoxide sinks. The first is provided by the soil surface. Thus, laboratory experiments show that the CO absorbing capacity of different soils can be very important (see Seiler, 1974). The generalization of the results of these laboratory works gives a value of  $450 \times 10^6$  t  $\text{yr}^{-1}$  for the global sink intensity (see Table 7). An other possibility is the reaction of carbon monoxide with OH radicals which removes CO rapidly from the air. In the previous section we have discussed the chemical destruction of CH<sub>4</sub> by OH. One end product of these processes is carbon monoxide (see [3.2]) which also reacts with free radicals to form carbon dioxide in the following way (e.g. Bortner *et al.* 1974)



It is assumed that the majority of carbon monoxide is removed from the atmosphere by these reactions. Seiler (1974) hypothesizes that the yearly CO loss in the troposphere due to [3.5] and [3.7], is  $(1940 - 5000) \times 10^6 \text{ t yr}^{-1}$ . The corresponding figure for the stratosphere is estimated to be  $110 \times 10^6 \text{ t yr}^{-1}$  (see Table 7). In contrast, Warneck (1974) speculates that the global atmospheric strength of this sink is much smaller than the Seiler's figure. Finally, according to the calculations of Ehhalt and Schmidt (1978) about  $(1500 - 2900) \times 10^6 \text{ t CO}_2$  is produced yearly from CH<sub>4</sub> by reaction steps [3.4], [3.2], [3.5] and [3.7]. On the basis of these data for the schematic representation of the atmospheric pathways of carbon a value of  $2800 \times 10^6 \text{ t yr}^{-1}$  expressed in CO<sub>2</sub> will be accepted (see Fig. 8, p. 46) for this sink term.

### 3.3.3 Non-methane organic carbon

This subsection surveys our knowledge of tropospheric non-methane organic compounds. The concentration and budget of organic substances containing no halogen will first be discussed. The gaseous phase in this case will be termed "organic vapours", while the particulate phase will be called "particulate organic carbon". After this short discussion the tropospheric concentration and sources of anthropogenic halocarbons will be mentioned. The role of halocarbons in stratospheric photochemistry is discussed in Subsection 3.4.3.

The importance of organic vapours in the chemistry of the clean atmosphere was stressed in several papers by Went (e.g. Went, 1966) in the sixties. He recognized that natural volatile organic vapours (mostly terpenes) play an important part in the formation of atmospheric aerosol particles. In spite of the importance of these materials in the budget of the particulate matter, "perhaps less is known about the global sources, distribution and fluxes of organic matter than any other major class of chemical substances in the atmosphere" (Duce, 1978). This situation is at least partially explained by the complexity of the problem. Thus, many organic compounds in vapour and particulate form can be found in the atmosphere as a result of different natural and anthropogenic sources as well as complicated atmospheric transformation processes. In the following, the results on organic vapours and particulate organic carbon will be presented as recently reviewed by Duce (1978). For further details the reader is referred to the original paper and to its references.

The concentration of vapour phase organic carbon in surface air over the oceans is  $5 - 10 \mu\text{g m}^{-3}$  STP. The corresponding range over non-urban North America was found to be  $10 - 50 \mu\text{g m}^{-3}$  STP. It should be noted, however, that much higher continental concentrations were measured in the Amazon jungle of Brazil.

Accepting average concentrations of  $8 \mu\text{g m}^{-3}$  STP and  $50 \mu\text{g m}^{-3}$  for oceanic and continental areas, respectively, the global tropospheric burden is calculated to be  $52 \times 10^6 \text{ t}$  if we assume a relatively constant mixing ratio for the tropopause. The source of these organic compounds is primarily plants. Unfortunately the value of the global plant emission is very uncertain; Went (1966) has estimated it at  $1000 \times 10^6 \text{ t yr}^{-1}$ , while Duce (1978) suggests for terpenoid hydrocarbons a value of  $(10-350) \times 10^6 \text{ t yr}^{-1}$ , calculated as carbon. The strength of total non-methane hydrocarbon sources due to human activity is around  $65 \times 10^6 \text{ t yr}^{-1}$  in carbon equivalents.

The particulate organic carbon level varies from  $0.5 \mu\text{g m}^{-3}$  STP (oceanic air) to about  $3 \mu\text{g m}^{-3}$  STP (clean continental air). The results of atmospheric measurements show that about 80 % of this carbon can be identified on aerosol particles with radii smaller than  $0.5 \mu\text{m}$ . Using  $0.5 \mu\text{g m}^{-3}$  STP as the average level in oceanic air and  $1.5 \mu\text{g m}^{-3}$  STP as the mean continental concentration, Duce (1978) has calculated that the burden of particulate organic carbon in the troposphere is  $2.2 \times 10^6 \text{ t}$ , which is about 2 % of the corresponding value for organic vapours. For his calculation he has assumed that particles with radii larger than  $0.5 \mu\text{m}$  have a constant mixing ratio from the surface up to 1000 m and then the concentration drops to one-third of its surface value from that level to the tropopause. On the other hand Duce has speculated that the mixing ratio of smaller organic particles is essentially constant to the top of the troposphere. This latter assumption was based partly on the particulate organic carbon measurements of Ketseridis *et al.* (1976) carried out at a mountain station (Jungfraujoch, Switzerland) and partly on the aircraft measurements of Gillette and Blifford (1971). It should be mentioned that these latter authors did not measure the organic compounds in particulate matter. They determined, however, among other things the vertical profile of sulfur particles of non-maritime origin having a size distribution similar to that of organic compounds (see Section 4.4).

An interesting consequence of Duce's speculations is the fact that he could calculate a reasonable residence time for smaller organic aerosol particles (4–7 days) only by assuming that a large quantity of these materials is formed from vapours in the atmosphere by gas-to-particle conversion. This argument leads to an atmospheric source intensity of  $(80-160) \times 10^6 \text{ t yr}^{-1}$ . He has also estimated that about  $20 \times 10^6 \text{ t}$  of anthropogenic hydrocarbons (expressed in carbon equivalents) are converted annually to aerosol particles in the troposphere. These anthropogenic organic compounds are mostly olefinic hydrocarbons emitted with automotive exhaust gases (see also Subsection 3.6.3).

Duce (1978) found an acceptable residence time (2 days) for larger organic particles when he took into account only primary sources. These primary aerosol particle sources are partly natural (e.g. materials from ocean waters, wind erosion of soil<sup>5</sup>, biospheric matter, forest wildfires) and partly anthropogenic (mostly from

<sup>5</sup> The formation of sea salt and mineral particles is discussed in Subsection 4.2.1.

combustion process). Annually they produce  $36 \times 10^6$  t of organic carbon particles with radii greater than 0.5  $\mu\text{m}$ . About 40 % of this quantity is due to pollution sources.

We can conclude from this short discussion that our knowledge of atmospheric non-methane organic vapours and particles is rather scanty. Much more research is needed to determine the source strength and atmospheric concentration of these materials. The measurement of the concentration of organic vapours and particles in the air over a wide variety of vegetation as well as the observation of vertical profile of the concentration would be of crucial interest. The more detailed investigation of removal mechanisms of organic vapours is also an important future task.<sup>6</sup> This research is indispensable to explain the role of organic compounds in the formation of aerosol particles and ozone in non-urban areas as well as to estimate the importance of non-methane hydrocarbons in the atmospheric cycle of carbon monoxide. Furthermore, it is not excluded that some petroleum hydrocarbons are transported to the ocean through the atmosphere. Clarification of this problem is also of interest for global environmental pollution studies.

Another class of organic compounds in the atmosphere comprises the various halocarbons. It can be demonstrated (Graedel and Allara, 1976) that these substances cannot be produced in the atmosphere by chemical transformations. While the majority of methyl chloride ( $\text{CH}_3\text{Cl}$ ) is of maritime origin, the other halocarbons arise from man's use of these compounds as refrigerants, solvents and propellants. According to McCarthy *et al.* (1977) the yearly release of anthropogenic fluorocarbon-11 ( $\text{CCl}_3\text{F}$ ) and fluorocarbon-12 ( $\text{CCl}_2\text{F}_2$ ) to the atmosphere in 1975 were  $0.34 \times 10^6$  t and  $0.41 \times 10^6$  t, respectively.

Measurement of atmospheric halogenated hydrocarbon started rather recently. The early measurements of Lovelock *et al.* (1973) show, among other things, that the background concentration of  $\text{CCl}_3\text{F}$ , observed over the Atlantic ocean from the United Kingdom to the Antarctic and back, depends upon the geographical latitude. At mid-latitudes in the Northern Hemisphere the  $\text{CCl}_3\text{F}$  level is about 25 % higher than the mean value (0.50 ppb) calculated on the basis of all observations.<sup>7</sup> The results of very numerous measurements carried out since about 1970 are reviewed by Jesson *et al.* (1977) and Graedel and Allara (1976). Graedel and Allara's estimates of mean tropospheric concentrations are tabulated in Table 8. These estimates are based on analyses of air samples carried out before 1975. The data suggest that the level of chlorofluoromethanes is steadily increasing in the troposphere even in the air over the Southern Hemisphere. Thus, over Australia (Fraser and Pearman, 1978a) the  $\text{CCl}_3\text{F}$  concentration increased at a rate of

<sup>6</sup> The particulate organic carbon is removed from the atmosphere by dry and wet deposition (see Chapter 5).

<sup>7</sup> More recent data suggest smaller interhemispheric gradient. For example, Rasmussen and his co-workers (see: Fraser and Pearman, 1978b) observed an 11 % decrease in concentration from 30° N to 15° S.

Table 8

Tropospheric concentration of halocarbons according to Graedel and Allara (1976)

Compound	Symbol	Concentration ppb
Methyl chloride	CH <sub>3</sub> Cl	~0.5 (partly of natural origin)
Dichlorodifluoromethane (F-12)	CF <sub>2</sub> Cl <sub>2</sub>	~0.1–0.2
Fluorotrichloromethane (F-11)	CFCl <sub>3</sub>	~0.1
Carbon tetrachloride	CCl <sub>4</sub>	~0.1
Methyl chloroform	CH <sub>3</sub> CCl <sub>3</sub>	~0.08

*Note:* The concentration of HCl in the troposphere is estimated to be around 1 ppb. Most of the gaseous chlorine is thought to be present as HCl. The tropospheric level of gaseous bromine is much less than the values given in the table (~0.01 ppb).

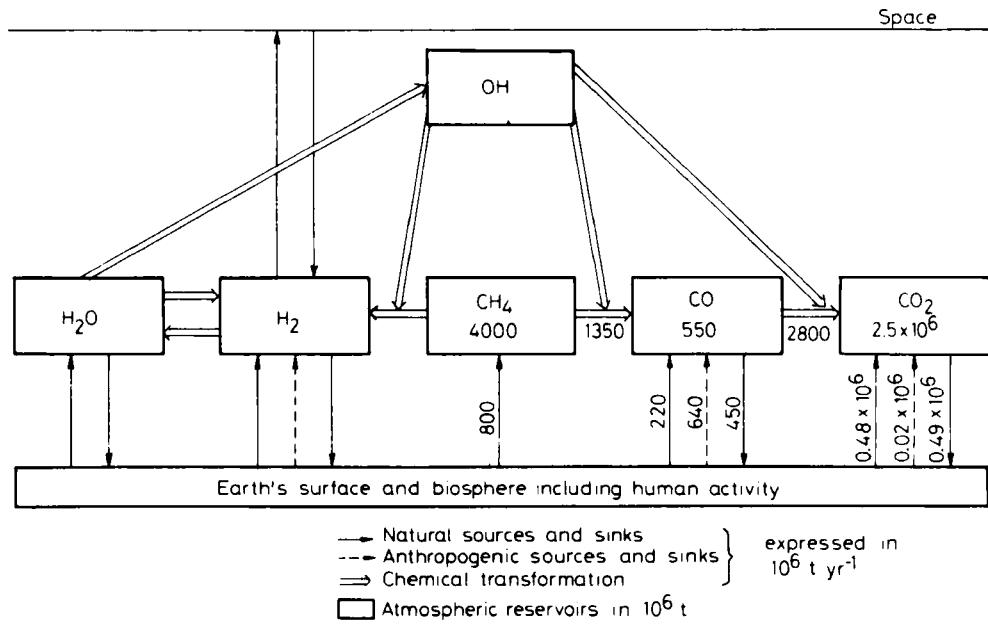
19 % yr<sup>-1</sup>. The concentrations measured in clean air are practically constant with increasing altitude.

The growing interest for the atmospheric study of halocarbons is explained by the fact that these substances rise by diffusion into the stratosphere where halogen compounds play a certain role in photochemical reactions. For the estimation of the importance of these processes the determination of the tropospheric residence time is of crucial interest. According to Sze and Wu (1976) the tropospheric lifetime of F-11 is about 10 years while the corresponding value for F-12 is probably between 10 and 20 years. Jesson *et al.* (1977) argue that the most probable tropospheric residence time for CCl<sub>3</sub>F lies between 15 and 20 yr. However, more recent data of Singh *et al.* (1979) make possible longer residence times: 65 to 70 years for fluorocarbon-12 and 40 to 45 years for fluorocarbon-11 but these estimates seem to be rather uncertain. It is obvious that much more investigation remains to be done in this important and interesting field.

### 3.3.4 The atmospheric carbon cycle

Figure 8 gives in a schematic way the atmospheric cycle of carbon compounds. The numerical values of the different budget terms are based on the results previously discussed in Sections 2.6 and 3.3. The cycle of hydrogen containing species taking part in the chemical processes illustrated is also given qualitatively. However, the atmospheric pathways of non-methane organic carbon vapours and particles are not plotted because of the uncertainties outlined in Subsection 3.3.3. The numbers at the arrows representing the chemical transformations are expressed as mass of the end products. The quantity of different compounds in the atmospheric reservoir is also illustrated.

It can be seen that the great majority of carbon is cycled in the atmosphere as carbon dioxide. Thus, although the oxidation of CO provides an important sink, the process does not supply an important CO<sub>2</sub> source. It follows from the data given that the residence times of methane, carbon monoxide and carbon dioxide are 5.0; 0.25 and 5.2 years, respectively.

**Fig. 8**

Atmospheric pathways of carbon compounds. Note : CH<sub>4</sub> released by paddy fields is considered biogenic and not anthropogenic pollution

### 3.4 Ozone

#### 3.4.1 Introduction

Ozone is an essential atmospheric trace substance. This gas plays an important role in the control of the radiation and heat balance of the stratosphere since it absorbs solar radiation with wavelengths shorter than about  $0.3 \mu\text{m}$ . An important consequence of this absorption is that UV radiation lethal to living species does not reach the lower layers of the atmosphere. Because of the importance of atmospheric O<sub>3</sub>, its study started rather early. Junge (1963) mentions that Dobson and his associates measured total ozone (see later) beginning in the twenties by a European network consisting of six stations. Later, this network became world-wide and even the determination of the vertical distribution of O<sub>3</sub> is now a routine measurement. Owing to these studies our knowledge of atmospheric ozone is rather substantial compared to that of other trace constituents.

A peculiarity of ozone is that O<sub>3</sub> molecules are both formed and partly destroyed in the atmosphere. Some decades ago it was believed that, according to the classical concept of Chapman (1930), the O<sub>3</sub> reaction chain involved only oxygen molecules

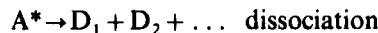
and atoms. In the last two decades it has become clear that free radicals, nitrogen oxides and halogens also play an important role in atmospheric photochemical processes. These "modern" theories have received considerable attention recently since man-made sources contribute to the stratospheric budget of the species mentioned.

The aim of this section is to present, mainly on the basis of coherent reviews (e.g. Junge, 1963; Crutzen, 1971; Dütsch, 1973; Rowland, 1976; Johnston and Podolske, 1978), the elements of the chemical aspects of the problem. Details of the relation between the general circulation and ozone formation can be found in specialized textbooks (e.g. Khrgian, 1973).

However, before discussion of the formation and destruction of atmospheric O<sub>3</sub> it seems to be necessary to define some basic notions of photochemistry and reaction kinetics for non-chemist readers. These definitions will also promote the understanding of other parts of this book.

### 3.4.2 Concepts of photochemistry and reaction kinetics

The principle of photochemical processes can be summarized as follows. A certain atmospheric gaseous component "A", absorbs a given band in the UV or visible solar spectrum. Due to the energy of the absorbed photon,  $h\nu$ , (where  $h$  is the Planck's constant and  $\nu$  is the frequency of the radiation) "A" is changed to an excited state. Because of this energy, the molecule decomposes or reacts with another compound "B" (disregarding quenching and fluorescence phenomena). The process may be symbolized in the following way (Leighton, 1961):



The last two steps in this sequence are termed primary photochemical processes. If the atmospheric concentration of the species is denoted by square brackets then

$$\frac{d[A^*]}{dt} = k_a [A],$$

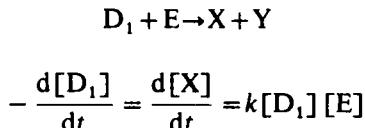
where  $k_a$  is the absorption rate of photons. The rate of the primary photochemical process will be:

$$\frac{d[D_1]}{dt} = k_a \Phi [A],$$

<sup>8</sup> Asterisk denotes the excited state.

where  $\Phi$  is the so-called quantum yield. Its value is equal to the ratio of the number of "A" reacted to that of excited molecules.

The primary photochemical processes are generally followed by secondary thermal reactions the energy of which is provided by the thermal agitation of molecules. In the case of a bimolecular reaction<sup>9</sup>:

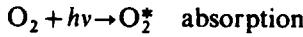


where  $k$  is the rate constant, which is equal to the quantity of  $\text{D}_1$  reacted per unit time if the  $[\text{D}_1]$  and  $[\text{E}]$  concentrations are also unity. It can be seen from the last equation that the loss rate of  $\text{D}_1$  is equal to the formation rate of  $\text{X}$  in molar units.

The above bimolecular reaction is said to be second order, since its rate depends on the product of two concentrations. Generally, the order of a reaction is the sum of the exponents of concentrations on the right-hand side of kinetic equations. Thus, the primary photochemical reaction discussed above is a first order process since its rate depends only on the concentration of A. In the case of photochemical reactions the rate constant is given by the product of the absorption rate and quantum yield.

### 3.4.3 Formation and destruction of $\text{O}_3$

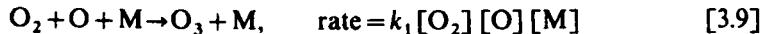
The "classical" ideas on ozone formation and destruction in the stratosphere are discussed on the basis of Paetzold's work as summarized by Junge (1963). As Chapman (1930) demonstrated the formation of ozone is initiated by the following photochemical processes:



which can be unified into one equation:



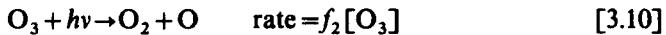
where  $[\text{O}_2]$  is the oxygen concentration expressed in molecules  $\times \text{cm}^{-3}$ , while  $f_1$  is the rate constant. This photodissociation is followed by a secondary thermal reaction leading to  $\text{O}_3$  formation:



<sup>9</sup> In these equations  $\text{D}_1$ ,  $\text{E}$ ,  $\text{X}$  and  $\text{Y}$  each denote an appropriate molecule.

where M is a third neutral body, generally oxygen or nitrogen (this means that strictly speaking the ozone formation also depends in some way on the concentration of nitrogen molecules). Molecular oxygen absorbs over the altitude range from 30 to 40 km in the band of 0.176–0.203 μm of the solar spectrum (Schumann–Runge band), while below that altitude range solar radiation with a wavelength of 0.210 μm also plays an important role in O<sub>2</sub> photolysis.

The decay of O<sub>3</sub>, according to the classical theory is due to the following reactions:



and



Ozone absorbs in the band of 0.200–0.320 μm (Hartley band) of the UV part of the spectrum and also in the visible range between 0.450 μm and 0.700 μm wavelengths (Chappuis band). A smaller absorption band can be identified in the infrared part of the spectrum. The strongest absorption is measured in the Hartley band.

It is to be noted that the possibility of other reactions between oxygen species cannot be ruled out. One might demonstrate, however, that these processes can practically be neglected. Thus, e.g. the rate of the reaction



is insignificant because of the low concentration of atomic oxygen. Further, the thermal decomposition of O<sub>3</sub> is also negligible at stratospheric temperatures.<sup>10</sup>

At equilibrium, equations [3.8]–[3.12] can be combined as follows:

$$\frac{d[\text{O}_3]}{dt} \equiv 0 \equiv k_1[\text{O}_2][\text{O}][\text{M}] - k_2[\text{O}_3][\text{O}] - f_2[\text{O}_3] \quad [3.13]$$

$$\frac{d[\text{O}]}{dt} \equiv 0 \equiv 2f_1[\text{O}_2] - k_2[\text{O}_3][\text{O}] - k_1[\text{O}_2][\text{O}][\text{M}] + f_2[\text{O}_3] \quad [3.14]$$

The combination of [3.13] and [3.14] yields:

$$f_2[\text{O}_3]^2 + f_1[\text{O}_3][\text{O}_2] - f_1k[\text{O}_2]^2[\text{M}] = 0 \quad [3.15]$$

<sup>10</sup> For this reason the decomposition of O<sub>3</sub> at night can be neglected.

where  $k = k_1/k_2$ . Since  $[M]$  is proportional to the sum of  $[N_2]$  and  $[O_2]$  we can write that  $[M] = s[O_2]$ , where  $s$  is a constant. The solution of equation [3.15] is:

$$[O_3] = \frac{-f_1[O_2] + \sqrt{f_1^2[O_2]^2 + 4f_2f_1ks[O_2]^3}}{2f_2} \quad [3.16]$$

From the fact that

$$f_1^2 \ll 4f_1f_2ks[O_2]$$

the equilibrium ozone concentration will be:

$$[O_3] = s^{1/2}[O_2]^{3/2}(kf_1/f_2)^{1/2} \quad [3.17]$$

By means of equation [3.17], the equilibrium vertical profile of the ozone concentration can be calculated. Thus,  $[O_2]$  on the right-hand side is known for various altitudes and  $k$  can be calculated for different temperatures.<sup>11</sup> The greatest problem is the determination of  $f_1$  and  $f_2$  as a function of altitude. The values of these latter parameters depend on the absorption of radiation, which varies in a complex way as solar radiation penetrates into the atmosphere. Theoretically  $f_1$  and  $f_2$  are calculated by the following two equations:

$$f_1 = \Phi_1 \int I(\lambda, h) \alpha_{O_3}(\lambda, p) d\lambda \quad [3.18]$$

$$f_2 = \Phi_2 \int I(\lambda, h) \alpha_{O_2}(\lambda) d\lambda \quad [3.19]$$

In these formulae  $I(\lambda, h)$  is the radiation intensity with wavelength  $\lambda$  at altitude  $h$ , while  $\alpha$  is the absorption coefficient of the gas specified by the subscript. Calculation using [3.18] is especially complicated by the fact that  $\alpha_{O_3}$  also depends on the pressure ( $p$ ). For these reasons the vertical profile of  $[O_3]$  cannot be calculated by analytical solution of the equations. Numerical integration, however, can be done stepwise down from the upper levels of the atmosphere.

Depending upon the assumptions employed, the equilibrium ozone concentrations, calculated by the classical theory, vary by a factor of no more than 2 or 3. Moreover the height of the maximum  $O_3$  concentration is nearly independent of the assumptions used and lies around 23 km.

It is evident that the equilibrium ozone concentration also depends on the temperature profile and on the zenith distance of the Sun. For this reason the equilibrium concentration at a given height decreases with increasing altitude. It

<sup>11</sup> According to a reaction rate table recently published by Vuppurturi (1977)  $k_1 = 1.07 \times 10^{-34} e^{(510/T)}$  and  $k_2 = 1.9 \times 10^{-11} e^{-2300/T}$ , where  $T$  is the absolute temperature.

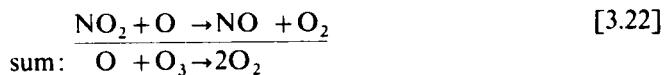
will be shown in the next section that atmospheric observations do not agree with this theoretical finding. This discrepancy can be explained by assuming that in the control of the ozone concentration atmospheric dynamics also plays an important part.

Theoretical investigations done in this field also show (Junge, 1963) that the time necessary to regain an equilibrium state again after it is disturbed varies as a function of altitude. This time can be expressed by the following equation:

$$\tau_1 = \frac{1}{4} (k[M]/f_1 \times f_2) \quad [3.20]$$

where  $\tau_1$  is the time for the deviation from the equilibrium to decrease to  $1/e$  of its initial value. According to the results of calculations obtained using equation [3.20],  $\tau_1$  is equal to 0.6 day at 40 km, while the respective figure at an altitude of 20 km is  $10^3$  days. This means that above 30 km equilibrium conditions are practically satisfied, while in lower layers of the stratosphere the ozone is a conservative property of the air.

In the sixties it became clear that the hydrogen containing free radicals formed from water (see equations [2.1] and [3.1]) also play a role in stratospheric photochemistry since these free radicals directly react with  $O_3$  and O (see Table 10). Recent studies of Johnston and Podolske (1978) suggest that these processes account for about 5–10 % of  $O_3$  destruction. Further, it was also found that the oxides of nitrogen<sup>12</sup> are involved in determining the stratospheric ozone budget in the following way (Crutzen, 1971):



If the effect of these reactions is included the decreases of the ozone and atomic oxygen concentrations are proportional to the  $NO_x$  concentration. Theoretical considerations also show that the effect of  $NO_x$  is particularly important in the stratosphere below 40 km. It is believed at present (Johnston and Podolske, 1978) that about 60 % of ozone molecules are removed by these processes (the corresponding figure for the “classical” removal is only 10 %). In the mid and lower stratosphere the equilibrium ozone concentration is approximately given by the following equation (Dütsch, 1973):

$$[O_3] \approx C [O_2]^2 \frac{f_1}{f_2 [NO_x]_{\text{mix}}} \quad [3.23]$$

<sup>12</sup> Their cycle in the atmosphere will be discussed in Section 3.5.

where  $C$  is a constant, while  $[NO_x]_{\text{mix}}$  is the mixing ratio of nitrogen oxides ( $f_1$  and  $f_2$  are as above). It can be seen that [3.23] differs from equation [3.17], in addition to  $NO_x$  mix, in the exponents of oxygen concentration and  $f_1/f_2$  ratio.

The indirect role of free radicals consists of decreasing the NO and  $NO_2$  levels. The end products of these reactions are nitric acid and nitrous acid vapours:



Thus, free radicals reduce the ozone loss due to the presence of nitrogen oxides.

It follows from this discussion that the activities of mankind can modify the natural photochemical processes in the stratosphere by adding nitrogen oxides and water vapour to stratospheric air. This possibility was first stressed by Crutzen (1971) and Johnston (1971). They stated that supersonic aircraft flying in the stratosphere could emit these species in a quantity sufficient to alter the chemical composition. Figure 9 gives numerical examples for these modifications (Dütsch,

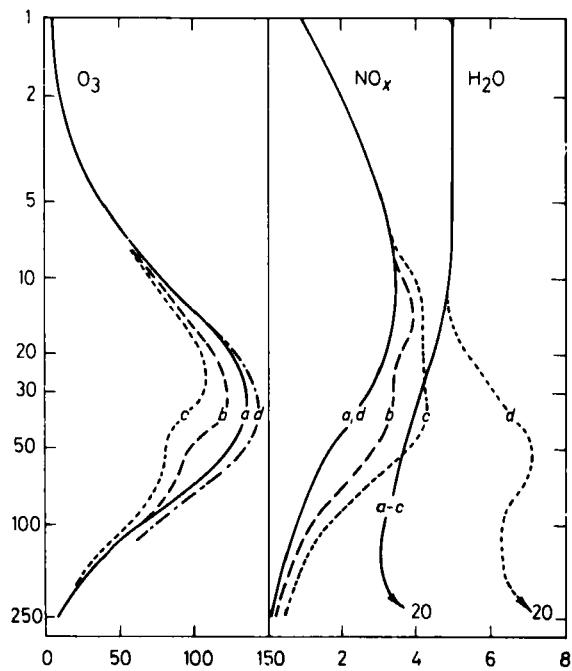


Fig. 9

The vertical profile of ozone expressed in nanobars as a function of atmospheric pressure (ordinate: millibar) for different  $NO_x$  (ppb) and  $H_2O$  (ppm) mixing ratios (Dütsch, 1973). (By courtesy of Birkhäuser Verlag and the author)

1973). On the left side of the figure the curve *a* represents the equilibrium ozone profile in case of "normal"  $\text{NO}_x$  vertical distribution (curve *a-d* in the middle) and  $\text{H}_2\text{O}$  concentrations (curve *a-c* on right). The ozone profiles *b* and *c* refer to a certain increase of the  $\text{NO}_x$  distribution (curves *b* and *c* for nitrogen oxides) without any variation in the  $\text{H}_2\text{O}$  profile. On the other hand the  $\text{O}_3$  vertical distribution labelled *d* gives the equilibrium ozone concentration as a function of the altitude (pressure) when  $\text{H}_2\text{O}$  level at different heights increases from *a-c* to *d* while  $\text{NO}_x$  concentrations remain "normal". One can see that the concentration increase of  $\text{NO}_x$  results in a rather significant decrease in the ozone concentration at some altitudes. Curves plotted in Fig. 9 also suggest that the effect of an increase in water content in the stratosphere is less important (see also Chapter 6) than that of nitrogen dioxides.

It thus appears from theory that nitrogen oxides may constitute a threat to ozone. However, more recent work has led to a total revision of the theory. While the details are more complex than it is possible to describe here, the key reactions are understandable. One possible sequence is given in Table 9. The result is that  $\text{NO}_x$  forms ozone by this sequence while destroying it by the previous one (Johnston and Podolske, 1978).

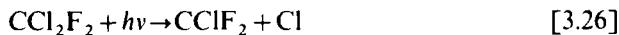
**Table 9**  
A possible reaction sequence in the stratosphere involving  $\text{NO}_x$  (Johnston and Podolske, 1978)

1	$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$
2	$\text{O} + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3$
3	$\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$
4	$\text{CH}_3 + \text{O}_2 \rightarrow \text{H}_2\text{CO} + \text{OH}$
5	$\text{H}_2\text{CO} + h\nu \rightarrow \text{H} + \text{HCO}$
6	$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$
7	$\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$
8	$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$
9	$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$
10	$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$
11	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$

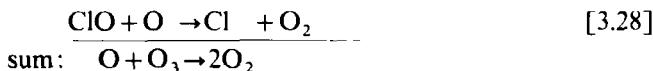
*Note:* These reactions are also of interest for tropospheric chemistry (see other parts of this book).

What actually happens is that  $\text{NO}_x$  destroys ozone at high altitude but forms it at low altitude. As a result, whether there is a net increase or decrease in total ozone depends on the altitude at which  $\text{NO}_x$  is injected. The transition from ozone formation to destruction appears to occur somewhat below 20 km, the precise level depending on details of the mathematical model (Johnston and Podolske, 1978). Thus the flight altitude of a supersonic transport is critical;  $\text{NO}_x$  from sources at the Earth's surface always seems to increase ozone (Turco *et al.*, 1978).

Some years ago Molina and Rowland (1974) demonstrated that chlorofluoromethanes (see Section 3.3) are photochemically destroyed in the stratosphere by solar radiation with wavelength shorter than  $0.23\text{ }\mu\text{m}$  to form chlorine atoms:

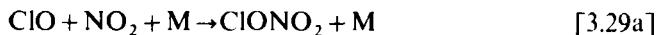


Thus, these substances, non-reactive under tropospheric conditions, give a species which reacts rather rapidly with  $\text{O}_3$  and the resultant  $\text{ClO}$  reacts with atomic oxygen to regenerate  $\text{Cl}$  (Rowland, 1976)<sup>13</sup>:



The halogenated hydrocarbons reaching the stratosphere through the tropopause by slow diffusion or through the tropopause gaps are mainly  $\text{CH}_3\text{Cl}$  (methyl chloride),  $\text{CCl}_4$  (carbon tetrachloride),  $\text{CFCl}_3$  (fluorotrichloromethane) and  $\text{CF}_2\text{Cl}_2$  (dichlorodifluoromethane). While  $\text{CH}_3\text{Cl}$  is predominantly of natural origin, the other compounds mentioned are man-made. Thus, we cannot exclude the possibility that man can modify the stratospheric photochemistry by the release of organochlorine species (see Chapter 6).

It is to be noted that the above concept was modified several times after the publication of the original paper of Molina and Rowland (1974). Thus it has been shown by Rowland, and his co-workers (see, e.g. Vuppurti, 1977) that the following reactions stabilize the ozone destruction by the  $\text{Cl}-\text{ClO}$  cycle in the mid-stratosphere:



Obviously the reactions [3.29a] and [3.29b] reduce substantially the ozone destruction due to anthropogenic F-11 and F-12 emissions. However, Howard and Evenson (1977) found that the rate of the chemical reaction



was much faster than previous indirect measurements had indicated. This finding again increased the value of the ozone reduction obtained by different model calculations<sup>14</sup> (see Chapter 6).

<sup>13</sup> For further details see e.g.: Rundel and Stolarski (1976).

<sup>14</sup> This is due to the fact that the reaction [3.30] removes  $\text{HO}_2$  which can react with  $\text{Cl}$ :  $\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$ . Furthermore by [3.30] OH radicals are formed. Thus the reaction  $\text{HCl} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{Cl}$  is accelerated.

It can be seen from reactions [3.27] and [3.28] that Cl and ClO are reformed by these processes. A temporary chemical sink for chlorine species is provided in the stratosphere by some reaction steps leading to the formation of hydrogen chloride. HCl can be removed from stratospheric air, like nitric acid, by slow downward mixing.

As in the case of nitrogen species, the value of theoretical predictions can be evaluated by comparing the measured stratospheric concentrations of halocarbons with calculated profiles. The results of stratospheric halocarbon analyses have been recently reviewed by Volz *et al.* (1978). Their data show that halocarbon levels decrease rather rapidly in the stratosphere with increasing altitude. The rate of this decrease is comparable to the theoretical value.

However, the experience of the change in direction of the effect of NO<sub>x</sub> must make us cautious in concluding that we understand the chemistry of the stratosphere. The recent past has included the discovery that one key reaction rate, supposedly well established by previous research, was in error by several orders of magnitude. Findings that do not agree with the models are coming to light. The field of stratospheric research, especially with regard to possible anthropogenic effects on essential trace gases, is certain to challenge researchers for a number of years to come.

#### **3.4.4 The distribution of total ozone. Vertical profile of the ozone concentration**

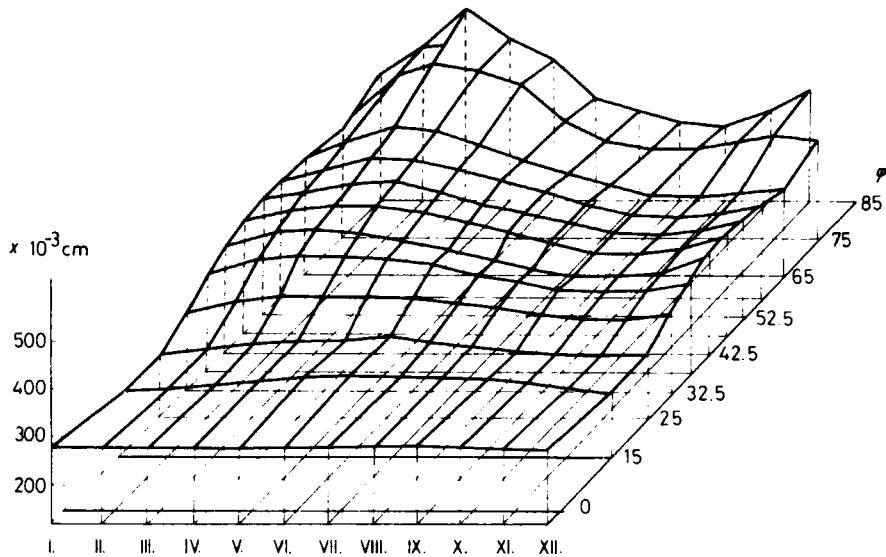
Generally, spectrophotometric methods are used to measure the atmospheric ozone concentration. By means of suitable optical devices<sup>15</sup> one detects the intensity of solar radiation in two narrow wavelength bands. In one of these bands ozone strongly absorbs the radiation while, in the other, O<sub>3</sub> has little absorption. The ozone content of the air can be calculated by comparing the two values measured. In this way the total ozone quantity in an air column is determined. This parameter expressed in cm is termed the total ozone. It represents the thickness of the layer which the same amount of ozone would form if it were separated from the air and held at normal temperature and pressure.

Figure 10 represents the average distribution of the total ozone (labelled x) as a function of geographical latitude and month of the year. Data refer to the Northern Hemisphere (Khrgian, 1969 and 1973). The curves in Fig. 10 were constructed on the basis of measurements carried out between 1957 and 1964. It can be seen that at tropical latitudes where changes in solar radiation are insignificant the variation of total ozone can be neglected. With increasing latitude the amplitude of variation increases and the maximum in late winter or early spring becomes more and more pronounced. The minimum can be found at mid-latitudes during autumn. It follows

<sup>15</sup> E.g. Dobson spectrophotometers.

from this distribution picture that the latitudinal gradient is greater in the early spring than during other seasons.

On the basis of photochemical considerations discussed in the last section we would expect a very different ozone distribution. For this reason it can be concluded that the pattern given by Fig. 10 can be explained only by the effect of atmospheric motions. This explanation is supported, together with other evidence by the fact that the results of individual measurements are also very much influenced by the atmospheric circulation.



**Fig. 10**  
Annual changes in the amount of total ozone ( $x$ ) in the Northern Hemisphere as a function of geographical latitude (Khrguijan, 1973). (By courtesy of Gidrometizdat)

Khrguijan's (1969) calculations based on data obtained in 1958 and 1959 show that on average  $x = 0.298$  cm in the Northern Hemisphere. The corresponding value for the Southern Hemisphere is equal to 0.307 cm. Based on these figures he calculated that the total  $O_3$  mass in the atmosphere is  $3360 \times 10^6$  t. Junge (1962) calculated the total ozone quantity in the atmospheric reservoir over the Northern Hemisphere on the basis of another data set. He found a value of  $1750 \times 10^6$  t. The two estimates are in good agreement.

The vertical profile of the ozone concentration can also be determined by spectrophotometric observations<sup>16</sup>. However, more accurate distributions are measured by ozone sondes lifted by balloons into the upper layers of the

<sup>16</sup> This procedure is called the "Umkehr" method (Götz, 1951).

atmosphere. These ozone sondes generally work on optical or chemical principles. The results obtained by chemical sondes (identifying ozone by iodometric methods) over the Northern Hemisphere have recently been compiled by Dütsch (1978). For levels above 10 mb and for the Southern Hemisphere he also used data gained by the Umkehr procedure. His average profiles for the Northern Hemisphere are reproduced in Fig. 11 as a function of latitude and season. One can see that, especially in winter and spring, there is a strong poleward gradient in the lower stratosphere. Above about 30 mb the poleward gradient becomes negative. Comparing Figs. 10 and 11 we can say that the late winter or early spring maximum in the value of total ozone observed over higher latitudes is caused by the huge quantity of ozone in the lower stratosphere at this time.

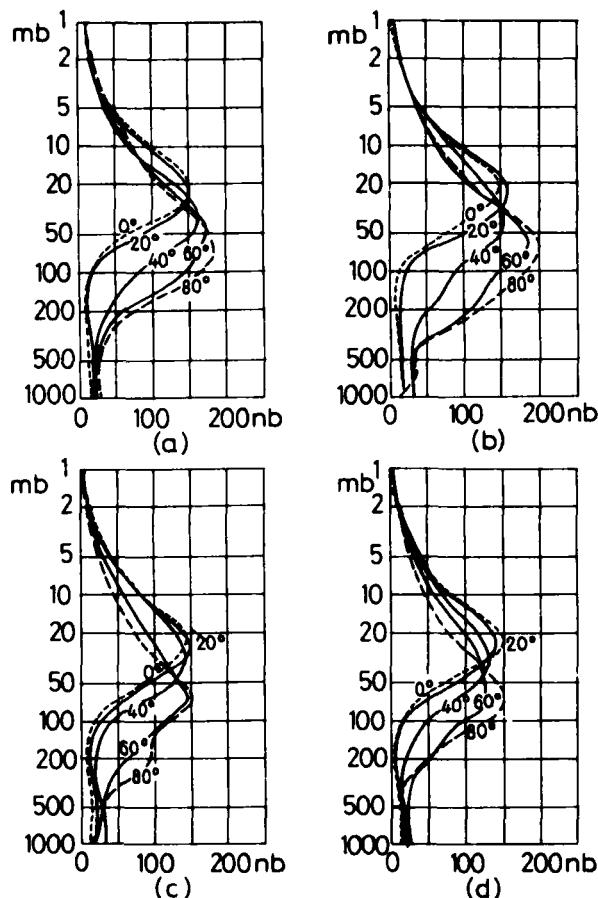


Fig. 11

Vertical ozone distribution at different latitudes in the Northern Hemisphere: (a) January; (b) April; (c) July; (d) October (Dütsch, 1978). (By courtesy of Birkhäuser Verlag and the author)

The distribution patterns shown in Fig. 11 can briefly be explained as follows. Stratospheric ozone formed by photochemical processes is transported in poleward direction by atmospheric motions. This circulation is particularly strong in winter and spring months when stratospheric air moves downward over polar regions. At the same time the lower stratosphere over the tropics is characterized by a slow updraft (Brewer, 1949). Thus, stratospheric dynamics lead to the accumulation of ozone rich air in the lower polar stratosphere. It should be recalled here that at this altitude  $O_3$  is a conservative property of the air. During the late spring and summer, especially, the stratospheric  $O_3$  reaches the troposphere first of all through the tropopause gaps. In the troposphere this species is removed from the air by various sinks, as this will be shown in the next section.

### 3.4.5 Tropospheric ozone

The ozone molecules formed in the stratosphere reach the troposphere where they move downward by turbulent diffusion. The stratospheric origin of  $O_3$  in the surface air is formally proved by Fig. 12. In this figure, on the basis of data gained by different workers, the mean tropospheric ozone concentration is plotted as a

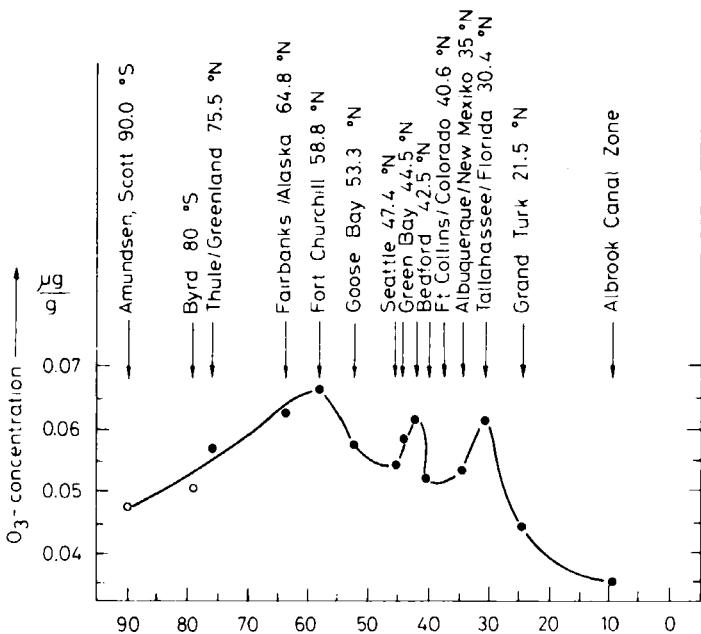


Fig. 12

The concentration of tropospheric ozone as a function of latitude (Pruchniewicz, 1973). (By courtesy of Birkhäuser Verlag and the author)

function of geographical latitude (Pruchniewicz, 1973). It can be seen that in the distribution three maximums are observed. The latitude of the three maximums might be related to the territory of frequent tropopause discontinuities. Thus, in the vicinity of  $30^{\circ}$  air masses of tropical origin usually meet the colder air of mid-latitudinal regions. At  $60^{\circ}$ , polar air is frequently in contact with warmer air of mid-latitudes. The contact of two air masses with different thermal structure produces a tropopause gap through which the mass exchange between the stratosphere and troposphere becomes very intensive. Furthermore, over latitudes of  $42^{\circ}$ – $45^{\circ}$  the same phenomenon can take place because of the tropopause fold between polar and tropical air masses. It follows from the observations represented by Fig. 12 that the most pronounced ozone maximum is found below the tropopause gap nearest to polar regions. This finding is explained by the fact that in the lower stratosphere the air with great ozone concentrations moves from the pole in the direction of the equator. One can also see that the tropospheric ozone concentration is very low over equatorial territories. This is not surprising, since tropical latitudes are characterized by a strong updraft in the troposphere.

The annual variation of the total ozone (see Fig. 10) can be approximated at the mid-latitudes by a sine curve. It should be noted that the tropospheric  $O_3$  level shows similar annual changes. The only difference is that maximum concentrations are observed in the troposphere 1–2 months later (see Fig. 13). On the basis of this time lag Junge (1962) estimated that the residence time of  $O_3$  in the troposphere is 2 months. In contrast the atmospheric residence time of  $O_3$  is calculated to be 1–2 years (Junge, 1963) that is, the lifetime of this species is very different in the stratospheric and tropospheric reservoirs.

According to the classical concept, the Earth's surface is a sink for stratospheric ozone. This is proved by the fact that a net downward ozone flux was measured in the lower tropospheric layers (e.g. Aldaz, 1969). By assuming a first-order process for ozone destruction and using the above residence time, Junge (1962) estimated that the ozone loss rate is  $780 \times 10^6 \text{ t yr}^{-1}$  at the surface. To calculate this rate he

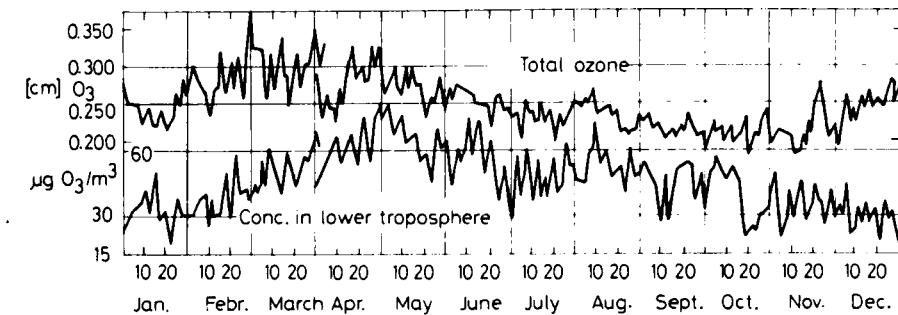


Fig. 13

Annual variation of total ozone and tropospheric ozone concentration in Arosa (Switzerland) between April, 1950 and March, 1951 (Junge, 1963). (By courtesy of Academic Press and the author)

also took into account the tropospheric ozone mass, which was found to be  $130 \times 10^6$  t. It should be noted that this latter figure is about one order of magnitude smaller than the global O<sub>3</sub> burden in the total atmospheric reservoir (see Subsection 3.4.4).

Table 10

Reaction chain leading to the destruction of ozone in the troposphere (Crutzen, 1974)

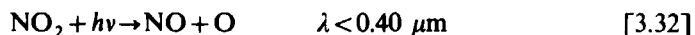
1	O <sub>3</sub> + hν → O* + O <sub>2</sub>	$\lambda \leq 0.32 \mu\text{m}$
2	O <sub>3</sub> + hν → O + O <sub>2</sub>	$0.45 < \lambda < 0.70 \mu\text{m}$
3	O + O <sub>2</sub> + M → O <sub>3</sub> + M	
4	O* + M → O + M	
5	O* + H <sub>2</sub> O → 2OH	
6	O <sub>3</sub> + OH → HO <sub>2</sub> + O <sub>2</sub>	
7	O <sub>3</sub> + HO <sub>2</sub> → OH + 2O <sub>2</sub>	
8	NO <sub>2</sub> + O <sub>3</sub> → NO <sub>3</sub> + O <sub>2</sub>	
9	NO + O <sub>3</sub> → NO <sub>2</sub> + O <sub>2</sub>	

Note: λ is the wavelength of radiation absorbed.

According to the above concept of ozone destruction, the troposphere is an inert medium concerning ozone chemistry. However, as Crutzen (1974) pointed out, there are several possible reaction steps for tropospheric O<sub>3</sub>. Thus ozone can be removed chemically from the air by transformation processes tabulated in Table 10. One reaction chain starts with the photolysis of O<sub>3</sub>, which is caused by radiations in the Hartley and Chappuis bands. The excited oxygen atoms, formed by R1, are partly transformed to ground state atomic oxygen by R4. However, they also react with water vapour to give OH radicals (R5). The sum of reactions 1–5 can be written in the following way:



Furthermore, O<sub>3</sub> combines with free radicals to form molecular oxygen and OH. An important consequence of these reduction processes is that OH radicals are formed which are very reactive species. Ozone is also removed from the troposphere by nitrogen oxides (R8 and R9). Under clean air conditions nitric oxide is of biological origin (see Section 3.5) while NO<sub>2</sub> comes from the oxidation of NO in the atmosphere. Fishman and Crutzen (1977) showed that the global reaction [3.31] could destroy about half of the stratospheric ozone before it reached the ground. However, we cannot rule out that an important amount of O<sub>3</sub> is also formed in the troposphere by the photolysis of NO<sub>2</sub>.



followed by reaction [3.9]. Thus, Fishman and Crutzen (1978) recently argue than over the Northern Hemisphere three times more O<sub>3</sub> is destroyed than over the

Southern Hemisphere due to the asymmetry in land area (over lands the downward ozone flux is much larger than over oceans, see Aldaz, 1969) and observed surface air ozone concentrations. Taking into account that this higher removal rate cannot be explained by differences in mass exchange between stratosphere and troposphere over the two hemispheres Fishman and Crutzen (1978) speculate that the higher ozone destruction rate over the Northern Hemisphere is probably balanced by tropospheric ozone formation<sup>17</sup> which might be very significant. Thus, they hypothesize that, in spite of the evidences of stratospheric origin discussed above, a part of O<sub>3</sub> in the troposphere is an *in situ* product. This tropospheric ozone formation is connected to the cycle of carbon monoxide, methane and other hydrocarbons since NO may be oxidized by HO<sub>2</sub> radicals formed during atmospheric reactions of some species (see, e.g. reaction [3.6]):



The concentration of CO (see Fig. 7), hydrocarbons and NO are higher in the air over the Northern Hemisphere than over the Southern Hemisphere, which leads to a higher tropospheric O<sub>3</sub> formation rate in these areas. Considering the complexity of the problem and our insufficient knowledge of some chemical processes we are not able at present to draw a final conclusion on the tropospheric ozone cycle. It is to be stressed, however, that there are several arguments in the literature (besides Fishman and Crutzen (1978) see, e.g. Ripperton *et al.*, 1971) supporting the hypothesis that tropospheric air also acts as an O<sub>3</sub> source.

The tropospheric processes discussed above are all homogeneous gas phase reactions. However, we cannot exclude the possibility that ozone is also removed from the air by chemical transformations taking place in liquid water (cloud and precipitation drops). Thus, Penkett (1972) and Penkett and Garland (1974) showed in laboratory experiments that ozone rather rapidly oxidized sulfur and nitrogen dioxides absorbed in artificial fog droplets. It was demonstrated that the SO<sub>2</sub> oxidation rate was proportional to the mixing ratio of O<sub>3</sub> in the air. If this latter is 0.05 ppm and the SO<sub>2</sub> concentration in the air is 0.1 ppm (this is too high for clean tropospheric air, Subsection 3.6.4), then in 1 minute 0.88 mg/l SO<sub>4</sub><sup>2-</sup> is formed in the fog water (temperature: 11 °C; pH = 5). This laboratory finding seems to be supported by atmospheric observations. In the annual variations of sulfate and nitrate concentrations of precipitation samples collected over different European territories (see Subsection 5.4.5) a spring maximum can be identified. This phenomenon may be explained (E. Mészáros, 1974a) by the effect of O<sub>3</sub> on SO<sub>2</sub> and NO<sub>2</sub> transformation. This follows from the fact (Fig. 13) that the concentration of tropospheric ozone has a maximum at this time of year.

<sup>17</sup> It has long been known that in locally polluted air ozone is formed in so-called photochemical smogs (see, e.g. Cadle, 1966). However, Fishman and Crutzen (1978) discuss the ozone formation in unpolluted tropospheric air.

The upper limit of the ozone reduced in this way can easily be estimated. According to Kellogg *et al.* (1972) the global yearly wet sulfate deposition is  $475 \times 10^6$  t. For the formation of such a sulfate mass,  $79 \times 10^6$  t of atomic oxygen is necessary, taking into account that sulfur dioxide transforms in water to  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$  ions (see Subsection 5.3.2). This atomic oxygen quantity is equal to  $237 \times 10^6$  t of  $\text{O}_3$  if we assume that each  $\text{SO}_2$  molecule absorbed is oxidized by one  $\text{O}_3$  molecule. This value is about one third of the estimate of Junge (1962) for total tropospheric ozone destruction. It follows from this high proportion that this process is probably a non-negligible  $\text{O}_3$  sink even if other species take part in  $\text{SO}_2$  oxidation, and if a part of the sulfate ions in atmospheric precipitation comes from sulfur containing aerosol particles.

### 3.5 Nitrogen compounds

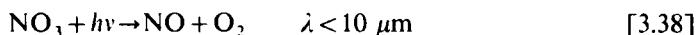
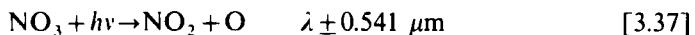
#### 3.5.1 Introduction

Several nitrogen oxides are known, including  $\text{N}_2\text{O}$  (nitrous oxide),  $\text{NO}$  (nitric oxide),  $\text{NO}_2$  (nitrogen oxide),  $\text{NO}_3$  (nitrogen trioxide),  $\text{N}_2\text{O}_3$  (dinitrogen trioxide),  $\text{N}_2\text{O}_4$  (dinitrogen tetroxide) and  $\text{N}_2\text{O}_5$  (dinitrogen pentoxyde). At normal temperatures and small partial pressures  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$  decompose according to the following equations (Junge, 1963):



For example, owing to this last decomposition, the  $\text{N}_2\text{O}_4$  concentration is  $10^{-6}$   $\mu\text{g}/\text{m}^3$ , if the nitrogen dioxide level is  $20 \mu\text{g}/\text{m}^3$ .

Furthermore under normal atmospheric conditions  $\text{NO}_3$  decomposes by photolysis or combines with  $\text{NO}$ . Thus Crutzen (1974) showed:



For these reasons, only nitrous oxide and  $\text{NO}_x$  ( $x = 1$  or 2) can be identified in practice in the air, if we disregard  $\text{HNO}_3$  formed by the interaction of nitrogen dioxide and water vapour (see later).

In addition to the above gases, ammonia ( $\text{NH}_3$ ) is also an important atmospheric trace substance. An essential characteristic of ammonia and  $\text{NO}_x$  is that these trace gases transform in the air into ammonium and nitrate-containing aerosol particles. These particles are of importance for the control of many atmospheric processes (see Chapter 4).

In the following, the atmospheric cycle of gaseous nitrous oxide will first be discussed. As we shall see, the pathway of this compound is related to the  $\text{NO}_x$  cycle. After the discussion of  $\text{N}_2\text{O}$ , the abundance of ammonia gas (ammonium particles) will briefly be presented; these can also be converted in the air to nitrogen oxides. Finally, the atmospheric cycle of  $\text{NO}_x$  will be outlined, including particulate nitrate.

### 3.5.2 Nitrous oxide

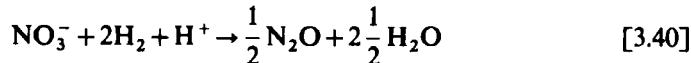
The presence of nitrous oxide in the atmosphere was first identified by optical methods (Adel, 1938). These early spectroscopic measurements gave a concentration interval of 0.25–0.60 ppm with a mean value of 0.40 ppm (Junge, 1963). Results of more recent gas chromatographic analyses show that the  $\text{N}_2\text{O}$  mixing ratio is near the lower limit of the range mentioned (Schütz *et al.*, 1970). These recent studies also demonstrate that the concentration of  $\text{N}_2\text{O}$  decreases only very slowly with increasing height in the troposphere. However, the decrease becomes significant in the stratosphere. This pattern is supported by the observations of Ehhalt *et al.* (1977), according to which the mixing ratio at an altitude of 35 km is one-tenth its value at the tropopause. The analyses of air samples collected in the vicinity of Mainz (Federal Republic of Germany) indicate no effects of industrial pollution on the level of this compound. This finding is confirmed by Soviet data showing no differences in  $\text{N}_2\text{O}$  content in air columns over Moscow and over Siberia (Achmedov *et al.*, 1978).

In the U.S.A.,  $\text{N}_2\text{O}$  was measured in Massachusetts by Goody (1969). His results suggested that  $\text{N}_2\text{O}$  concentration increased during 1967 and 1968. More recently Rasmussen and Pierotti (1978) have studied the  $\text{N}_2\text{O}$  level in the air over Antarctica, the Pacific Ocean and eastern Washington. Their data do not show hemispheric differences. The mean concentration has been found to be  $0.33 \pm 0.003$  ppm, which is larger than the average tropospheric  $\text{N}_2\text{O}$  level (0.26 ppm) reported by Schütz *et al.* (1970). However, Rasmussen and Pierotti's results also show a uniform mixing ratio in the troposphere. It is believed that this discrepancy is at least partly due to analytical problems. However, as Rasmussen and Pierotti (1978) point out, data gained in 1976 and 1977 at a rural station in eastern Washington do not exclude a small temporal increase of the concentration. The rate of this increase is estimated to be less than 2 %. Considering that the measurement precision is at best 1 %, it is obvious that further observations are needed in this field.

Schütz *et al.* (1970) estimated, on the basis of their measurements, a  $\text{N}_2\text{O}$  column concentration of  $3.30 \times 10^{-4} \text{ g cm}^{-2}$  in the troposphere. The corresponding stratospheric figure is  $0.625 \times 10^{-4} \text{ g cm}^{-2}$ . Taking into account the surface of the

Earth ( $5.1 \times 10^{18} \text{ cm}^2$ ), a rounded-off value of  $1700 \times 10^6 \text{ t}$  can be calculated for the whole of the troposphere, while the global atmospheric  $\text{N}_2\text{O}$  burden is equal to  $2000 \times 10^6 \text{ t}$ . The data of Rasmussen and Pierotti (1978) lead to a somewhat higher total quantity in the troposphere. However, on the basis of several recent vertical profile measurements, Ehhalt *et al.* (1977) give a global tropospheric nitrous oxide mass of  $1660 \times 10^6 \text{ t}$  which is in excellent agreement with Schütz's estimate.

It was shown by experiments carried out under laboratory conditions that nitrous oxide can be liberated from different soils since under some conditions bacterial denitrification processes lead to the formation of  $\text{N}_2\text{O}$  gas (Delwiche, 1978):

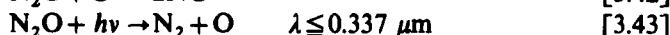


Schütz *et al.* (1970) estimate that the global strength of this source is  $50 \times 10^6 \text{ t yr}^{-1}$ , while Robinson and Robbins (1970) propose a value of  $592 \times 10^6 \text{ t yr}^{-1}$ . In a recent and careful study Söderlund and Svensson (1976) speculate that this source yields between  $25$  and  $110 \times 10^6 \text{ t yr}^{-1}$  which essentially confirms Schütz's estimate. Moreover, Hahn (1974) demonstrated that ocean water was supersaturated with  $\text{N}_2\text{O}$  as compared to atmospheric concentration. In another paper he hypothesizes that oceanic denitrification deliberates yearly  $(30\text{--}130) \times 10^6 \text{ t}$  of  $\text{N}_2\text{O}$  (see: Söderlund and Svensson, 1976). On the basis of the above data it can be proposed with caution that the global strength of the  $\text{N}_2\text{O}$  biological source is around  $100 \times 10^6 \text{ t yr}^{-1}$ . Taking into account the total global burden of  $2000 \times 10^6 \text{ t}$ , we can calculate a value of 20 years for the atmospheric residence time.

It has been mentioned in Section 1.1 that for atmospheric constituents the residence time linearly increases with the decrease of the variability of the concentration. Junge (1974) speculates that the product of the residence time and the relative standard deviation of the concentration is constant and equal to 0.14. By using this relation Rasmussen and Pierotti (1978) estimate, on the basis of their measurements, residence times of between 25 and 30 years, which is in acceptable agreement with the above figure.

It should be stressed that the activity of man also produce atmospheric  $\text{N}_2\text{O}$ . Several authors argue (e.g. Bremner and Blackmer, 1978) that  $\text{N}_2\text{O}$  can be released to the atmosphere through denitrification of fertilizer-derived nitrate and ammonia. This concept seems to be supported by the possibility that the  $\text{N}_2\text{O}$  mixing ratio is increasing in the troposphere. It is obvious, however, that much work remains to be done to clarify this problem.

Unfortunately, the sinks of the atmospheric nitrous oxide are very poorly understood. In any case we can accept the view that a part of  $\text{N}_2\text{O}$  is chemically removed from the air by the following reactions (Crutzen, 1973):



Robinson and Robbins (1970) think that these processes are effective mainly in the stratosphere. This concept is reasonable since  $O^*$  concentrations in the stratosphere are greater than in the troposphere. Furthermore, the intensity of UV radiations is also greater above the tropopause. According to Ehhalt *et al.* (1977) the flux of  $N_2O$  from the troposphere to the stratosphere is between  $6 \times 10^8$  and  $30 \times 10^8$  molecules  $cm^{-2} s^{-1}$  which are equivalent to  $(7-35) \times 10^6 t yr^{-1}$ . These values are based partly on the  $N_2O$  concentration gradient measured in the lowest three kilometers of the stratosphere and partly on the net transport coefficient of  $1 \times 10^3 cm^2 s^{-1}$  and  $5 \times 10^3 cm^2 s^{-1}$ . Taking into account the average tropospheric column concentration given by these authors ( $4.5 \times 10^{18}$  molecules  $cm^{-2}$ ) calculations of the tropospheric residence time range between 47 and 233 years. Since these values are high compared to the atmospheric lifetimes calculated above (20–30 years) we can conclude that other sink mechanisms must operate in the troposphere. The nature of this tropospheric sink is not yet clear. We cannot exclude the possibility (Schütz *et al.*, 1970) that chemical removal processes are also effective in the troposphere. Robinson and Robbins (1970) speculated that a large part of atmospheric  $N_2O$  returns to the pedosphere. It should be mentioned in this respect that Brice *et al.* (1977) demonstrated in England that  $N_2O$  concentration varied during the day inversely with the level of radon of soil origin. On the basis of this finding they postulated that soils provide a nitrous oxide sink with a strength sufficient to balance the sources mentioned.

An important consequence of reaction [3.42] is that  $N_2O$  plays a certain role in the chemistry of ozone formation. Although a small part of the nitric oxide formed in this way returns into the troposphere by slow diffusion (see later Fig. 15), the majority of NO molecules takes part in stratospheric chemistry as discussed in Subsection 3.4.3. This suggests that  $N_2O$  arising from the use of nitrogen containing fertilizers may pose a threat to the stratospheric  $O_3$  layer.

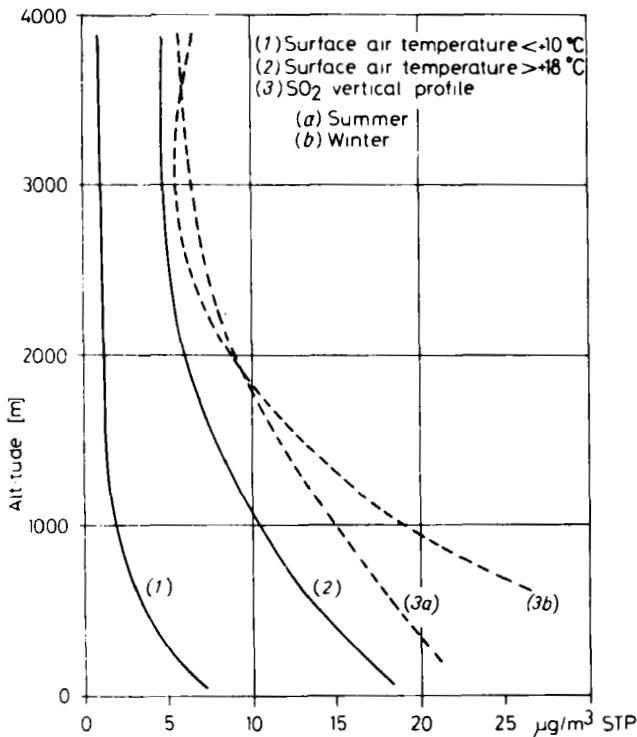
### 3.5.3 Ammonia

Ammonia was first identified in atmospheric precipitation (Junge, 1963).  $NH_3$  molecules (actually ammonium ions) in precipitation water are due to ammonia gas and ammonium containing aerosol particles in the air (see Chapter 5). Results of atmospheric measurements show that the ammonia concentration in surface air is between 4–20  $\mu g m^{-3}$  for unpolluted continental areas (Georgii, 1963). The corresponding range for the oceanic environment is 0.2–1.3.  $\mu g m^{-3}$  (Junge, 1963; Tsunogai and Ikeuchi, 1968). In tropical continental air  $NH_3$  concentrations are relatively high (Lodge *et al.*, 1974). Robinson and Robbins (1970) propose a value of 6 ppb ( $4.6 \mu g m^{-3}$  STP) for the mean atmospheric concentration, which seems too high on the basis of the above data. In the recent compilation of Söderlund and Svensson (1976) figures between 0.4 and 12 ppb ( $0.3-9.1 \mu g m^{-3}$  STP) can be found.

The first aircraft flights to measure  $NH_3$  concentration in the troposphere over continents were carried out by Georgii and Müller (1974), while Gravenhorst (1975)

published the first oceanic vertical profiles. The solid lines of Fig. 14 represent the mean results of Georgii and Müller obtained over Germany. These authors divided their data in two categories:

- (1) when the surface air temperature was higher than 18 °C (summer);
- (2) when the surface air temperature was below 10 °C (late fall, winter, early spring).



**Fig. 14**  
Vertical profile of NH<sub>3</sub> (solid lines) and SO<sub>2</sub> (dashed lines) concentrations according to Georgii and Müller (1974). (By courtesy of *Tellus*)

According to the observations of Georgii and Müller (1974) the following conclusions can be drawn concerning the vertical profile of NH<sub>3</sub>:

- (a) The profiles suggest that NH<sub>3</sub> sources are at the surface.
- (b) The concentration decreases with increasing height in the lower two kilometers of the troposphere, then it becomes nearly constant.
- (c) When the temperature is higher, concentrations are also greater, especially near the surface.

(d) The annual variation can be detected even at an altitude of 3000 m, where the SO<sub>2</sub> level is already independent of seasons. The vertical transport of NH<sub>3</sub> is influenced by thermal structure and convection.

(e) In the lowest 2 kilometers the SO<sub>2</sub> concentration is greater in the winter, while the NH<sub>3</sub> level has a maximum during summertime. Since a large part of the sulfur dioxide over continents is due to combustion processes (see later) this inverse relationship means that NH<sub>3</sub> is of biological origin.

On the basis of data obtained in the atmosphere Söderlund and Svensson (1976) propose that the atmospheric ammonia burden is  $0.9 \times 10^6$  t expressed in nitrogen. For the calculation of this figure the authors mentioned assumed characteristic mixing heights for different climatic regions. This height varied between 1 and 2 km.

A significant fraction of NH<sub>3</sub> is converted into ammonium containing aerosol particles in the atmosphere. These particles are generally composed of ammonium sulfate, the formation of which will be discussed later (Subsection 3.5.3). We only note here that the concentration of NH<sub>4</sub><sup>+</sup> in the lower troposphere is comparable to that of NH<sub>3</sub> gas. Even, in the upper troposphere the particulate concentration may be greater than the level of gaseous NH<sub>3</sub>. For this reason Söderlund and Svensson (1976) speculate that the atmospheric NH<sub>4</sub><sup>+</sup> burden is twice the global mass of NH<sub>3</sub> (both expressed as nitrogen).

There is a considerable body of evidences suggesting that the major part of the NH<sub>3</sub> is of biospheric origin. This biological source is provided by the decomposition of nitrogenous organic matters in aquatic and terrestrial ecosystems. Animal urea is also believed to be an important source of atmospheric NH<sub>3</sub> as proposed by Healy *et al.* (1970). The global strength of ammonia sources was estimated originally by Robinson and Robbins (1970). They gave, however, a very high figure ( $1160 \times 10^6$  t yr<sup>-1</sup>) as compared to more recent and more reliable estimates<sup>18</sup> (Galbally, 1975; Söderlund and Swensson, 1976; Dawson, 1977; Georgii and Lenhard, 1978). Thus Söderlund and Swensson's speculations led to a global emission of  $(113-244) \times 10^6$  t yr<sup>-1</sup>. Other workers give values of less than  $100 \times 10^6$  t yr<sup>-1</sup>; e.g. Dawson calculates a source intensity of  $47 \times 10^6$  t yr<sup>-1</sup>.

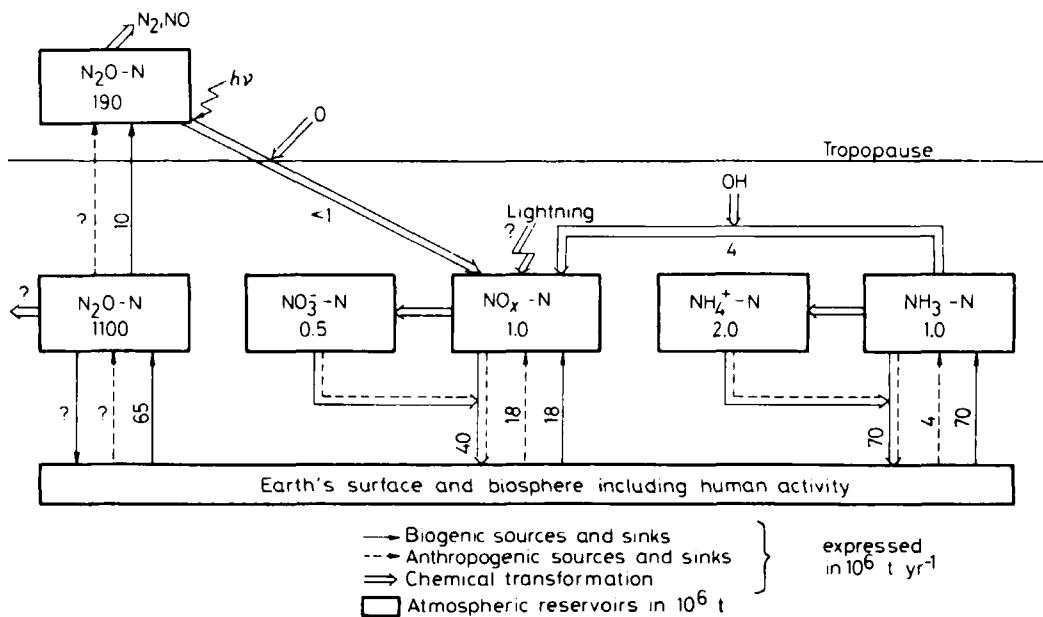
Combustion of coal was also suggested as a source of NH<sub>3</sub>-N. In the study of Söderlund and Svensson (1976) a figure of  $(4-12) \times 10^6$  t yr<sup>-1</sup> is proposed for the global strength of this anthropogenic source, which is in acceptable agreement with earlier estimate of  $3.5 \times 10^6$  t yr<sup>-1</sup> given by Robinson and Robbins (1970).

A large part of the NH<sub>3</sub>, and of particulate ammonium formed from the gaseous phase, is washed out of the air by cloud and precipitation elements. The size of this sink term can be estimated on the basis of the results of chemical analyses of atmospheric precipitation (e.g. Eriksson, 1952). Söderlund and Svensson (1976) propose global values between  $38 \times 10^6$  and  $85 \times 10^6$  t yr<sup>-1</sup> for wet deposition. The

<sup>18</sup> This is due to the fact that Robinson and Robbins (1970) wanted to balance a very high unrealistic dry deposition rate ( $\sim 900 \times 10^6$  t yr<sup>-1</sup>).

greater amount of this quantity is deposited on land:  $(30-60) \times 10^6 \text{ t yr}^{-1}$  (expressed as nitrogen). Another fraction of  $\text{NH}_3$  and ammonium particles is removed from the air by dry deposition. Many authors assume in calculating this sink strength that the dry deposition velocity<sup>19</sup> is equal to the observed value for sulfur dioxide ( $\sim 1 \text{ cm s}^{-1}$ ) in the atmosphere. It is also argued (see Subsection 5.2.1) that the corresponding value for ammonium particles is much smaller. Thus Söderlund and Svensson (1976) computed by this questionable procedure dry deposition values between  $19 \times 10^6$  and  $53 \times 10^6 \text{ t yr}^{-1}$  for ammonia-nitrogen over the terrestrial system. For oceanic areas the corresponding figure is  $(6-17) \times 10^6 \text{ t yr}^{-1}$ . In contrast to this estimate Dawson (1977) speculates that the dry deposition of ammonia can be neglected. The author of this book believes that lower limit given by Söderlund and Svensson is more realistic than the upper one.

It was also proposed in the literature (e.g. Crutzen, 1974) that a non-negligible part of  $\text{NH}_3$  is converted in the troposphere into nitrogen oxides. The first step of this conversion is the reaction between ammonia and OH free radicals:



**Fig. 15**  
Atmospheric pathways of nitrogen compounds. Note:  $\text{NH}_3$  released from domestic animal urea is considered biogenic and not pollution

<sup>19</sup> Deposition velocity is defined by the ratio of the deposition (quantity deposited per unit time on a unit surface) to the concentration (see Subsection 5.2.1).

which is followed by the  $\text{NH}_2 \rightarrow \text{NO}_x$  transformation. Crutzen argues that this process is a very important source of nitrogen oxides, while Söderlund and Svensson's work indicates values between  $3 \times 10^6$  and  $8 \times 10^6 \text{ t yr}^{-1}$ .

On the right-hand side of Fig. 15 the atmospheric pathways of  $\text{NH}_3$  are plotted. Values of different terms are based on the references mentioned. In the figure,  $\text{NH}_3$  and  $\text{NH}_4^+$  burdens are also given. All numbers are expressed in nitrogen equivalents. In the total deposition value, a dry deposition of  $10 \times 10^6 \text{ t yr}^{-1}$  is postulated. It should be noted that the accuracy of the values is not better than a factor of 2 or 3. It follows from these data that the residence time of  $\text{NH}_3$  in the atmosphere is around 5 days.

### 3.5.4 Nitrogen oxides

During denitrification processes in acidic soil  $\text{NO}$  is produced by chemical destruction of nitrite. Under aerobic conditions or in the air,  $\text{NO}$  is oxidized to form  $\text{NO}_2$ <sup>20</sup>:



If the  $\text{O}_2$  partial pressure is large, the equilibrium  $\text{NO}$  concentration is small. Thus, if the  $\text{NO}_2$  concentration in the air is  $10 \mu\text{g m}^{-3}$  the  $\text{NO}$  level is theoretically equal to  $10^{-5} \mu\text{g m}^{-3}$  (Junge, 1963). For this reason the majority of earlier nitrogen oxide analyses carried out in clean tropospheric air aimed to determine the  $\text{NO}_2$  concentration. However, further studies, done by oxidizing  $\text{NO}$  to  $\text{NO}_2$  before sampling, showed that in background air the concentration of  $\text{NO}$  is comparable to the  $\text{NO}_2$  level (Lodge and Pate, 1966; Lodge *et al.*, 1974). This means that  $\text{NO}$  gas is released from the soil and that equilibrium is not attained in the time available.

On the basis of the results of different authors Robinson and Robbins (1970) estimated concentrations of 2 ppb ( $\text{NO}$ ) and 4 ppb ( $\text{NO}_2$ ) for continental areas between  $65^\circ \text{N}$  and  $65^\circ \text{S}$ , while for other territories they proposed 0.2 ppb and 0.5 ppb, respectively. On the other hand, Söderlund and Svensson (1976) speculate that the sum of  $\text{NO}$  and  $\text{NO}_2$  concentrations in clean tropospheric air, except temperate regions, is less than 1 ppb. Over temperate regions the  $\text{NO}_x$  level is about 4 ppb. The above  $\text{NO}_x$  levels for remote areas were confirmed recently by Cox (1977), who measured mean concentration of 0.12 ppb  $\text{NO}$  and 0.34 ppb  $\text{NO}_2$  mean concentrations on the Irish West Coast.

Söderlund and Svensson (1976) calculate for the global  $\text{NO}_x-\text{N}$  burden values between  $1 \times 10^6$  and  $4 \times 10^6 \text{ t}$  by using the above tropospheric concentrations.

As mentioned earlier, a large portion of  $\text{NO}_x$  is of biological origin. The global strength of this source was calculated to be  $(21-89) \times 10^6 \text{ t yr}^{-1}$  by balancing source and sink terms (Söderlund and Svensson, 1976). Another  $\text{NO}_x$  source at the Earth's surface is provided by man's activities. This source mainly arises from coal, gasoline

<sup>20</sup> Other possible routes of oxidation are reactions [3.21] and [3.33].

and oil combustion.<sup>21</sup> Robinson and Robbins (1970) estimate that the anthropogenic NO<sub>x</sub>—N production is  $16 \times 10^6$  t yr<sup>-1</sup>. This figure is essentially confirmed by the more recent speculation of Söderlund and Svensson (1976) who give for this source strength a value of  $19 \times 10^6$  t yr<sup>-1</sup>.

There are different opinions in the literature concerning the role of lightning in NO<sub>x</sub> production. According to earlier estimates (Junge, 1963; Georgii, 1963) the effect of this process can be neglected. However, some more recent papers (e.g. Noxon, 1976; Chameides *et al.*, 1977) indicate that this source is at least comparable to the NO<sub>x</sub> source intensities discussed above. It is obvious from this discrepancy that much more research is needed in the future to establish this production rate in a reliable way.

It is well documented that NO<sub>2</sub> can be transformed in the air to particulate nitrate. For this reason the nitrate content of aerosol particles in clear air is around  $0.1 \mu\text{g m}^{-3}$  (Söderlund and Svensson, 1976). This gas-to-particle conversion process is initiated either by reaction [3.24] or by the gas phase hydrolysis of nitrogen dioxide:



The nitric acid vapour produced in this way condenses together with H<sub>2</sub>O molecules to form acid solution droplets which can be neutralized by some cations. Theory shows (Kiang *et al.*, 1973) that the homogeneous condensation of HNO<sub>3</sub> vapour is rather improbable under normal atmospheric conditions. This means that the condensation takes place mainly on existing aerosol particles which serve as nuclei for the phase transition.

An interesting version of this process is the interaction of nitric acid vapour and sea salt particles (Cadle, 1973). These particles are composed mainly of sodium chloride, so that sodium nitrate is formed as a result with the liberation of gaseous hydrochloric acid. It is very probable that the high nitrate content of seaside atmospheres may be explained by this interaction (Junge, 1963).

It is reasonable to expect that nitric acid vapour should react with atmospheric NH<sub>3</sub> to form an aerosol of ammonium nitrate, NH<sub>4</sub>NO<sub>3</sub>. However, Stelson *et al.* (1979) calculate from the available thermodynamic data that solid NH<sub>4</sub>NO<sub>3</sub> should be in equilibrium with NH<sub>3</sub> and HNO<sub>3</sub> such that, at 20 °C,  $11 \mu\text{g m}^{-3}$  of an equimolar mixture of the two gases would remain in the atmosphere. At 30 °C the figure is  $38 \mu\text{g m}^{-3}$ . Since these figures are of the order of magnitude of concentrations in only slightly polluted air, NH<sub>4</sub>NO<sub>3</sub> can form during cold nights and decompose during the day, and it can be collected on filters and lost when the filter samples are brought into a warm laboratory. This finding raises questions about the adequacy of our understanding of atmospheric particulate nitrate.

<sup>21</sup> It should be mentioned here that, due to this pollution source, the NO<sub>2</sub> level in polluted cities can reach 100 ppb and under these conditions nitrogen dioxide can stimulate a chain reaction by photolysis (see [3.32]) leading to smog formation (e.g. Cadle, 1966; Haagen-Smit and Wayne 1976).

It should be mentioned that  $\text{NO}_2$  can take part in many other chemical conversions leading to the formation of particulate matter. However, these reactions were studied mainly in polluted air (e.g. Cadle, 1966 and 1973). Thus, application of the results obtained to clean air would be questionable. Nevertheless, it is possible that under background conditions terpenoid hydrocarbons (see Subsection 3.3.3.) play an important part in these transformations. Furthermore, as we shall see in the next section, the presence of  $\text{NO}_2$  can also be important in the oxidation of sulfur dioxide.

On the basis of the results of nitrate measurements in the atmosphere Robinson and Robbins (1970) calculated that the total atmospheric nitrate mass is  $0.9 \times 10^6 \text{ t}$ , which is comparable to the nitrate-nitrogen burden ( $0.5 \times 10^6 \text{ t}$ ) given by Söderlund and Svensson (1976).

It is believed that a large proportion of both  $\text{NO}_x$  and nitrate-containing particles is removed from the troposphere by wet deposition. Söderlund and Svensson (1976) propose a global wet deposition between  $18 \times 10^6 \text{ t yr}^{-1}$  and  $46 \times 10^6 \text{ t yr}^{-1}$  (expressed as nitrogen) on the basis of nitrate concentration analyses in precipitation. The corresponding value used by Robinson and Robbins (1970) is  $70 \times 10^6 \text{ t}$  which arose from a wet deposition calculation of Eriksson (1952).

Another possible sink mechanism is the dry deposition. Robinson and Robbins (1970) assumed in their study a value of  $1 \text{ cm s}^{-1}$  for  $\text{NO}_2$  dry deposition velocity. This value was based on experimental data obtained over alfalfa and oats by Tingey (see Robinson and Robbins (1970)). Using this figure they calculated a very high  $\text{NO}_2$  dry deposition. In contrast, Söderlund and Svensson (1976) applied a dry deposition velocity of  $0.3\text{--}0.8 \text{ cm s}^{-1}$  for  $\text{NO}_x$ . Taking into account their model concentrations mentioned above, their calculation resulted in a dry deposition term of  $(25\text{--}70) \times 10^6 \text{ t yr}^{-1}$ . Although the above deposition velocity range is in good agreement with the result of laboratory studies made by Judeikis and Wren (1978) with selected soil and cement surface, the laboratory model experiments of Bötger (1978) indicate an order of magnitude smaller  $\text{NO}_2$  deposition velocities than the above values<sup>22</sup> (see Chapter 5). Thus, the deposition values given by Söderlund and Svensson would have to be decreased by a factor of ten. Furthermore, the dry deposition of nitrate particles was found to be insignificant due to the small nitrate concentration in the air and to the small deposition velocity of aerosol particles. The Swedish workers mentioned give a nitrate-nitrogen dry deposition range of  $0.3 \times 10^6\text{--}3 \times 10^6 \text{ t yr}^{-1}$ .

On the basis of the foregoing discussion a schematic atmospheric  $\text{NO}_x\text{--N}$  and  $\text{NO}_3\text{--N}$  cycle has been constructed as shown in Fig. 15. It has been postulated that the sum of dry deposition of gases ( $4 \times 10^6 \text{ t yr}^{-1}$ ) and particles ( $2 \times 10^6 \text{ t yr}^{-1}$ ) is only  $6 \times 10^6 \text{ t yr}^{-1}$ . For the wet deposition a global value of  $34 \times 10^6 \text{ t yr}^{-1}$  has been accepted, the midpoint of the range proposed by Söderlund and Svensson (1976). The strength of biological sources has been calculated by balancing the source and

<sup>22</sup> According to Bötger's experiments the dry deposition velocity of NO is even smaller.

sink terms<sup>23</sup>. One can see that biological source intensity received is equal to the NO<sub>x</sub> production rate by pollution sources. It should be mentioned that our figure for global natural source intensity essentially agrees with the emission rate calculated by Galbally (1975) by using the 50 % concentration difference between altitudes of 1 m and 2 km. In Fig. 15 no value for the NO<sub>x</sub> formation by lightning is given due to the uncertainties mentioned above. This does not exclude the possibility, however, that this term might be significant in the atmospheric pathways of nitrogen oxides. It goes without saying that the numbers represented have a considerable uncertainty which is not less than a factor of 2–3. It follows from the data given that the residence time of nitrogen oxide molecules in the atmosphere is about 9 days.

Finally, for the sake of completeness, the cycle of N<sub>2</sub>O is also plotted in Fig. 15. The values of the budget terms in this case are also very uncertain. However, the global N<sub>2</sub>O burden is rather well established by atmospheric measurements (see Subsection 3.5.2). We have to emphasize here that the quantity of NO<sub>x</sub> molecules of surface origin reaching the stratosphere is relatively small as compared to the mass of nitrous oxide, owing to the relative atmospheric concentrations of these species.

## 3.6 Sulfur compounds

### 3.6.1 Introduction

Sulfur compounds are very important atmospheric constituents, since in clean tropospheric air as well as in the stratosphere the majority of aerosol particles are composed of ammonium sulfate or sulfuric acid (see Chapter 4). This finding is particularly interesting since with the exception of sea salt sulfur, a predominant portion of sulfur emission is in gaseous form.

The study of the atmospheric sulfur cycle is a rapidly expanding field because human activity provides an important sulfur dioxide source. In the atmosphere SO<sub>2</sub> is converted to sulfate containing aerosol particles which can modify the radiation balance of the Earth-atmosphere system, the optical properties and the precipitation forming ability<sup>24</sup> of the air.

### 3.6.2 Origin of atmospheric sulfur

Sulfur compounds in the atmosphere are provided by the decomposition of organic matter, combustion of fossil fuels, production of sea salt particles and volcanic activity. We can rather well quantify the strength of these sources, except the intensity of biological sulfur production.

<sup>23</sup> If the role of lightning in NO<sub>x</sub> production is significant the value of the biological source strength is less.

<sup>24</sup> By acting as condensation nuclei. It is well documented (e.g. Twomey, 1971) that atmospheric condensation nuclei consist mainly of ammonium sulfate.

The emission rate of anthropogenic sulfur dioxide (95 % of sulfur due to pollution sources is SO<sub>2</sub>) was estimated by Katz (see Kellogg *et al.* 1972) to be  $77 \times 10^6$  t yr<sup>-1</sup> in 1943. According to more recent estimates (Friend, 1973)  $130 \times 10^6$  t of anthropogenic SO<sub>2</sub> is released into the atmosphere annually. Comparison of the two figures makes it evident that during about two or three decades the emission increased by a factor of 1.7. This huge quantity of SO<sub>2</sub> is mainly due to combustion of fossil fuels containing sulfur. However, the effect of some industrial processes has also to be taken into consideration (Table 11). It is believed that the increase of SO<sub>2</sub> emission will continue in the future. Kellogg *et al.* (1972) speculate that the source strength will be  $300 \times 10^6$  t yr<sup>-1</sup> in 2000.

**Table 11**  
Strength of different global anthropogenic SO<sub>2</sub> sources  
according to Friend (1973)

Source	Emission rate [ $10^6$ t yr <sup>-1</sup> ]	Relative emission [%]
Coal-burning	45.4	70
Oil-burning	5.5	8.4
Industrial (smelting and petroleum refining)	13.6	21
Transportation	0.4	0.6
Total	64.9	100

Note. The emissions are expressed as sulfur

The next important sulfur source is the biosphere. A large part of gaseous sulfur of biological origin is hydrogen sulfide. This gas is liberated into the air because of the reduction of sulfate in anaerobic swamps, muds and eutrophic waters by microorganisms (Jaeschke *et al.*, 1978). This H<sub>2</sub>S may escape into the air when the anaerobic zone is close to the atmosphere. It is also shown by measurements (Rasmussen, 1974) that the release of dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) is also possible due to the activity of bacteria and fresh water green and blue-green algae. Some other reduced sulfur species (e.g. carbon disulfide, see Lovelock, 1974) were also proposed to explain the biological part of the sulfur cycle. Unfortunately, the global flux produced by micro-biota is not well known. Friend (1973) gives a value of  $62 \times 10^6$  t yr<sup>-1</sup> for continental biospheric production rate. He obtains this figure by balancing the pedospheric sulfur budget. He calculates the global oceanic flux by difference, requiring the atmosphere to be balanced. By using this procedure Friend's calculation results in an oceanic production rate of  $51 \times 10^6$  t yr<sup>-1</sup>. Thus, the total biological release is  $106 \times 10^6$  t yr<sup>-1</sup>, calculated as sulfur.

The main problem with the calculation of biological source intensity by difference is the fact that the figure obtained varies as a function of other terms in budget

equation. Thus, Granat *et al.* (1976) calculated only  $32 \times 10^6 \text{ t yr}^{-1}$  (expressed in sulfur) for the natural source strength since they used smaller deposition values than Friend. It follows from this latter figure that, in contrast to Friend's conclusion, the activity of man now produces more atmospheric gaseous sulfur than natural sources do. Considering the importance of this question it is obvious that an acceptable determination of global biological sulfur release, independent of the budget, would be of crucial interest.

The third sulfur source is provided by the formation of sea salt particles at the surface of the ocean (see Section 4.2). According to Eriksson (1960) the sulfur mass in sea salt particles produced yearly is  $44 \times 10^6 \text{ t}$ . This figure seems to be rather well established, and for this reason, we shall not discuss it in more detail.

Finally, we must quantify the annual production rate due to volcanos. According to Friend (1973), volcanic activity produces  $0.8 \text{ km}^3$  of magma per year, which is equivalent to a mass of  $2200 \times 10^6 \text{ t yr}^{-1}$ . The composition of gases released by volcanic eruptions is roughly the following: 95%  $\text{H}_2\text{O}$ , 4%  $\text{CO}_2$  and 1%  $\text{SO}_2$ . Since the mass of  $\text{H}_2\text{O}$  vapour is 5% of that of the magma emitted, a  $2 \times 10^6 \text{ t yr}^{-1}$  global volcanic sulfur emission can be calculated. This figure is in good agreement with the estimate of other workers (Kellogg *et al.* 1972; Granat *et al.* 1976). We can conclude that sulfur production by volcanos is quantitatively small as compared to the intensity of other sources. We must emphasize, however, that a significant fraction of this sulfur quantity, emitted into the atmosphere in a very short time<sup>25</sup>, can reach the stratosphere to contribute to the stratospheric sulfate layer (see Section 4.3). This means that we cannot neglect volcanic activity when studying the pathways of sulfur in the atmosphere.

Table 12 lists the strength of different sulfur sources as proposed by Friend (1973) and Granat *et al.* (1976). One can see from Friend's data that around 1/3 of atmospheric sulfur is provided by man's activity. Taking into account that

**Table 12**  
Absolute and relative intensities of different sulfur sources according  
to Friend (1973) and Granat *et al.* (1976)

Source	Friend		Granat	
	[ $10^6 \text{ t yr}^{-1}$ ]	[% of total]	[ $10^6 \text{ t yr}^{-1}$ ]	[% of total]
Anthropogenic	65	30	65	45
Biological (cont.)	58	27	5	4
Biological (oceanic)	48	22	27	19
Sea-salt	44	20	44	30
Volcanic activity	2	1	3	2
Total	217	100	144	100

<sup>25</sup> According to a recent study of Hauguet *et al.* (1977) the  $\text{SO}_2$  production rate during the eruption of Etna in June, 1973 was found to be  $3.7 \times 10^3 \text{ t day}^{-1}$ .

according to Granat *et al.* (1976) this proportion is even greater (approximately 50 %) we conclude that man contributes substantially to the atmospheric inventory of sulfur compounds.

### 3.6.3 Transformation of sulfur compounds in the atmosphere

The sulfur compounds, except the sulfate of sea salt particles, are released into the atmosphere in gaseous form. In spite of this fact the majority of atmospheric sulfur in clean air is found in particulate matter as sulfate (see later). Thus, the aim of studies on transformations of sulfur compounds is to determine the nature and rate of oxidation processes leading to sulfate formation.

Unfortunately, our knowledge about the  $\text{H}_2\text{S} \rightarrow \text{SO}_2$  transformation is very scanty, although it is speculated that this reaction is the only important sink for hydrogen sulfide of biological origin. According to Kellogg *et al.* (1972)  $\text{SO}_2$  forms by the interaction of  $\text{H}_2\text{S}$  and atomic oxygen or ozone. These authors believed that the oxidation takes place on the surface of aerosol particles as well as in cloud and precipitation water since the rate of gas phase reactions was found to be insignificant. The reaction with ozone is as follows:



However, it was demonstrated by Penkett (1972) that the oxidation of  $\text{H}_2\text{S}$  in solutions is a very slow process.  $\text{H}_2\text{S}$  can also react with atomic oxygen:



which is followed by a reaction chain resulting in the formation of  $\text{SO}_2$ ,  $\text{SO}_3$  and sulfuric acid vapour. It is very doubtful, however, whether reaction [3.48] is important in the troposphere where the level of atomic oxygen is low.

According to the laboratory experiments of Cox and Sandalls (1974) OH radicals play an important role in the oxidation of  $\text{H}_2\text{S}$ . They stated that the oxidation of  $\text{H}_2\text{S}$  is initiated by the gas phase reaction



The HS radical formed in this way reacts with molecular oxygen:



The rate constant of [3.49] is reported as  $3.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Jaeschke *et al.* (1978) have shown the importance of this process in the following indirect way. They measured the vertical concentration gradient of  $\text{H}_2\text{S}$  and calculated the vertical flux by using the gradient method (see Section 5.1). They have

found, on the basis of the decrease of  $\text{H}_2\text{S}$  flux with increasing height, that the mean removal coefficient of hydrogen sulfide is  $2.27 \times 10^{-5} \text{ s}^{-1}$ . This coefficient is equal to the product of the reaction rate and OH concentration ( $k [\text{OH}]$ ), since

$$-\frac{d[\text{H}_2\text{S}]}{dt} = k[\text{OH}][\text{H}_2\text{S}] \quad [3.51]$$

This permits calculation of the steady-state OH concentration in the air layer studied (150–1000 m). Since Jaeschke *et al.* (1978) have calculated values comparable to measured OH levels (Perner *et al.*, 1976), it can be concluded that reaction [3.49] accounts for most of the observed  $\text{H}_2\text{S}$  transformation. From the mean removal coefficient, Jaeschke *et al.* (1978) were also able to determine the mean lifetime of  $\text{H}_2\text{S}$  as about 12 hr.

Cox and Sandalls (1974) also studied during their laboratory work the oxidation of DMS by using ppm concentrations (which are much higher than possible atmospheric levels). They found that photochemically generated free radicals such as O and OH reacted rapidly with DMS. An important finding was the absence of  $\text{SO}_2$  during DMS oxidation. However, the appearance of aerosol particles was evident in the system. Cox and Sandalls stated that, due to this process, the residence time of DMS in the atmosphere is only a few hours.

Recently, Paugam (1978) published an interesting atmospheric observation which may be related to the oxidation of DMS. He observed a substantial photolytic aerosol formation on the coast of Brittany (France) during low tide. Paugam believes that this phenomenon is due to the photooxidation of DMS emitted by algae. He also mentioned, on the basis of  $\text{SO}_2$  measurement, that sulfur dioxide does not play an important part in the gas-to-particle conversion.

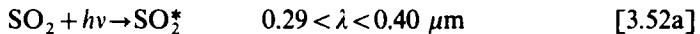
Our knowledge of the oxidation of sulfur dioxide is more complete because this transformation was studied in more detail, owing to its importance for local air pollution. It is generally accepted that sulfate can be formed from  $\text{SO}_2$  in the following ways:

- (a) Sulfuric acid vapour is an end product of homogenous gas phase reactions, including photochemical and thermal steps. Sulfuric acid droplets are formed by vapour condensation.
- (b)  $\text{SO}_2$  is oxidized in fog- and cloud drops after its absorption. Sulfate particles are formed by the evaporation of drops.<sup>26</sup>
- (c)  $\text{SO}_2$  is oxidized on the surface of existing aerosol particles.

The study of homogenous gaseous reactions leading to sulfate formation started at the beginning of the fifties. The results of early laboratory works are reviewed by

<sup>26</sup> If the cloud evaporates. In case of precipitation formation the  $\text{SO}_4^{2-}$  formed is removed from the air by wet deposition (see Chapter 5).

Leighton (1961). A general feature of these studies was the fact that authors assumed direct photooxidation of  $\text{SO}_2$  gas. Thus, Gerhard and Johnstone (1955) speculated that the processes could be summarized by the following three reactions:



Their experiments showed that the  $\text{SO}_2$  loss is a first-order process:

$$-\frac{d[\text{SO}_2]}{dt} = k[\text{SO}_2] = k_a \Phi[\text{SO}_2] \quad [3.54]$$

Gerhard and Johnstone (1955) demonstrated that  $k$  was  $10^{-3} \text{ hr}^{-1}$  when they used solar radiation to illuminate the reaction chamber containing only purified air,  $\text{SO}_2$  and  $\text{H}_2\text{O}$ . In a more recent paper, Cox (1972) published  $\Phi$  values ( $\Phi$  is the quantum yield, see Subsection 3.4.2) between  $1 \times 10^{-3}$  and  $5 \times 10^{-3}$ , which implies that  $k_a$  in reaction [3.54] should be about  $1 \text{ hr}^{-1}$ .

Further studies pointed out that the homogeneous oxidation of  $\text{SO}_2$  becomes faster when the air also contains nitrogen dioxide and ozone. Thus,  $\text{NO}_2$  absorbs solar radiation in the visible spectrum and dissociates (see [3.32]) to give atomic oxygen. Oxygen atoms produce ozone or react with  $\text{SO}_2$  to form sulfur trioxide (Cadle and Powers, 1966):

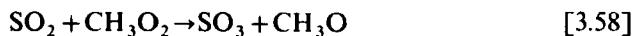


This oxidation is of third order and its reaction rate is independent of the temperature. Using reaction rate values measured under laboratory conditions and the concentrations of M and O for different levels of the atmosphere, Cadle and Powers calculated that this process can be significant only above 10 km if the  $\text{SO}_2$  concentration is  $1 \mu\text{g m}^{-3}$  STP. The residence time of sulfur dioxide molecules is estimated to be  $10^3 \text{ hr}$  at an altitude of 10 km, while at 30 km the corresponding figure ranges from 5 hr to 10 hr. Hence it seems probable that this reaction is not important in the troposphere. However, it may play an important role in the formation of the stratospheric sulfate layer (Subsection 4.4.3).

In the  $\text{SO}_2 \rightarrow \text{H}_2\text{SO}_4$  transformation organic materials play an important part. Thus, if organic substances are added to air containing  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_2$  and  $\text{O}_3$  the  $\text{SO}_2$  oxidation rate is observed to accelerate. According to the laboratory experiments of Cox and Penkett (1972) the photooxidation rate of  $\text{SO}_2$  is as large as 1-10 % per hr if the air contains appropriate olefins and ozone. Olefins can be detected, however, only in air polluted by exhaust gases. However, Cadle (1972) has

speculated that, under clean tropospheric conditions.  $\text{SO}_2$  oxidation is stimulated by the presence of terpenoid hydrocarbons (see Subsection 3.3.3).

It is believed at present (Calvert *et al.* 1978) that "the direct photooxidation of  $\text{SO}_2$  by way of the electronically excited states of  $\text{SO}_2$  is relatively unimportant for most conditions which occur within the troposphere". Among others, Calvert *et al.* (1978) argue that, in the air containing the species noted above, many radicals are formed by photochemical processes. These radicals (e.g.  $\text{OH}$ ,  $\text{HO}_2$ ,  $\text{CH}_2$ ,  $\text{CH}_3\text{O}_2$ ) oxidize  $\text{SO}_2$  by the following processes:



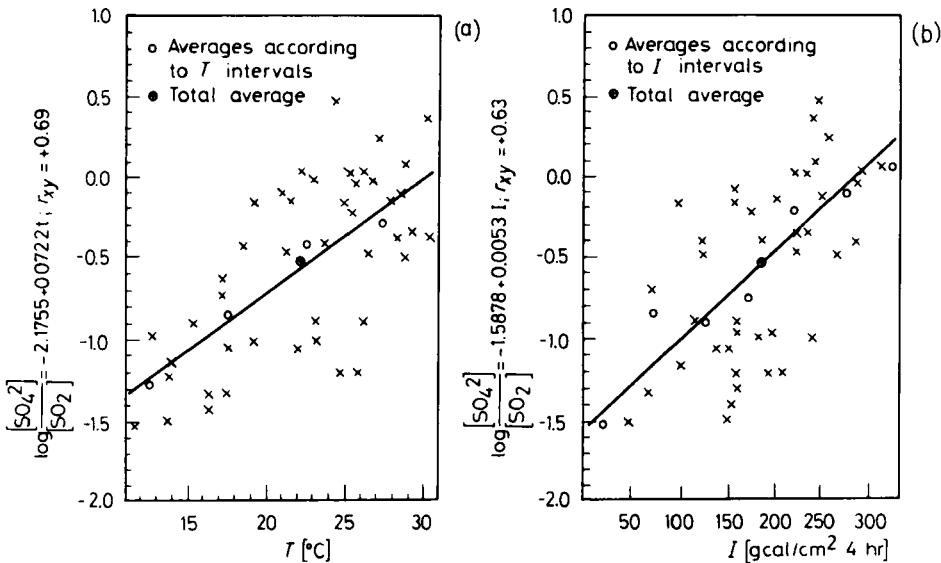
where reaction [3.56] is the dominant path. In the case of  $[\text{OH}]$ ,  $[\text{HO}_2]$  and  $[\text{CH}_3\text{O}]$  concentrations typical for the clean troposphere,  $\text{SO}_2$  transformation rates with an order of  $0.1 \text{ } \mu\text{mol m}^{-3} \text{ hr}^{-1}$  can be calculated, which is equivalent to a residence time of 5 days. However, the rate is calculated to be greater than  $1 \text{ } \mu\text{mol m}^{-3} \text{ hr}^{-1}$  in the more polluted lower part of the troposphere, because of the higher concentrations of free radicals.

By homogeneous reactions, vapour phase sulfuric acid is formed. This vapour condenses in the air by bimolecular condensation ( $\text{H}_2\text{O}$  molecules also take part in the phase transition). The rate of this process depends, among other things, on the concentration of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  molecules as well as on the temperature (Kiang *et al.*, 1973). In the presence of suitable aerosol particles the condensation is heterogeneous, that is vapour molecules condense on the surface of aerosol particles (Cox, 1974).

Relatively few direct observations supports the photochemical sulfate formation concept; it derives primarily from laboratory experiments.<sup>27</sup> Thus, Atkins *et al.* (1972) demonstrated in Southern England that airborne sulfuric acid concentrations correlate generally with the intensity of solar radiation and the  $\text{O}_3$  level. Similarly, near Budapest during summer daylight, E. Mészáros (1973) found a good positive correlation between the sulfate content of particulate matter and solar radiation intensity, as well as between radiation and the logarithm of  $[\text{SO}_4^{2-}]/[\text{SO}_2]$  molar ratios. The chemical parameters mentioned also correlated well with the temperature. The results obtained are plotted in Fig. 16. It can be seen that the linear correlation coefficient between  $\log([\text{SO}_4^{2-}]/[\text{SO}_2])$  and radiation intensity is +0.63. In the case of temperature the corresponding coefficient is +0.69. These results strongly suggest that sulfate ions in particulate matter are formed by

<sup>27</sup>The expression "direct" means that we speak about such measurements when it was chemically proved that particles were composed of sulfate.

photochemical reactions followed by thermal processes. It is emphasized, however, that the above effect cannot be identified in the winter months (E. Mészáros, 1974b), which means that the sulfate formation in these months is due to other transformation paths.



**Fig. 16**  
Variation of the ratio of molar concentration of sulfate to that of  $\text{SO}_2$  as a function of temperature ( $T$ ) and solar radiation intensity ( $I$ ) during summer daylight (E. Mészáros, 1973) (By courtesy of *J. of Aerosol Science*)

One possible alternative process has already been mentioned: the oxidation of  $\text{SO}_2$  in cloud and fog drops by different absorbed oxygen species. Since this oxidation plays an important role also in the wash-out of sulfur dioxide from the troposphere, we will discuss it in more detail in Chapter 5. We will note here only that this oxidation is promoted by the presence of metal (iron, manganese etc.) ions (Junge and Ryan, 1958). Moreover, considering that the rate of this process depends upon the pH of the solution, the presence of  $\text{NH}_3$  also increases the rate of this conversion. Thus, Georgii (1970) found by calculation with the model of Scott and Hobbs (1967) that the quantity of sulfate ions formed depends more on the  $\text{NH}_3$  concentration than on the  $\text{SO}_2$  level, both measured in the air. The aircraft measurements of the same author and his associate (Georgii and Müller, 1974) show, however, that the concentration of ammonia at different altitudes is sufficient for this process only during summertime (see Fig. 14). It was also proposed (see Subsection 3.4.5) that ozone absorbed by atmospheric liquid water is important as a reaction partner for the oxidation. The present author believes that  $\text{O}_3$  plays an

essential role in these transformation processes, feeling that it is very improbable that the concentration of the metal catalysts mentioned is significant in the clean troposphere (see Chapter 5).

The amount of observational support for the formation of sulfate particles by the evaporation of cloud water is also very limited. Thus, according to Jost (1974) the concentration of larger sulfate particles below the clouds might be high even if their number is low at the cloud levels. Hobbs (1971) showed that downwind from dissipating clouds, a great number of condensation nuclei active at 0.5 % supersaturation can be detected. This observational fact, of course, supports the foregoing hypothesis only on the reasonable assumption (see Twomey, 1971), that active cloud nuclei are composed of sulfates. However, Hobbs (1971) did not make any chemical analyses.

The oxidation of  $\text{SO}_2$  can also take place on the surface of existing aerosol particles. According to the laboratory work of Urone *et al.* (1968) the rate of the  $\text{SO}_2$  oxidation can be rapid in the presence of aerosol particles, even without illumination. In case of  $\text{Fe}_2\text{O}_3$  particles the  $\text{SO}_2$  loss in the laboratory chamber air is as much as 100 %  $\text{hr}^{-1}$ , while high loss rates were found in the presence of aluminum, calcium, chromium and other metal oxides as well. It is questionable, however, whether the  $\text{SO}_2$  loss is due to chemical conversion or to simple physical adsorption (Corn and Cheng, 1972). Furthermore, in Urone's experiments the mass concentration of aerosol particles was 100–200 times greater than that of  $\text{SO}_2$  which is unrealistic under atmospheric conditions. Finally, the experimental results of

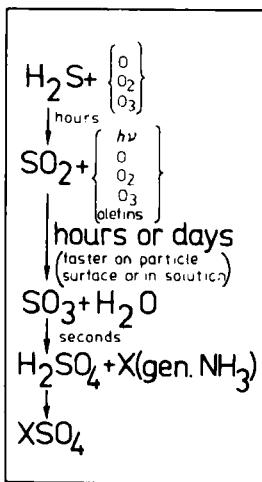


Fig. 17

Schematic representation of the transformation of sulfur compounds in the atmosphere according to Kellogg *et al.* (1972). (Copyright 6.2.1979 by the American Association for the Advancement of Science and by courtesy of the authors)

Urone and his associates are supported to date only by atmospheric observations carried out in locally polluted environment (e.g. Benarie *et al.*, 1973). For this reason it is believed that this process is probably unimportant under background conditions.

The foregoing discussion, excluding the photooxidation of DMS, is summarized in Fig. 17 (Kellogg *et al.*, 1972). It can be seen that the sulfuric acid droplets formed are generally neutralized by ammonia. This is the reason why background aerosol particles consist mainly of ammonium sulfate (see Chapter 4).

### 3.6.4 Concentration of sulfur compounds

We know rather well the concentration of oxidized sulfur compounds ( $\text{SO}_2$  and  $\text{SO}_4^{2-}$ ) over industrialized North America and Europe as well as over the Atlantic Ocean. However, our knowledge of the concentration of reduced sulfur is much poorer because of analytical problems.

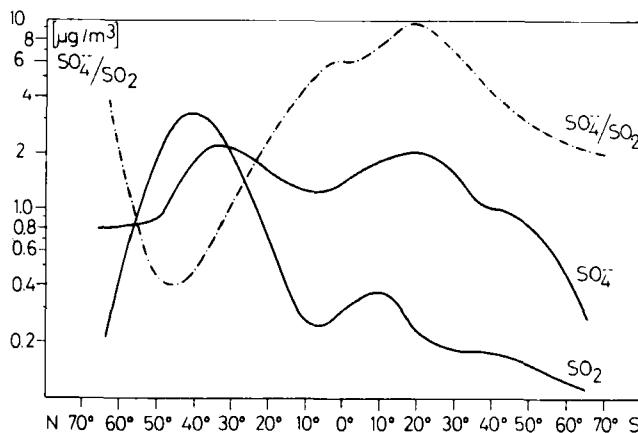
In the atmosphere of the Northern equatorial Atlantic Ocean the concentration of hydrogen sulfide has been recently studied by Slatt *et al.* (1978) using a sensitive fluorescence technique. They report concentrations ranging from  $5 \times 10^{-3}$  to  $5 \times 10^{-2}$  ppb ( $0.0076\text{--}0.076 \mu\text{g m}^{-3}$  STP) which are much lower than the mean level of 0.2 ppbm used by Friend (1973). Slatt and her co-workers also state, on the basis of their results, that the residence time of  $\text{H}_2\text{S}$  in the atmosphere cannot be more than a few hours. On the other hand, they estimate that the oceanic production rate of this substance given by Friend is probably correct.

Jaeschke *et al.* (1978) have carried out  $\text{H}_2\text{S}$  analyses over different parts of the F.R.G., using a similar procedure. According to their data the continental concentration level of hydrogen sulfide is generally in the range of  $0.05\text{--}0.1 \mu\text{g m}^{-3}$  STP at a height of 1m above the ground. This agrees reasonably with the values of Breeding *et al.* (1973) obtained in the central United States. The aircraft measurements of Jaeschke show that the concentration of  $\text{H}_2\text{S}$  decreases rather rapidly with increasing height, which also suggests that the lifetime of  $\text{H}_2\text{S}$  in air is relatively low. An interesting finding of Jaeschke and his co-workers is that the concentrations are higher over industrialized regions, which demonstrates some anthropogenic production.

Unfortunately, very little information is available concerning the concentrations of other reduced sulfur species in the atmosphere. According to Maroulis and Bandy (1977) the DMS level is around 0.005 ppb on the Atlantic Coast, and generally below 0.03 ppb in Virginia (both in U.S.A.). The preliminary results of Sandalls and Penkett (1977) show that in Harwell, England, the mean carbonyl sulfide (COS) level is 0.51 ppb, while the concentration of carbon disulfide ( $\text{CS}_2$ ) is found on average to be 0.19 ppb. Much work has to be done, however, before generally accepted values of mean atmospheric levels are obtained.

The results of surface air concentration measurements of gaseous  $\text{SO}_2$  and particulate  $\text{SO}_4^{2-}$  have recently been reviewed by E. Mészáros (1978). The

compilation of data gained over the Atlantic Ocean is summarized in Fig. 18. The most interesting fact emerging from this figure is the maximum in the sulfur dioxide concentration over northern mid-latitudes. These high concentrations were published by Georgii and Vitze (1971) who attributed this finding to the  $\text{SO}_2$  advection from continental sources. The much lower values over the southern Atlantic Ocean were found by Nguyen Ba Cuong *et al.* (1974). Since these latter authors used the same chemical method (West and Gaeke, 1956) as Georgii and Vitze the maximum found in the  $\text{SO}_2$  distribution is probably real.



**Fig. 18**

Concentration of sulfur dioxide and sulfates as a function of the latitude over the Atlantic Ocean according to information available (E. Mészáros, 1978). (By courtesy of *Atmospheric Environment*)

The sulfate distribution has two maxima. One of them is connected to the  $\text{SO}_2$  maximum, while the other is in the proximity of the equator. It thus appears that without the anthropogenic disturbance in sulfur dioxide distribution there would be only one  $\text{SO}_4^{2-}$  maximum at low latitudes. It is postulated that this is caused by a higher conversion rate of  $\text{SO}_2$  over these areas. Thus, it is reasonable to suppose that, in the vicinity of the equator, meteorological conditions are very favourable for photochemical and thermal reactions. It can also be seen from the figure that the  $\text{SO}_4^{2-}/\text{SO}_2$  ratio, considered as a measure of these transformations, also shows a maximum at the equator. The sea salt sulfate in the samples collected varies considerably. If we consider that "excess" sulfate (i.e., that not originating in sea salt) forms much smaller particles than does sea salt, we can say that on a number basis the sulfate particles formed from gaseous compounds are very important even over the oceans (see Chapter 4).

On the basis of data compiled, E. Mészáros (1978) proposes model background concentrations for different part of rural and remote areas of Europe, as tabulated in Table 13. One can see that the  $\text{SO}_2$  level may be as high as  $15 \mu\text{g m}^{-3}$ , while the sulfate concentration ranges from 0.3 to  $10.5 \mu\text{g m}^{-3}$  STP. The values given agree reasonably well with data gained in North America, as discussed by the same author.

Table 13

Model sulfur concentrations for various areas of Europe  
(E. Mészáros, 1978)

Area	$\text{SO}_2-\text{S}$	$\text{SO}_4-\text{S}$	%
Clean N. areas	0.35	0.1	12
Areas with low conc. (e.g. S. Sweden)	3.5	1.0	22
Moderately polluted areas (e.g. Central and E. Europe)	4.0	1.7	34
Areas with high conc. (e.g. W. Europe)	7.5	3.0	12
Southern Europe	1.0	3.5	14

Note: All concentrations are expressed in  $\mu\text{g m}^{-3}$  as sulfur. Percentage values give the area of the region considered relative to the total area of Europe

The vertical profile of  $\text{SO}_2$  concentration was first studied in the troposphere by Georgii and Jost (1964). Their mean results obtained over the F.R.G. are plotted in Fig. 14. It is seen that the  $\text{SO}_2$  concentration decreases rapidly with increasing altitude under continental conditions. At a height of about 1000 m the concentration drops to half its value in the surface air. Above 2 km the annual variation disappears and above 3 km the concentration decrease becomes insignificant. This constant concentration is approximately  $5 \mu\text{g m}^{-3}$  STP. However, more recent aircraft flights (e.g. Rodhe, 1972a; Trägårdh, 1978; Várhelyi, 1978) resulted in a smaller concentration at this height. Várhelyi (1978), for example, found the corresponding figure over Hungary to be about one order of magnitude smaller than the concentration proposed by Georgii and Jost (1964). In contrast, the results of aircraft flights, carried out by Gravenhorst (1975) over the Bay of Biscay, indicate much less  $\text{SO}_2$  vertical decrease over the sea than over continental areas.

An interesting peculiarity of the vertical sulfate profile is the small value of the concentration gradient compared to the  $\text{SO}_2$  concentration decrease (Georgii, 1970; Várhelyi, 1978). It follows from this fact that the  $\text{SO}_4^{2-}/\text{SO}_2$  ratio increases with increasing height. This is due, in part to the gradual conversion of  $\text{SO}_2$  to sulfate particles in updrafts as well as to the difference in deposition velocity of gases and particles (see later). The observations of Várhelyi (1978) lead to sulfate concentrations around  $1 \mu\text{g m}^{-3}$  at an altitude of 3 km, which is about twice the corresponding  $\text{SO}_2$  level (see above).

Concerning sulfate concentration in surface air, the level of this species has no maximum in the winter (Bónis, 1968), in contrast to the annual variations of  $\text{SO}_2$ . That is, high winter  $\text{SO}_2$  concentrations do not necessarily coincide with a high sulfate content of particulate matter. This phenomenon can be explained by the interaction of different conversion processes (E. Mészáros, 1974b) of sulfur gases. According to the observations of Kolb (1973), carried out in a very clean environment (Tromsø, N. Norway), the annual variation of  $\text{SO}_4^{2-}$  shows a spring maximum and a minimum during the fall like the tropospheric  $\text{O}_3$  concentration (see Fig. 13). However, more numerous American studies indicate a summer maximum in the annual distribution of sulfate level (Hidy *et al.* 1978).

Another interesting feature of sulfate concentration is the increase above the tropopause. Thus, in the stratosphere around 16 and 18 km a sulfate layer can be found, the formation and characteristic of which will be discussed elsewhere (Subsection 4.4.3).

On the basis of his data compilation, including the results of some aircraft flights, E. Mészáros (1978) estimates values for atmospheric  $\text{SO}_2-\text{S}$  and  $\text{SO}_4-\text{S}$  burden as shown in Table 14. The figures proposed by Friend (1973) are also given for comparison. All values are expressed in sulfur equivalents. The agreement between the two authors on  $\text{SO}_2-\text{S}$  burden is excellent. However, more atmospheric sulfate-sulfur mass was calculated by E. Mészáros. Thus, Mészáros' estimates show a greater sulfate-sulfur burden than that of  $\text{SO}_2-\text{S}$ . It is to be noted that stratospheric  $\text{SO}_4-\text{S}$  is not included in sulfate burden. However, the total quantity of sulfate-sulfur in the stratosphere (Karol, 1977) is at least one order of magnitude less than the global mass in the troposphere.

Table 14

Global atmospheric sulfur burden over the oceans and continents according to Friend (1973) and E. Mészáros (1978)

Surface	$\text{SO}_2-\text{S}$		$\text{SO}_4-\text{S}$	
	Friend	Mészáros	Friend	Mészáros
Oceans	—	0.17	0.09	0.30
Continents	—	0.28	0.16	0.50
Total	0.52	0.45	0.25	0.80

Note: All values are expressed in  $10^6 \text{ t}$

The tropospheric burden of sulfur in reduced compounds is very speculative. Nevertheless, for  $\text{H}_2\text{S}$  the following figure is proposed. Let us assume that the global  $\text{H}_2\text{S}$  concentration in surface air over the ocean is  $0.05 \mu\text{g m}^{-3}$  STP, while it is  $0.1 \mu\text{g m}^{-3}$  STP above the continents (see above). From these data a global concentration of  $0.065 \mu\text{g m}^{-3}$  STP can be calculated by averaging according to the relative area of continents and oceans. Based on vertical profiles published by Jaeschke *et al.* (1978),

it is speculated with caution that the hydrogen sulfide scale height<sup>28</sup> is around 1000 m. This leads to a global H<sub>2</sub>S—S burden of  $0.03 \times 10^6$  t. However, this mass does not include the quantity of sulfur in other reduced species. The burden of *all* reduced sulfur, however, can hardly be more than  $0.1 \times 10^6$  t.

### 3.6.5 Atmospheric cycle of sulfur

On the basis of the foregoing discussion and further considerations the schematic atmospheric sulfur budget represented in Fig. 19 is proposed. The terms in the cycle were determined as follows. We accepted the figures of Friend (1973) for the strength of anthropogenic sources and for the sulfur production rate by volcanoes ( $65 \times 10^6$  t  $\text{yr}^{-1}$  and  $2 \times 10^6$  t  $\text{yr}^{-1}$ , respectively). On the other hand, we assumed, in accordance

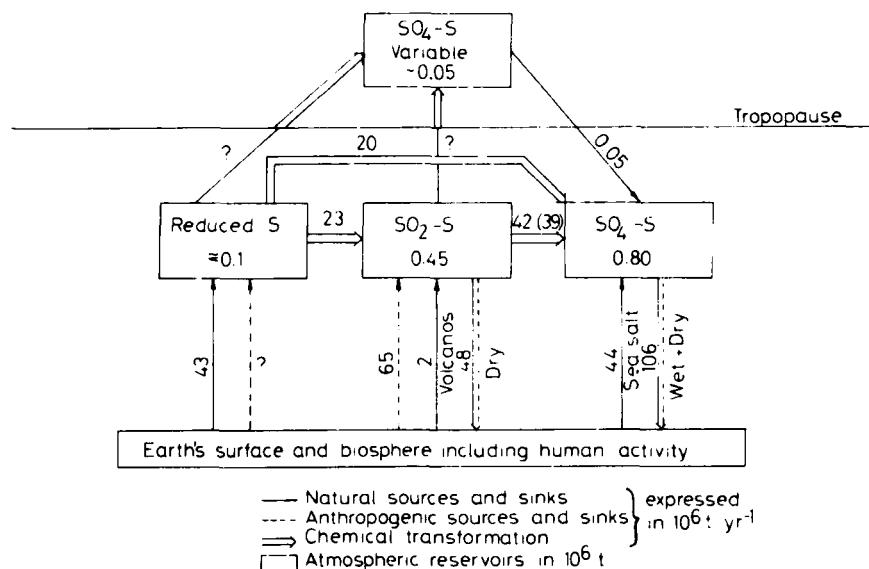


Fig. 19  
Cycle of sulfur compounds in the atmosphere

<sup>28</sup> The scale height,  $H$ , is a hypothetical altitude defined as

$$H = \int_0^x c(z)dz/c(0),$$

where  $c(z)$  is the concentration at level  $z$ , while  $c(0)$  is the same parameter for surface level air. The integral gives the column concentration of the substance considered. The weakness of this approach to calculating global burdens is the linear dependence of the burden on the surface level concentration, which often is not well established.

with the careful study of Granat *et al.* (1976), that the sum of the total wet deposition and the dry deposition of sea salt particles is  $106 \times 10^6 \text{ t yr}^{-1}$  (for further details see the original paper). The dry deposition of sulfate particles formed by gaseous reactions was neglected since their deposition velocity is estimated to be no more than  $0.1 \text{ cm s}^{-1}$  (Garland, 1978). The source intensity of sea salt-sulfur was taken from data of Eriksson (1960). The natural biological sulfur release was calculated by balancing the cycle. It is proposed with caution that  $23 \times 10^6 \text{ t yr}^{-1}$  from the value obtained is provided by  $\text{H}_2\text{S}-\text{S}$ . This latter figure was calculated by using the above  $0.03 \times 10^6 \text{ t H}_2\text{S}-\text{S}$  burden and a global residence time of half a day (e.g. Jaeschke *et al.*, 1978).

The dry deposition of  $\text{SO}_2$  was calculated from a  $1 \mu\text{g m}^{-3}$  mean continental concentration (expressed in sulfur) and a  $0.1 \mu\text{g m}^{-3}$  mean oceanic surface air concentration, which were multiplied by respective deposition velocities of 1.0 and  $0.7 \text{ cm s}^{-1}$ . These latter figures are provided by observational findings showing that soil and vegetation are important  $\text{SO}_2$  absorbers (Garland, 1978; see Chapter 5). On the other hand it was demonstrated, among others by Beilke and Lamb (1974), that the ocean surface provides a sulfur dioxide sink. Thus, it is not excluded that the same oxidation processes that occur in cloud water (see Chapter 5) also occur in the ocean surface layer, where the relatively high pH ( $8.1 \pm 0.2$ ) does not limit the reaction rate. In this way  $48 \times 10^6 \text{ t yr}^{-1}$   $\text{SO}_2-\text{S}$  global dry deposition was obtained.

The wash-out of reduced sulfur compounds was neglected owing to the small solubility in water of these species. Furthermore it was assumed that the dry deposition of reduced compounds is negligible as compared to the strength of chemical sinks. Thus, Judeikis and Wren (1977) demonstrated by laboratory studies that the dry deposition velocity of DMS and  $\text{H}_2\text{S}$  on selected soil samples ranges from  $0.015$  to  $0.28 \text{ cm s}^{-1}$ . They mention, however, that these values are likely to be upper limits due to a possible reversible physical adsorption.

The term characterizing the transformation of  $\text{H}_2\text{S}$  to  $\text{SO}_2$  is determined by the source strength of  $23 \times 10^6 \text{ t yr}^{-1}$  calculated above. The chemical conversion of  $\text{SO}_2$  is estimated by assuming a global overall reaction rate of  $1\% \text{ h}^{-1}$  including processes in cloud water. In this way we obtained a value of  $39 \times 10^6 \text{ t yr}^{-1}$  which was normalized by requiring the  $\text{SO}_2-\text{S}$  reservoir to be balanced. The direct sulfate formation rate from reduced sulfur gases was obtained by balancing the budget of reduced S and  $\text{SO}_4-\text{S}$ . The accuracy of these terms is not better than within a factor of 2.

For completeness the stratospheric inventory is also plotted in Fig. 19. The value of stratospheric sulfur burden is based on data for 1971–1973 as reported by Karol (1977). The term representing the sedimentation of sulfate particles from the stratosphere to the troposphere is estimated by assuming a 1 year stratospheric residence time (Junge, 1963). Moreover, the arrow going from the tropospheric reduced S reservoir to the  $\text{SO}_4-\text{S}$  one in the stratosphere represents the possibility, proposed by Crutzen (1976), that COS may be a source of stratospheric  $\text{SO}_2$ .

It follows from data given in Fig. 19 that the overall residence time of sulfur compounds in the atmosphere is

$$\tau = \frac{1.35 \times 10^6 \text{ t}}{154 \times 10^6 \text{ t yr}^{-1}} = 0.0088 \text{ yr}$$

which is equivalent to about 3 days. The corresponding figures for  $\text{SO}_2-\text{S}$  and  $\text{SO}_4-\text{S}$  are 2 days and 3 days, respectively. Further, the global lifetime of reduced sulfur compounds in the atmosphere is less than 1 day.

We have to emphasize here that the majority of the sulfate-sulfur in the tropospheric reservoir is not sea salt. Friend (1973) estimated that the atmospheric sea-salt burden is around  $0.1 \times 10^6 \text{ t}$ . By subtracting this value from the sulfate-sulfur loading given in Fig. 19 and considering only the strength of chemical sources ( $62 \times 10^6 \text{ t yr}^{-1}$ ), a residence time of more than 4 days is obtained for the "excess" sulfate.

### 3.6.6 Atmospheric sulfur cycle over continents

Kellogg *et al.* (1972) estimated that 90 % of the anthropogenic sulfur is emitted into the atmosphere over the Northern Hemisphere. The sulfur emission due to human activity is  $17 \times 10^6 \text{ t yr}^{-1}$  over the U.S.A. (Urone 1976, based on data of 1970), while the corresponding figure for the whole of Europe is estimated to be  $25 \times 10^6 \text{ t yr}^{-1}$  (Semb, 1978, data for 1973). The combination of these values with the strength of the global anthropogenic emission ( $65 \times 10^6 \text{ t yr}^{-1}$ ) leads to the conclusion that 65 % of all man-made sulfur emission is provided by the U.S.A. and the European countries. It is obvious from this high proportion that the strength of anthropogenic sources may be much greater over some areas of the world than is the intensity of biological production. The aim of this book is to study the pollution of the global atmosphere. In spite of this fact, it seems meaningful to discuss the problem of continental pollution at least for one pollutant.  $\text{SO}_2$  is particularly suitable for this purpose since some information is available in the field.

The sulfur budget over the U.S.A. was studied by Junge (1960). On the basis of data obtained by a precipitation chemistry network operated during 1955–1956 he was able to calculate the sulfur deposition of this country ( $3.5 \times 10^6 \text{ t yr}^{-1}$ ). Junge speculated that 90 % of this deposition comes from continental sources. In 1957 the anthropogenic source strength was  $8.6 \times 10^6 \text{ t yr}^{-1}$  over the United States. By neglecting the effect of natural production it is easy to show that only 40 % of the sulfur emission is deposited. Since at these latitudes in the troposphere westerly winds prevail, it is tempting to explain the  $\text{SO}_2$  concentration maximum over the Atlantic Ocean (see Fig. 18) by this sulfur export. We have to recognize, however, that Junge (1960) neglected the dry deposition of  $\text{SO}_2$ , which may be comparable with the wet deposition. Furthermore, the  $\text{SO}_4^{2-}$  distribution over the Atlantic Ocean does not clearly support this assumption.

An atmospheric sulfur inventory for the whole European continent has been recently constructed by E. Mészáros *et al.* (1978). These authors show on the basis of the comparison of anthropogenic sulfur emission (Semb, 1978) and sulfur advection from the Atlantic that the sulfur gained by advection is small. 70–85 % of the sulfur emitted and imported is removed over the continent equally by dry (mostly in form of  $\text{SO}_2$ ) and wet deposition. Mészáros and his associates have estimated the dry deposition of  $\text{SO}_2$  by using an average European  $\text{SO}_2-\text{S}$  concentration calculated from data in Table 13 ( $3.2 \mu\text{g m}^{-3}$ ) and a dry deposition velocity of  $1 \text{ cm s}^{-1}$  (Garland, 1978). The value of wet deposition was based on precipitation chemistry measurements. It follows from this quantitative calculation that Europe contributes 15–30 % of its sulfur emission to the tropospheric sulfur cycle of other areas.

The regional sulfur budget for the northwestern part of the European continent was studied in several papers. Thus, Rodhe (1972b) investigated the sulfur budget of the two regions shown in Fig. 20. Over the region labelled II the anthropogenic sulfur emission is nearly  $10 \times 10^6 \text{ t yr}^{-1}$ , which means that about 15–16 % of the total man-made sulfur (see Table 12) is emitted into the air over this region, what

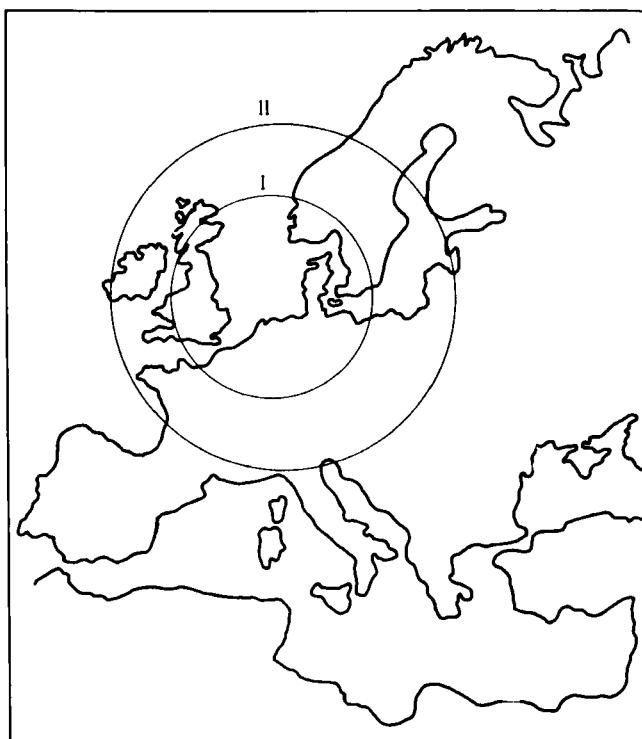


Fig. 20

The two regions used for sulfur budget studies over N. W. Europe (Rodhe, 1972b). (By courtesy of *Tellus*)

comprises 1 % of the surface of the Earth. Rodhe speculated that the natural source intensity over this area (estimated on the basis of Friend's data in Table 12) is at least one order of magnitude less than the strength of anthropogenic sulfur production. Table 15 tabulates the results. The wet deposition values given were estimated on the basis of data on the chemical composition of precipitation. The wet deposition due to anthropogenic sources was determined by subtracting the negligible natural sulfur deposition from these figures. Rodhe assumed, as seems reasonable, that the sum of dry and wet deposition is at most twice the wet removal alone. In this way he calculated that over region I 20–40 % of the sulfur emitted is removed from the air. The corresponding figure for region II is estimated to be between 40 and 75 %. Thus 25–60 % of the emission of region II is exported into the air of other regions. This result indicates that sulfur emission cannot be considered as a purely national problem. Well organized international projects are needed (see e.g. Ottar, 1978) to study the long-range transport of pollutants across national boundaries.

**Table 15**  
Atmospheric sulfur inventory over two regions of N. W. Europe (see Fig. 20)  
according to Rodhe (1972b)

Region	Anthropogenic emission	Wet deposition	Wet deposition minus natural wet dep.	Total anthropogenic deposition	Deposition in % of anthropogenic emission
I	5.9	1.5	1.2	1.2–2.3	20–40
II	8.4	4.5	3.2	3.2–6.4	40–75

*Note:* Values tabulated are expressed in  $10^6 \text{ t S/yr}$

### 3.7 Summary

Table 16 summarizes our discussion of atmospheric trace gases. In this table, besides source strengths and burdens, the relative rates of biological and anthropogenic production expressed as a percentage of global source intensities is also given. Concerning the tabulated values we have to mention that the fraction of hydrogen and carbon monoxide from methane is considered biological. The same is true for the total ozone formed from  $\text{O}_2$  released by the biosphere (see Chapter 2). Furthermore, the global  $\text{NO}_2$  source is taken as the sum of NO produced by the biosphere and  $\text{NO}_2$  emitted by man. The biological portion of  $\text{SO}_2$  is provided by the oxidation of  $\text{H}_2\text{S}$ . The question-marks denote that the possible anthropogenic fraction is uncertain or low.

One can clearly see from the data tabulated that the preponderance of trace gases is of biological origin. They are mostly produced by microbiological processes (for further details see Schlegel, 1974). This means that the biosphere plays an important role not only in cycling the main atmospheric constituents, but also in the

production of different trace gases. It is interesting to note that, while the production rate of the highly variable gases (e.g. NH<sub>3</sub>, NO<sub>2</sub>, SO<sub>2</sub>) is comparable to that of some variable components (N<sub>2</sub>O, H<sub>2</sub>), their atmospheric burden is much smaller. This fact is due to the very short residence time caused by aerosol formation and wet deposition.

Finally, it can also be seen that the inventory of certain trace constituents is considerably modified by human activity (H<sub>2</sub>, CO, NO<sub>2</sub>, SO<sub>2</sub>). The anthropogenic proportion is particularly high in the case of sulfur dioxide, which yields an essential fraction of tropospheric aerosol particles (see Chapter 4). This inadvertent effect can be very dangerous from the point of view of climatic variation (see Chapter 6).

**Table 16**

Production rate (*F*) and atmospheric burden (*M*) of trace constituents on the basis of data of different authors (see text). Figures expressed as percentage of *F* give the relative source strengths due to biological and anthropogenic (in parentheses) sources

Gas	<i>F</i> [10 <sup>6</sup> t yr <sup>-1</sup> ]	"% of <i>F</i> biological (anthropogenic)	<i>M</i> [10 <sup>6</sup> t]
H <sub>2</sub>	20-25	40-50 (50-60)	200
CH <sub>4</sub>	500-1000	95-98 (2-5)	4000
CO	1000	~50 (~50)	550
O <sub>3</sub>	1600	100 (?)	3400
N <sub>2</sub> O	100	100 (?)	2000
NH <sub>3</sub>	50-100	90-95 (5-10)	1
NO	40	100 (?)	
NO <sub>2</sub>	100	50 (50)	1-2
H <sub>2</sub> S	25	100 (?)	0.1
SO <sub>2</sub>	150-200	25 (75)	1

*Note:* In the case of nitrogen and sulfur compounds *F* and *M* are given in the mass of species and not in nitrogen or sulfur equivalents

## 4. The atmospheric aerosol

### 4.1 Introduction

#### 4.1.1. Definition of the aerosol

An *aerosol* is defined as a dispersed system containing solid or liquid particles suspended in a gas. In our case the gaseous medium is the air in which *aerosol particles* of different composition and size are suspended.

In more rigorous terms an aerosol or aerocolloidal system exists, if (Hidy and Brock, 1970):

- (a) the sedimentation velocity of the particles is small;
- (b) inertial effects during particle motions can be neglected (the ratio of inertial forces to viscous forces is small);
- (c) the Brownian motion of the particles, due to the thermal agitation of gas molecules, is significant and
- (d) the surface of the particles is large compared to their volume.

The physical meaning of the above criteria is as follows. The external force acting on an aerosol is generally gravitation. This means that the lifetime of a particle in the system is determined by its sedimentation velocity. If the particle radius is greater than the mean free path of gas molecules, the  $v_s$ , falling velocity is given by the well-known Stokes equation:

$$v_s = \frac{2}{9} \frac{r^2 \rho_p g}{\mu} \quad [4.1]$$

where  $r$  and  $\rho_p$  are the radius and density of the particle, assumed spherical,  $\mu$  is the dynamic gas viscosity (equal to  $1.81 \times 10^{-4}$  poise at a temperature of  $20^\circ\text{C}$ ) while  $g$  is the gravitational constant. In the atmosphere,  $v_s$  in equation [4.1] depends on altitude above the sea level. Furthermore, the updraft motions in the troposphere make the interpretation of the sedimentation velocity rather complicated. In spite of these problems in the surface air a value of  $10 \text{ cm s}^{-1}$  can be accepted with caution as an upper limit, which gives the falling speed of a spherical particle of  $30 \mu\text{m}$  radius if the density is taken to be unity. We have to emphasize, however, that due to the presence of updrafts, larger particles also can be found in the atmosphere at significant distances from their sources.

The ratio of inertial forces to viscous forces is *per definitionem* the Reynolds number (Re) of particles. In this way the second criterion can be written in the form:

$$\frac{\rho v r}{\mu} = \text{Re} < 1 \quad [4.2]$$

where  $\rho$  is the air density, while  $v$  is the speed of the particle motion caused by some external force. Physically [4.2] means that in a stable system the product of the particle speed and particle size cannot exceed a given value. Thus, under normal atmospheric conditions the speed of motion of a particle of  $10 \mu\text{m}$  radius could not exceed  $30 \text{ cm s}^{-1}$ . In the case of  $r = 30 \mu\text{m}$  the critical velocity is  $10 \text{ cm s}^{-1}$ . If the external force arises from the gravitational field, this condition is obviously equivalent to the first criterion.

A very characteristic property of aerosol particles is their Brownian motion. This random motion is a result of the fluctuations in the impact of gas molecules on the particles. It goes without saying that the speed of this motion increases with decreasing size. Generally, Brownian motion is considered significant if the particle radius is smaller than  $0.5 \mu\text{m}$ .

Finally, the fourth criterion is satisfied if the particle surface (in  $\text{cm}^2$ ) exceeds the particle volume (in  $\text{cm}^3$ ) at least a thousand times. For this reason, surface phenomena play an important role in the behaviour of aerocolloidal systems.

The foregoing conditions determine the upper limit of the particle size. The lower limit can be specified in a very simple way. A system is considered an aerosol when the radius of the particles is greater than that of gas molecules. At the same time  $m_a \gg m_g$ , where  $m_a$  and  $m_g$  are the mass of aerosol particles and gas molecules, respectively. Bearing in mind the size of molecules in the air we might define the lower limit to be around  $10^{-7} \text{ cm} (= 10^{-3} \mu\text{m})$ .

An important consequence of the Brownian motion of aerosol particles is their collision and subsequent coalescence. This so-called coagulation process can be characterized by the particle loss per unit time (Hidy and Brock, 1970):

$$-\frac{dN}{dt} = 8\pi D r N^2 \quad [4.3]$$

where  $N$  is the number of particles per unit volume,  $t$  is the time and  $D$  is the diffusion coefficient of particles:

$$D = \frac{kT}{6\pi\mu r} \left( 1 + \frac{Al}{r} \right) \quad [4.4]$$

In equation [4.4]  $k$  is the Boltzmann constant ( $1.3803 \times 10^{-16} \text{ erg/degree} \times \text{molecule}$ ),  $T$  is the absolute temperature,  $A$  is the Stokes-Cunningham

correction<sup>1</sup>, while  $l$  is the mean free path of gas molecules<sup>2</sup>. Thus, the coagulation equation may be written in the following form:

$$-\frac{dN}{dt} = \frac{4 k T}{3 \mu} \left( 1 + \frac{Al}{r} \right) N^2 \quad [4.5]$$

It is concluded on the basis of equation [4.5] that the intensity of the particle loss due to the thermal coagulation is directly proportional to square of the particle concentration, while the coagulation efficiency increases with decreasing particle radius. This means that the coagulation of small particles at a high concentration is a very rapid process. Equation [4.5] is valid only for monodisperse aerosols, i.e. aerosols composed of particles of uniform size. However, the same qualitative conclusion can also be drawn in the case of polydisperse systems.

It should be emphasized that there is no intention here to discuss the dynamics of aerocolloidal systems. For further details the reader is referred to textbooks specialized in the field (e.g. Hidy and Brock, 1970).

#### 4.1.2 Classification and measurement of atmospheric aerosol particles

With regard to their formation process and size, aerosol particles can be divided into two distinct groups: fine and coarse particles (Whitby, 1978). Fine particles with radius smaller than  $0.5\text{--}1.0 \mu\text{m}$  are formed by condensation and coagulation (see Subsection 4.2.2), while coarse particles arise mostly from surface disintegration (see Subsection 4.2.1). Since this classification provides an explanation of the form of the particle size distribution, we will discuss Whitby's ideas in more detail in Subsection 4.3.2.

Another possibility is to classify particles simply according to their size. In atmospherics physics and chemistry the classification of Junge (1963) is widely used. Junge divided aerosol particles in three groups:

- Aitken<sup>3</sup> particles:  $r < 0.1 \mu\text{m}$ ;
- large particles:  $0.1 \leq r < 1.0 \mu\text{m}$ ;
- giant particles:  $r \geq 1.0 \mu\text{m}$ .

This division is very convenient from the point of view of particle characterization and measurement. Thus, in the range of Aitken particles diffusion effects are significant and particle coagulation is rapid. However, in case of giant particles these phenomena can be neglected and the behaviour of aerosol particles is mostly determined by their sedimentation due to gravitation. The large particles constitute

<sup>1</sup>  $A \approx 1.257 + 0.400 \times \exp(-1.10 r/l)$

<sup>2</sup>  $l = 6.53 \times 10^{-6} \text{ cm}$ , at a temperature of  $20^\circ\text{C}$  and a pressure of  $760 \text{ mmHg}$ .

<sup>3</sup> The concentration of these particles is generally measured by means of expansion chambers, the first versions of which were constructed by Aitken.

a transition between the two characteristic ranges mentioned. Since their size is comparable to the wavelength of visible light these particles play a great role in the optical properties of the air. Large and giant particles have a significant inertia which can be utilized for their measurement (see below). Moreover, the giant particles and significant portion of the large particles can be studied with an optical microscope.

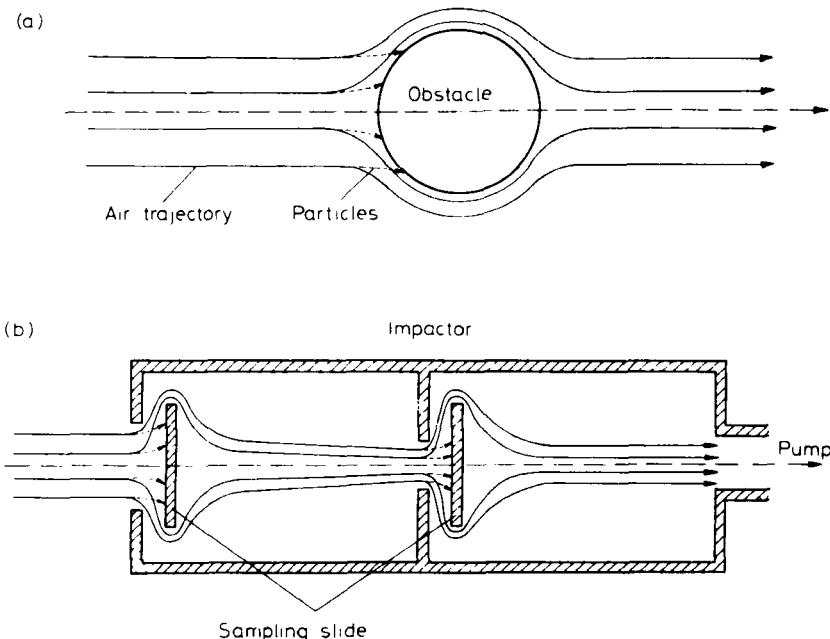
Because of their small radius, the size and size distribution (see Subsection 4.3.2) of Aitken particles may be determined with a diffusion battery. This device is composed by an ensemble of capillary tubes, through which the air is drawn at low velocity. As a result of their Brownian diffusion, the smaller aerosol particles are deposited on the walls of the tubes during the aspiration. This particle loss is a function of the diffusion coefficient and consequently of the size of the particles (see equation [4.4]).

The total number concentration of aerosol particles can be measured with expansion chambers. In these devices the air sampled is humidified and suddenly expanded to produce a significant water vapour supersaturation. In the supersaturated environment, water condenses on the aerosol particles. The number of droplets formed in this way is equal to the particle concentration. The droplets are generally counted allowing them to settle on a microscope slide or, after calibration, by the extinction of a light beam through the chamber. This type of measurement actually determines the total number concentration of particles. However, since the concentration of Aitken particles is much larger than that of large and giant particles (see later), the result essentially gives the number of particles with radius smaller than  $0.1 \mu\text{m}$ .

The smaller aerosol particles can be captured from the air for subsequent counting and size measurement by means of so-called thermal precipitators. In these instruments, metal wires are heated to produce a temperature gradient. Aerosol particles move away from the wire in the direction of a cold surface, since the impact of more energetic gas molecules from the heated side gives them a net motion in that direction. The particles captured are studied with an electron microscope. Another possible way to measure Aitken particles is by charging them electrically under well-defined conditions. The charged particles are passed through an electric field and are captured as a result of their electrical mobility (see equation [4.6]). Since size and electrical mobility are related, the size distribution of particles can be deduced. These devices are called electrical mobility analyzers.

There are several methods to detect large particles. Thus, particles can be studied *in situ* in the gaseous medium. In single particle optical counters, the particles are illuminated and the light scattered individually by each particle is measured photoelectrically at a given angle. The number of such scattering signals is a measure of the particle number while the amplitude of each signal gives, after suitable calibration, the particle size. In another type of optical device, we detect the light scattered by a cloud of particles in a fixed solid angle. In this case the counter is called an integrating nephelometer.

Generally, the large and giant particles are collected from a given air sample by inertial deposition. Inertial sampling is carried out by placing an obstacle or collector in the air stream as shown in Fig. 21(a). As can be seen the air goes around the obstacle, while the trajectory of particles with a higher inertia than the air molecules deviates from their trajectory, and the particles strike the collector. With increasing gas stream velocity, and with decreasing collector size, the radius of the particles collected decreases.<sup>4</sup> In other words this means that the efficiency of the collection (impaction) increases. The impaction efficiency "is defined as the ratio of the volume of gas cleared of particles by the collection element to the total volume swept out by the collector" (Friedlander, 1977). During aircraft sampling the collector (e.g. a microscopic slide) is exposed directly in the moving air. If the aircraft has a velocity of  $200 \text{ km hr}^{-1}$ , large particles can be captured with an acceptable efficiency on slides 0.1 mm wide. For giant particles this characteristic size is 1 mm.



**Fig. 21**  
Inertial collection of aerosol particles by an obstacle and by a two-stage impactor

In the surface air the wind speed is generally not high enough for the direct collection of large particles. However, a suitable relative velocity can be achieved by attaching the collecting slide to the end of a rotating arm. Alternatively, the air can be accelerated by pumping it into or through a tube. In this latter case the stream

<sup>4</sup> See Subsection 5.2.1.

velocity can be further increased by passing the air through narrow slits. Such a device is called an impactor; its collection efficiency is an inverse function of the slit size. A great advantage of this sampling procedure is that particles with different dimensions can be separated by means of an impactor containing slits (jets) with different sizes. Fig. 21(b) represents in a schematic way such an instrument of two stages, termed a cascade impactor. As we see the air is sucked gradually through progressively narrower slits. This allows the capture of smaller and smaller particles by the slides placed at an appropriate distance behind the jets. The particles collected are counted and their size is measured by an optical or electron microscope or they may be analyzed chemically (see Subsection 4.4.1).

The different collection procedures are combined by suitable filters consisting of fine fibers or membranes. These filters remove large and giant particles from the air by inertial impact on the fibers (e.g. glass fibers) or around the holes of membranes, while Aitken particles are collected by making use of their Brownian diffusion. If the filter material is electrically charged, electric forces have to be also taken into account. For the microscopic study of aerosol particles, the membrane filters are very suitable. These filters consist of synthetic organic membranes containing holes of approximately cylindrical form. To obtain filters with holes of uniform size, the filter mentioned is bombarded with fission recoil fragments, and the nuclear tracks are then etched out chemically (Nuclepore filters).

Experimental methods for aerosol studies have recently been reviewed by Friedlander (1977). The reader can find further details and references in his book.

#### 4.1.3 Importance of the study of atmospheric aerosol

We have mentioned several times that the study of aerosol particles contributes to the solution of many problems in atmospheric science. Figure 22 shows some of the branches of atmospheric physics that involve aerosol studies.

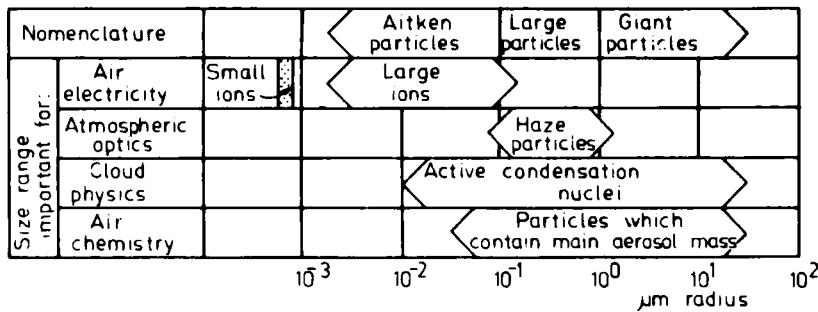


Fig. 22

Importance of particle size for various fields of meteorology (Junge, 1963). (By courtesy of Academic Press and the author)

First, aerosol particles are important from the point of view of atmospheric electricity. A fraction of the air molecules is electrically charged (small ions), as a result of ionizing radiation. Measurements show (Bricard and Pradel, 1966) that in 1 cm<sup>3</sup> of surface air about 10 ion-pairs are formed each second. Eight out of ten are produced by the radioactivity of the air and soil, while the other two are produced by cosmic radiation. The electrical properties of the air are determined by the electrical mobility ( $B$ ) of ions formed:

$$B = \frac{v}{E} \quad [4.6]$$

where  $E$  is the potential gradient, while  $v$  is the ion velocity. Small ions of opposite sign can combine with one another, or they can coagulate with existing aerosol particles. The ion mobility decreases as a result of coagulation, since the mass of aerosol particles is much greater than that of air molecules. For this reason there is an inverse relation between the aerosol concentration and the electrical mobility of the air.

It is well known that particles suspended in a gas absorb and scatter radiation. These processes depend on the size, form and composition of the particles as well as on the wavelength of the radiation. If the particle size is much smaller than the wavelength, the scattering is described by the Rayleigh theory. However, if the two parameters are of comparable magnitude the theory developed by Mie must be applied (see Friedlander, 1977). Mie scattering is particularly important in the visible range. Since the wavelength of visible light coincides with the size of the large particles, these play an important role in the control of the atmospheric visibility. Fogs and clouds are the only other major controlling factors over most of the Earth: their particle size is larger, but they exert their influence by virtue of much higher mass concentrations<sup>5</sup>. Owing to the above extinction process, large particles also play a part in the regulation of the radiation and heat balance of the Earth-atmosphere system (see Chapter 6).

Another important property of aerosol particles is their role in the atmosphere as condensation nuclei for water vapour. Potentially, all particles may be condensation centres. However, under normal atmospheric conditions only a proportion of the particles take part in the formation of clouds. According to recent studies of Twomey (1971 and 1972) the majority of active condensation nuclei consists of ammonium sulfate and have a radius of the order of 10<sup>-2</sup> µm (see Subsection 5.3.1).

It follows from this discussion that the study of properties and effects of atmospheric aerosol particles exceeds the scope of air chemistry. Considering the complexity of the problem, we restrict our discussion in the following to the presentation of formation processes and principal physical and chemical properties of background aerosol in the troposphere and stratosphere.

<sup>5</sup> In this book, except for the discussion of removal process in Chapter 5 we always deal with unsaturated air, that is, with "dry aerosol".

## 4.2 Origin of atmospheric aerosol particles

### 4.2.1 Dispersal of particles of surface origin

The majority of atmospheric particulate matter arises from two basic processes<sup>6</sup>:

- (a) dispersal of materials from the Earth's surface;
- (b) chemical reaction and condensation of atmospheric gases and vapours.

The dispersal of surface materials produces particles in two major categories: sea salt and soil or mineral particles.

Sea salt particles can be formed by the direct dispersal of the ocean water from the foam of the waves. However, these particles are generally too large to remain airborne, even after evaporation of the water. A much greater number of particles is produced by the bursting of gas bubbles reaching the water surface. According to the laboratory work of Moore and Mason (1954) this process takes place in two stages. In the first stage, when the bubble arrives to the surface, small particles are ejected from the bursting water film. In the second stage, a thin jet is formed by the water flowing into the cavity remaining in the surface after the rupture. The particles formed in the second stage are less numerous and their size are in the giant range (Woodcock, 1953).

The sea salt particles produced in this way are composed mostly of sodium chloride, which reflects the composition of sea water. Among other substances, marine particulate matter also contains a large amount of sulfates (see Subsection 3.6.2). Furthermore, during their rise through the water, bubbles scavenge a lot of surface active organic materials which are partly injected into the air when the bubbles burst (see Subsection 3.3.3).

Woodcock (1953) as well as Moore and Mason (1954) demonstrated that the rate of bubble formation increases with increasing wind speed. In more recent work A. Mészáros and Vissy (1974) reported that over the oceans the correlation between the number of sea salt particles and the wind speed becomes gradually weaker as the particle size decreases. Thus, it is not excluded that the smallest sea salt particles ( $r < 0.3 \mu\text{m}$ ) originate from a type of bubbles the formation of which is independent of the wind speed.

The relation between the bubble size and the number of airborne particles produced upon bursting was studied by Day (1963) during his laboratory investigation. He pointed out that the number of particles increases with increasing bubble size. A bubble with a size of several millimeters forms some hundreds of particles when it bursts. On the basis of his atmospheric observations made in Hawaii, Blanchard (1969) speculated that the intensity of sea salt particle formation

<sup>6</sup> Such processes as particle coagulation may also produce new large particles, but not new particulate matter.

is between  $25\text{--}100 \text{ cm}^{-2} \text{ s}^{-1}$  at the surface of the ocean. This range is in a good agreement with the laboratory results of Moore and Mason (1954).

Airborne sea salt particles are transported to higher levels and over the continents by atmospheric motions. Because of the relationship between relative humidity and particle size (see Section 4.5), low relative humidity promotes the transport of sea salt particles.

The other category of particles arise from the solid surface of the Earth. This dispersal is obviously due to the effect of wind on rocks and soils. A well-known and highly visible example of this process is the formation of dust clouds and storms. However, the quantitative explanation of this particle production mechanisms is not easy, except when some external mechanical force agitates the surface (vehicles, animals, people etc.). The main reason for the difficulties in the explanation is the decrease of the wind speed with decreasing height above the surface, usually extrapolating to zero wind speed at the surface. It is believed that turbulent flow is necessary (see Twomey, 1977) for the detachment of grains. According to the most acceptable estimates the global strength of this source is  $(100\text{--}500) \times 10^6 \text{ t yr}^{-1}$  (SMIC, 1971)<sup>7</sup>.

An important proportion of mineral particles produced by wind erosion is insoluble in water. The particles are composed of silicates (Junge, 1963). Their radius is generally greater than  $0.1\text{--}0.5 \mu\text{m}$ . Some particles are removed from the air in the vicinity of sources, while another fraction is transported at great distances. This has been proved by the analyses of snow and ice in Greenland, which reveals potassium and calcium in concentrations that cannot be interpreted by the effect of maritime particles (Junge, 1963). Furthermore, particulate matter collected over the Atlantic Ocean contains a significant quantity of Saharan dust under some conditions (Junge and Jaenicke, 1971); in fact, such dust particles were collected and identified even over the West Indies (Prospero, 1968; Blifford, 1970).

#### 4.2.2 Formation of atmospheric aerosol particles by chemical reaction and condensation

Particles formed by the dispersal of surface materials generally have radii larger than about  $0.1 \mu\text{m}$ . This means that Aitken-size particles must be produced by another mechanism, namely by condensation of vapours, preceded in many cases by gaseous chemical reactions. These reactions are generally initiated by photochemical processes.

Thus, a large set of data obtained by McWilliams (1969) in clean air (W. Ireland) by means of expansion chambers showed that the concentration of Aitken particles is lower in the winter than in the summertime. Furthermore, McWilliams' observations also demonstrated that more aerosol particles can be detected during daylight than at night. This finding was confirmed by the investigations of Vohra *et*

<sup>7</sup> SMIC: Study of Man's Impact on Climate.

*al.* (1970) and A. Mészáros and Vissy (1974) according to which, in a clean maritime environment, the number of Aitken particles is at a maximum during the afternoon. It was also shown by atmospheric measurements (e.g. Lopez *et al.*, 1973) that after sunrise the aerosol concentration increases, which also points in the direction that particles with radii smaller than  $0.1 \mu\text{m}$  are produced by photochemical reactions. Recently, Hogan and Bernard (1978) have reported that over Antarctica there is a steady increase in the concentration after astronomical sunrise. Moreover, in Antarctic winter very small concentrations can be measured.

The formation of aerosol particles from gaseous components is appropriately investigated under laboratory conditions. In so-called aerosol chambers an artificial atmosphere is created to which small quantities of appropriate trace gases (e.g.  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and organics) is added. It is also possible to use ambient air purified from particulate matter. The chamber may be illuminated to initiate photochemical processes, and the behaviour of particles formed is studied by the methods outlined in Subsection 4.1.2, e.g. by electrical mobility analyzers (Whitby *et al.*, 1972).

An important result from aerosol chamber studies was the discovery of the indirect photochemical process. Thus, Bricard *et al.* (1968) found that intense aerosol particle production can be observed in the chamber in the dark if ambient filtered air is sampled from a sunlit atmosphere. It is speculated that in the atmosphere some gaseous substance is excited by sunlight and is not collected by the filter used to obtain air which is free of aerosol particles. In the chamber these photochemically excited molecules initiate secondary thermal reactions leading to the formation of some supersaturated vapour (e.g.  $\text{H}_2\text{SO}_4$ ) which subsequently condenses (see also Subsection 3.6.3).

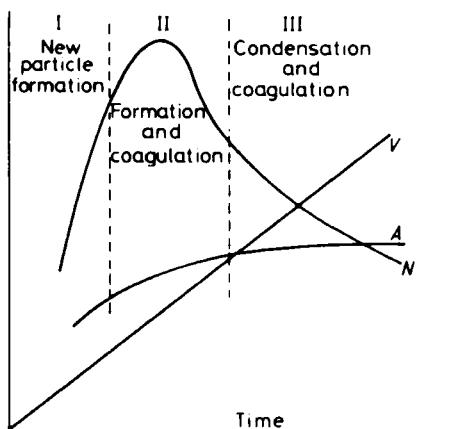


Fig. 23

Aerosol formation in an irradiated chamber (Friedlander, 1978).  $N$ : particle number;  $V$ : volume of particles;  $A$ : total particle surface. (By courtesy of *Atmospheric Environment*)

It was also demonstrated by aerosol chamber investigations that the behaviour of particles formed by condensation varies as a function of time. Figure 23 reproduces schematically the change in particle number ( $N$ ), particle surface ( $A$ ) and particle volume ( $V$ ) according to Friedlander (1978). The curves are based on irradiation chamber experiments by Husar and Whitby (1973). It can be seen that three separate domains are identified. In domain I the formation of new particles is the dominant process. In this stage the number, surface and volume of particles all steadily increase. With increase in particle number (domain II) coagulation becomes more and more important (see Subsection 4.1.1). When the  $N$  curve has a maximum the coagulation loss just balances the particle formation rate. In domain III coagulation and condensation of the vapour on existing particles are the dominant processes. The number concentration decreases in this time interval, while particle volume further increases. The value of the surface area remains approximately constant.

A good atmospheric example of the above particle formation is the production of sulfate particles from gaseous precursors (see Subsection 3.6.3). It is further believed that the smaller organic particles discussed in Subsection 3.3.3 are also formed by gas-to-particle conversion. However, a large quantity of aerosol particles can form during the cooling of vapours with low saturation pressure, which are produced by combustion processes. This aerosol formation is obvious in urban and industrial environments. However, natural forest, brush and grass fires also provide an important atmospheric aerosol particle source (see Cadle, 1973).

The formation rate of small Aitken-size aerosol particles in the atmosphere was estimated by Lopez *et al.* (1974) on the basis of their aircraft measurements carried out over S. W. France. They argued that in an air column with base area of  $1 \text{ cm}^2$   $3 \times 10^4$  particles are formed each second. A quarter of this quantity is due to human activity. In a more recent paper Bigg and Turvey (1978) speculate that the natural particle production rate is only  $170 \text{ cm}^{-2} \text{ s}^{-1}$ , two orders of magnitude smaller than the above estimate. Bigg and Turvey establish this rate by using the results of their observations, carried out over Australia, together with an acceptable residence time of  $3 \times 10^5 \text{ s}$ . It follows from this figure that the total Australian source strength is about  $10^{19} \text{ s}^{-1}$ . This may be compared with the total particle flux of  $4 \times 10^{19} \text{ s}^{-1}$  produced by only one industrial area (Perth) which exceeds the global natural emission of the continent! The present author feels that the natural production rate proposed by Lopez *et al.* (1974) is too high, while Bigg and Turvey's value is too low, at least for the European continent. Thus, according to Selezneva (1966), who made a large number of aircraft measurements over the European part of Soviet Union, the particle number is  $6 \times 10^8 \text{ cm}^{-2}$  in a tropospheric air column. Using a residence time of  $3 \times 10^5 \text{ s}$ , we calculate an acceptable production rate of  $2 \times 10^3 \text{ cm}^{-2} \text{ s}^{-1}$ .

#### 4.2.3 Other formation mechanisms

Besides the major aerosol formation mechanisms discussed in the previous section other processes also produce atmospheric particles. The strength of these sources can be neglected on global scale. However, the effect of particles formed in

these ways may be important under special conditions. For this reason these sources are briefly enumerated in this subsection.

First of all, volcanic activity must be mentioned; it introduces both gases (see Section 2.3 and Subsection 3.6.2) and particles into the atmosphere. The particles play an important temporary role in the control of atmospheric optical properties and radiation balance. Thus, after the eruption of Krakatoa in 1883 unusual darkness was observed over Batavia and the height of the volcanic cloud reached the altitude of nearly 30 km (18 miles). After the violent eruption of the Agung volcano in 1963 the optical effect of ash particles was identified at several points of the Earth and a temperature increase of 2 °C was measured in the stratosphere (see Cadle, 1973) due to the radiation absorption of particles. While an important part of volcanic particulate matter consists of dispersed lava, sulfuric acid also was detected in volcanic fume (Cadle, 1973).

Another special class of particles is meteoritic dust of cosmic origin. Smaller meteoritic particles ( $r < 1 \mu\text{m}$ ) can reach the lower layers of the atmosphere without significant modifications. However, larger meteorites falling through the atmosphere partly or totally evaporate due to frictional heating. In the troposphere, spherical droplets from the condensation of the resulting vapour can be identified (e.g. Wirth and Prodi, 1972). Pettersson estimates (see Cadle, 1973) that  $14 \times 10^6 \text{ t}$  of meteoritic materials are collected annually by the atmosphere of our planet.

It is believed by some workers that meteoritic particles may play an important role in the formation of precipitation, since they serve as ice forming nuclei in clouds of appropriate negative temperatures. Since ice crystal formation may initiate precipitation formation in mixed clouds (i.e. clouds containing liquid as well as solid phase), Bowen argues (see Fletcher, 1962) that the distribution of precipitation is controlled to some degree by meteor showers reaching the atmosphere. It is to be noted, however, that this theory is far from generally accepted by cloud physicists (Fletcher, 1962).

Finally, many viruses, bacteria, pollens and spores can be found in the lower atmosphere. The size of viruses and bacteria is small, while the pollens and spores are in the giant size range. According to A. Mészáros (1977), on an average 20 % of the giant particles in clean continental air are composed of pollen and spores during the appropriate seasons. The biological importance of these airborne materials is obvious.

#### 4.2.4 Comparison of the strength of different aerosol sources

The strength of various natural and anthropogenic aerosol sources is tabulated in Table 17 (SMIC, 1971). The precision of estimates is represented by the intervals given. For further details, the interested reader is referred to the original work.

The most important fact emerging from the data given is the ratio of the intensity of anthropogenic sources to the strength of natural production mechanisms. It can be seen that on a mass basis emission by natural sources exceeds anthropogenic

production by a factor of 4–5. The other essential thing shown by the table is the importance of gas-to-particle conversion in the formation of aerosol particles. The fraction of particles formed by gaseous reactions is particularly significant in the case of man-made emissions.

**Table 17**

Formation rate of atmospheric aerosol particles with radii smaller than 20 µm (SMIC, 1971)

<i>Natural aerosol sources</i>	
Soil and rock debris*	100–500
Forest fires and slash-burning*	3–150
Sea salt	(300)
Volcanic debris	25–150
Particles formed from gases	
Sulfate from H <sub>2</sub> S	130–200
Ammonium salts from NH <sub>3</sub>	80–270
Nitrate from NO <sub>x</sub>	60–430
Hydrocarbons from plants	75–200
<b>Subtotal</b>	<b>773–2200</b>
<i>Man-made aerosol sources</i>	
Particles (direct emission)	10– 90
Particles formed from gases	
Sulfate from SO <sub>2</sub>	130–200
Nitrate from NO <sub>x</sub>	30– 35
Hydrocarbons	15– 90
<b>Subtotal</b>	<b>185–415</b>
<b>Total</b>	<b>958–2615</b>

*Note:* Values are expressed in 10<sup>6</sup> t yr<sup>-1</sup>. Asterisk denotes unknown amounts of indirect man-made contributions

### 4.3 Concentration and size distribution of atmospheric aerosol particles

#### 4.3.1 Concentration and vertical distribution of Aitken particles

We can characterize the particle concentration of an aerosol in two different ways. Firstly, the number concentration can be employed which is the number of the particles in a unit gas volume. Secondly, like the concentration of trace gases, the particle mass in a unit volume (mass concentration) can be given as we have seen in Chapter 3. In this subsection we will always use the number concentration of all particles which is practically equivalent to the number of Aitken size particles (see

Subsection 4.1.2). All values discussed in the following were obtained using expansion chambers.

The early results of particle concentration measurements carried out under different conditions were compiled by Landsberg (see Junge, 1963). Some of his data are reproduced in Table 18. The figures tabulated make it evident that the majority of particles are of continental origin. It is also obvious that man's activity plays an important role in particle production. Furthermore, one can see from Table 18 that the number concentration of atmospheric aerosol particles decreases with increasing height.

**Table 18**

Average concentration of Aitken particles under various conditions according to Landsberg (see Junge, 1963)

Location	Number of observations	Average concentration cm <sup>-3</sup>
Cities	2500	147 000
Towns	4700	34 300
Country	3500	9 500
Sea shore	7700	9 500
Mountains		
500-1000 m	870	6 000
1000-2000 m	1000	2 130
2000 m	190	950
Islands	480	9 200
Oceans	600	940

More recent observations demonstrated that in remote oceanic and continental areas smaller concentrations can be measured than those listed in the table. Thus, according to Junge and Jaenicke (1971) over the northern Atlantic Ocean the concentration is  $600 \text{ cm}^{-3}$  on an average. Hogan *et al.* (1973) suggest that the lowest concentrations in the surface air over the North Atlantic can be measured between 20–25° N and 30–50° W. Over this area the mean value is only about  $300 \text{ cm}^{-3}$ . In clean oceanic air of the Southern Hemisphere a smaller average concentration ( $\sim 400 \text{ cm}^{-3}$ ) can be detected (A. Mészáros and Vissz, 1974) than the value reported by Junge and Jaenicke (1971). Moreover, according to information published by Japanese workers (Ohta and Ito, 1974), concentrations are generally between  $150\text{--}200 \text{ cm}^{-3}$  over the Pacific Ocean. Recent results obtained by Hogan and Bernard (1978) over Antarctica demonstrate that the concentration is less than  $50 \text{ cm}^{-3}$  in wintertime. During Antarctic summer the number of aerosol particles is around  $100\text{--}200 \text{ cm}^{-3}$  in agreement with the findings of Ohta and Ito (1974).

It is questionable whether the higher values reported for the Northern Atlantic Ocean are caused by anthropogenic pollutant emissions. Unfortunately, it is very

difficult to answer to this important question, since we have no suitable homogeneous data sets to estimate possible secular concentration trends. However, some information is available concerning variations in the electrical mobility of the air over different oceans. These data show (Cobb and Wells, 1970) that electrical mobility of the surface air over the northern part of the Atlantic Ocean decreased by a factor of 2 during the last 70 years. In contrast this electrical parameter remained constant over the southern regions of the Pacific Ocean. Taking into account the relation between electrical mobility and aerosol particle concentration (Subsection 4.1.3) this finding suggests that the particle number concentration doubled during this century in remote areas of the Northern Hemisphere.

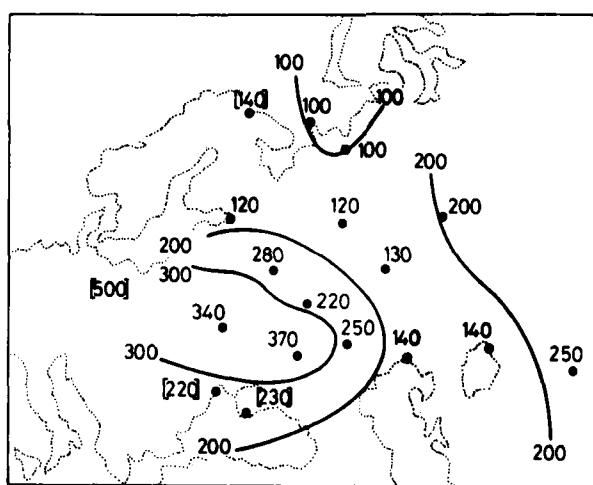
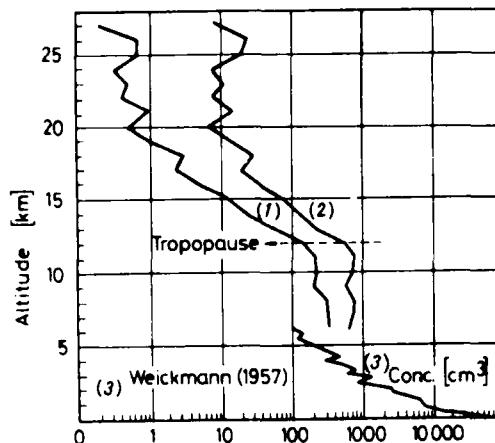


Fig. 24  
Spatial distribution of the concentration of the Aitken particles at 3000 m over the European part of the U.S.S.R. (Selezneva, 1966). (By courtesy of *Tellus*)

The vertical profile of aerosol particle concentration in the troposphere was widely studied by Soviet research workers. A great number of data obtained by aircraft flights is reviewed by Selezneva (1966). Her compilation indicates that on average the concentration drops to one-fourth of its ground level value at an altitude of 900 m on an average, and that above 3000–4000 m the particle number becomes constant. Selezneva speculates that this vertical distribution is mostly controlled by atmospheric exchange and particle coagulation (flights were made generally under weather situations without precipitation). In Fig. 24 the average results at 3000 m altitude are plotted. One can see that concentrations increase with increasing continental source density. It can also be seen that the concentrations measured at this altitude agree well with those reported for remote oceanic surface air (see above). This means that, except the first few kilometers above the continents,

the troposphere is filled with aerosol particles of the same concentration. Disregarding sea salt particles of small number concentration, the composition of this aerosol, termed the tropospheric background aerosol (Junge, 1963), is also independent of place and time (see Section 4.4).



**Fig. 25**

Vertical profile of Aitken particles according to Junge (1963) and Weickmann (1957). (1) under ambient conditions; (2) at standard temperature and pressure. (By courtesy of Academic Press and Junge)

The concentration of aerosol particles in the stratosphere was firstly measured by Junge (1963) by balloon flights over the Central U.S.A. He found (see Fig. 25) that the number of aerosol particles, in agreement with the Soviet data discussed above, does not change with altitude in the upper troposphere. This constant concentration is around  $300 \text{ cm}^{-3}$ . Above the tropopause the concentration rapidly decreases with increasing height. Since the character of the vertical profile plotted in Fig. 25 was more recently confirmed by several workers (e.g. Käselau *et al.*, 1974; Podzimek *et al.*, 1977), it can be considered acceptable for use in further studies. On the basis of the stratospheric concentration distribution, it is believed that particles in this atmospheric domain may be of tropospheric origin. However, it is also possible that stratospheric Aitken particles, formed *in situ* by gaseous reactions, coagulate to create the stratospheric aerosol layer consisting of large particles.

#### 4.3.2 The size distribution

Since the size of atmospheric particles covers several orders of magnitude (see Subsection 4.1.1) the concentration alone is not sufficient to characterize atmospheric particles. For more complete aerosol characterization the size

distribution function must be used, which is defined as follows (Fuchs, 1964):

$$\frac{1}{N} \frac{dN}{dr} = f(r) \quad [4.7]$$

where  $N$  is the total number concentration while  $dN$  is the same parameter for particles with radius between  $r$  and  $r+dr$ . It follows from [4.7] that

$$\int_0^r f(r) dr = 1 \quad [4.8]$$

It is obvious that a similar size distribution function can be given for the surface, volume and mass of aerosol particles. Thus, e.g. the volume concentration (aerosol volume per unit volume of air) distributes according to particle radius in the following way:

$$\frac{1}{V} \frac{dV}{dr} = F(r) \quad [4.9]$$

with the condition

$$\int_0^r F(r) dr = 1 \quad [4.10]$$

It goes without saying that the number size distribution may be converted to volume size distribution, given an assumed particle shape. Furthermore by using a constant particle density the size distribution of particle mass can be calculated from equation [4.9] by a simple calculation.

It is customary, in the interconversion of these distribution functions, to assume that the particles are spherical; this simplifies the mathematics, but is somewhat questionable physically. The method of measurement determines the nature of the reported radii of these hypothetical spheres; e.g. in the case of microscopic sizing, the so-called "surface radius" is obtained, which is the radius of a circle having the same surface area as the orthogonal projection of the particle.

On the basis of his atmospheric impactor measurements Junge (1963) proposed a power law to describe the size distribution of large and giant particles:

$$\frac{dN}{dr} = C_1 r^{-(\beta + 1)} \quad [4.11]$$

where  $C_1$  and  $\beta$  are constant. Considering the large range of particle size, equation [4.11] is best rewritten in the following form:

$$\frac{dN}{d \log r} = C_2 r^{-\beta} \quad [4.12]$$

In this formula  $C_2$  is a function of concentration, while  $\beta$  characterizes the slope of the distribution curve. According to Junge (1963),  $\beta$  is about 3 under continental conditions.

More recently, Whitby (1978) has analyzed the results of much more numerous size distribution observations carried out mainly by his group who used a combination of expansion chamber, electrical mobility and optical counter techniques. This analysis clearly shows that the complete size distribution is composed of three separate log-normal distributions as demonstrated in Fig. 26. Whitby speculates that the first distribution, the nuclei mode, is controlled by the condensation of vapour, (predominantly  $H_2SO_4$ ) formed by chemical reactions. Thus, the concentration of these small particles was found to be very significant in irradiated polluted atmosphere. On the other hand, the so-called accumulation

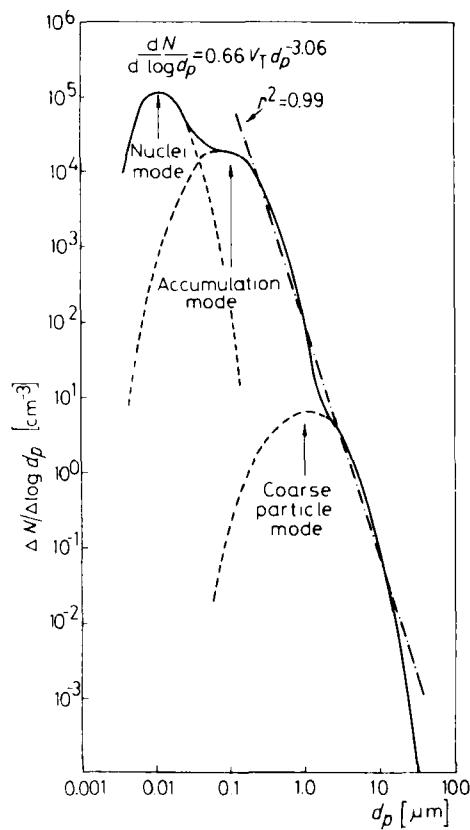


Fig. 26

Number size distribution of aerosol particles under urban conditions according to Whitby (1978).  $N$ : number of particles;  $d_p$ : diameter of particles;  $V_T$ : total volume concentration;  $r$ : correlation coefficient between power law given in the figure and experimental data. (By courtesy of *Atmospheric Environment*)

mode is due to the coagulation of primary particles or to the vapour condensation on secondary particles formed by coagulation or on existing aerosol particles. It follows from this idea that the accumulation mode is a consequence of aging of the primary aerosol. In the air far from gaseous sources the nucleation mode may well be partly or totally missing. The third log-normal distribution consists of particles formed mostly by mechanical disintegration of the material of the Earth's surface. This is the coarse particle mode, which is independent of the first two distributions. For this reason the chemical composition of the coarse particles is different from the composition of the smaller particles (see later), called "fine" particles.

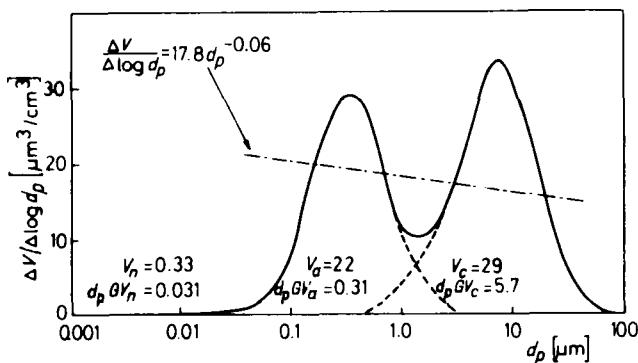


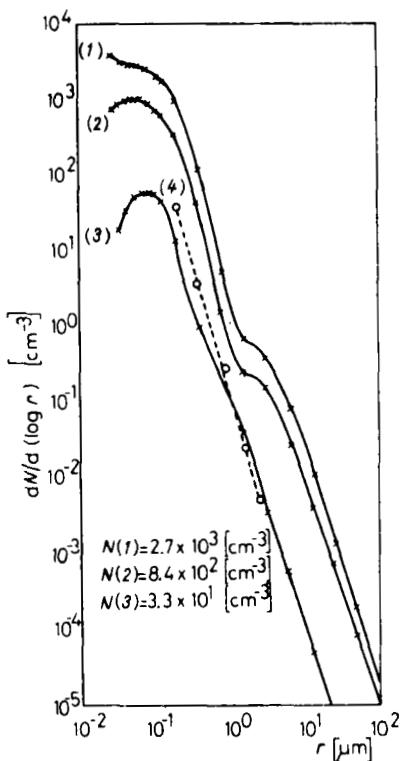
Fig. 27

Size distribution of the volume of aerosol particles (solid line) according to Whitby (1978). Dotted line corresponds to the power law of Fig. 26.  $V$ : particle volume;  $n$ : nuclei mode  $a$ : accumulation mode;  $c$ : coarse particle mode;  $d_p GV$ : geometric volume mean size. (By courtesy of *Atmospheric Environment*)

To gain further insight into the character of particle size distribution, the volume distribution calculated from the curve of Fig. 26 is also presented in Fig. 27. It can be seen that on a volume basis the nuclei mode, which determines the particle number, cannot be identified owing to the small size of the primary particles. One can also see that a large fraction of the aerosol mass is found in the range of coarse particles. However, the mass of particles in the accumulation mode is also significant. In our case the particle volume in the two modes is nearly the same. Generally speaking 2/3 of the total mass is in the coarse and 1/3 in the accumulation mode. Finally, Figs 26 and 27 show that, while the number size distribution of large and giant particles can be well approximated by the power law, Junge's formula is very poor for characterizing the volume distribution. In other words this means that minor deviations from the power law in the number distribution cause significant deviations in the volume distribution.

It should be mentioned that the size distributions presented in Figs 26 and 27 are typical of a polluted atmosphere. Unfortunately, very little information is available about the background aerosol filling 80–90 % of the troposphere. These

background particles can be studied over oceanic areas remote from continents if we disregard sea salt particles. The other possibility for such a study is the direct sampling above a height of about 5 km in the troposphere. Examples of the first method are provided by the work of Junge and Jaenicke (1971), A. Mészáros and Vissz (1974) and Tymen *et al.* (1975).



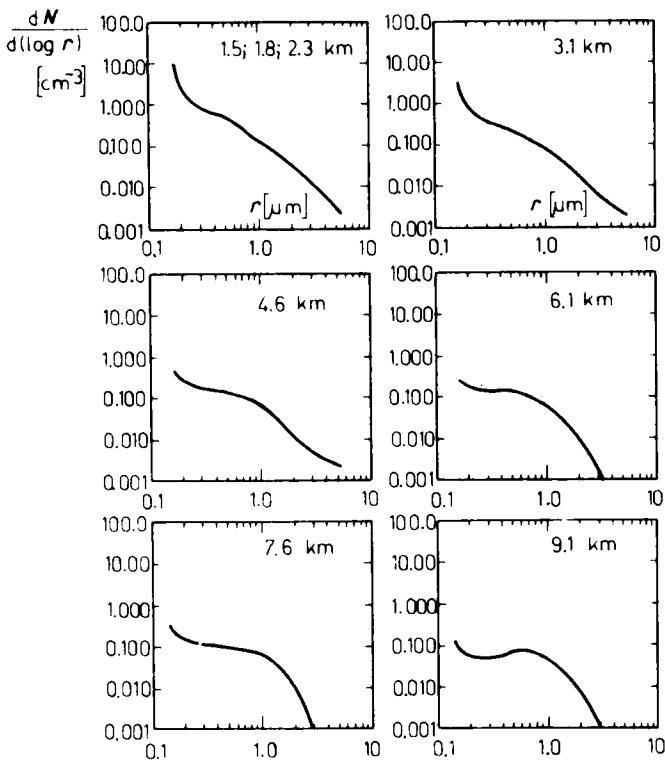
**Fig. 28**

Size distribution of atmospheric aerosol particles under various conditions. (1): urban (2): continental; (3): tropospheric background; (4): continental at 3000 m above inversions;  $N$ : total number of particles with radius larger than 0.03  $\mu\text{m}$ . (Data of A. Mészáros)

Curve 3 of Fig. 28 represents the size distribution of atmospheric aerosol particles obtained by A. Mészáros and Vissz (1974) from samples collected on membrane filters over the oceans of the Southern Hemisphere. The samples were evaluated by optical and electron microscopy in the radius range of 0.03–64  $\mu\text{m}$ <sup>8</sup>. The total concentration of these particles is also shown. It can be seen that the maximum of the distribution occurs around 0.1  $\mu\text{m}$  radius, a value in the range of the

<sup>8</sup> This means that the nuclei mode was not studied.

accumulation mode. The coarse mode is practically missing since the curve does not contain the distribution of sea salt particles (see later). It should be mentioned that the form of this spectrum agrees fairly well with the distributions found over the North Atlantic by other workers (Junge and Jaenicke, 1971; Tymen *et al.*, 1975). However, the maximum of the distribution over the Northern Hemisphere is shifted to smaller sizes probably as a result of indirect anthropogenic effects. We have to note in this respect that Junge and Jaenicke (1971) identified, by the diffusion channel technique, another maximum in the aerosol particle spectrum below 0.01  $\mu\text{m}$  which proves the presence of primary particles formed by reaction and subsequent condensation (nuclei mode). No such measurements were performed by A. Mészáros and Vissny (1974). However, comparison between the concentration of particles with radii larger than 0.03  $\mu\text{m}$  and the total particle concentration ( $\approx 400 \text{ cm}^{-3}$ ) make evident the presence of the nuclei mode even over the Southern Hemisphere.



**Fig. 29**

Size distribution of large and giant particles at various altitudes (Blifford, 1970). (By courtesy of the American Geophysical Union)

Also shown in Fig. 28 are three other size distributions. Curve 1 was measured near Budapest, Hungary in a locally polluted atmosphere (A. Mészáros, 1977), while spectrum 2 refers to rural air, also in Hungary. Finally, the curve labelled 4 is the size distribution of large and giant particles observed at an altitude of 3 km above inversion layers over Central Europe by A. Mészáros (1969). It is seen by comparing these size distributions that the aerosol structure varies considerably as a function of the pollution of the place considered. The difference between curves 1 and 3 is particularly great in the range of smaller particles. The coarse particle mode is also evident in distributions 1 and 2. The concentration of coarse (or giant) particles is  $0.40$  and  $0.12 \text{ cm}^{-3}$ , respectively. Unfortunately, when distribution 4 was measured, only optical microscopic evaluation was made. However, comparison of curves 3 and 4 shows that the distribution of large and giant particles at an altitude of 3 km over continents practically coincides with the spectrum of aerosol particles measured in remote oceanic areas. This fact also supports the concept of a tropospheric background aerosol.

In the upper troposphere the size distribution of large and giant particles was investigated by Soviet (Kondratyev *et al.*, 1969) and American (Blifford, 1970) research workers. Particles were collected by impactors in both cases. Figure 29 shows Blifford's size distributions for different altitudes, obtained over Nebraska, U.S.A. An interesting feature emerging from the distributions presented is the decrease in the steepness of the slope in the distributions (that is the value of  $\beta$  in equation [4.12] decreases). It is very difficult to explain this peculiarity of aerosol behaviour. However, it is believed that the removal of aerosol particles by cloud elements (Chapter 5) plays an important role in control of the size distribution of aerosol particles in the troposphere.

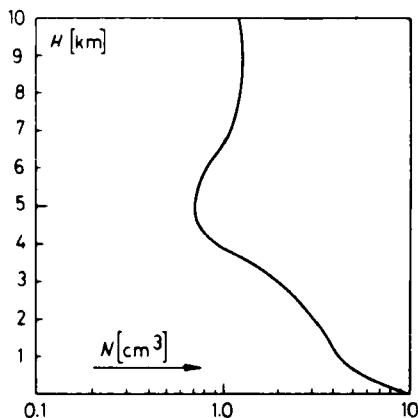


Fig. 30

Vertical distribution of the concentration of large particles according to Blifford (1970).  $H$ : height;  $N$ : number concentration. (By courtesy of the American Geophysical Union)

#### 4.3.3 Concentration and vertical profile of large and giant particles

A vertical profile of the concentration of large and giant particles was constructed on the basis of two profiles by Blifford (1970), measured over California. Blifford's vertical distributions are based on the results of 12 flights. His two curves were averaged and smoothed. The resulting curve is plotted as Fig. 30. It can be seen that the shape of the vertical profile of large and giant particles in the troposphere is practically the same as that of Aitken particles (see also Fig. 25). In the lower troposphere the concentration decreases with increasing height, while in the upper troposphere a practically constant concentration of  $1\text{--}2 \text{ cm}^{-3}$  is found.

The stratospheric profile of the concentration of large and giant aerosol particles was first studied by Junge and his co-workers (see Junge, 1963) by means of impactors lifted by balloons and aircraft. These studies demonstrated that between 15–20 km a concentration maximum can be observed. This finding is very interesting in view of the fact that the profile of Aitken particles showed no such maximum at that time (around 1960). It was also shown by measurements (see Subsection 4.4.3) that these large particles are composed of sulfates apparently formed *in situ* from gaseous sulfur compounds.

Since its discovery the existence of the stratospheric aerosol layer has been proved by many investigators (e.g. Mossop, 1965; Friend, 1966; Kondratyev *et al.*, 1969). A mathematical model of the particles in the aerosol layer, constructed by Friend (1966), led to a size distribution with a maximum in the vicinity of  $0.3 \mu\text{m}$  particle radius. However, according to the results of more recent measurements by Bigg (1976) the actual distribution has its maximum at smaller sizes. The observations of Kondratyev *et al.* (1974) show that the stratospheric concentration of aerosol particles with radii larger than  $0.2 \mu\text{m}$  may be as great as  $1 \text{ cm}^{-3}$ . However, this concentration is strongly time dependent (Bigg, 1976) as we shall discuss in Subsection 4.4.3.

### 4.4 Chemical composition of atmospheric aerosol particles

#### 4.4.1 The main methods of the identification

Effects of the atmospheric aerosol depend not only on the concentration and size but also on the chemical composition of particles. For this reason the study of the chemical nature of particulate matter in the atmosphere is of crucial importance. This study is rather complicated because of the small mass and concentration of the particles. Furthermore, due to coagulation, condensation and gas adsorption processes, one particle can contain several different materials, that is, the aerosol is internally mixed<sup>9</sup>.

<sup>9</sup> By contrast, an external mixture contains particles, each of which is composed of a pure substance.

There are at least four different classes of methods of identifying the chemical nature of particles in the atmosphere. In the first three classes, particles are captured from the air, and the composition of the sample is subsequently determined. The first procedure (Lodge, 1962) consists of the collection of particles on a substrate sensitized chemically before (e.g. gelatin layers) or after (e.g. membrane filters) the sampling. The reaction spots produced by each particle can be studied individually under a microscope. This is called a single particle method. In the second procedure (bulk analysis, see Lodge, 1962) particles are collected on chemically inert impactor slides or filters. The samples are washed off of the substrate by appropriate solvents and the solution obtained is analyzed by standard wet chemistry. Although the chemical nature of individual particles is missed in this way, bulk analysis can determine the composition of very small internally mixed particles. Despite the fact that size information is lost when the particles are dissolved the size distribution can be estimated by separating particles according to their size during sampling, e.g. by cascade impactors and suitable filters.

Modern bulk analysis methods make possible non-destructive chemical identification, which means that the sample remains intact after the analysis. Such a procedure is provided by electron microprobe or X-ray fluorescence analyses, in which the sample is irradiated by electron beams or X-rays and the elemental composition is determined on the basis of induced characteristic X-ray emissions. These methods have been successfully employed to study both stratospheric (Junge, 1963) and tropospheric (Gillette and Blifford, 1971) aerosol particles. Neutron activation analysis is also widely used to identify the chemical composition of atmospheric particulate matter (e.g. Duce *et al.*, 1966; Rahn *et al.*, 1971); this is also a non-destructive procedure.

The third major class of analytical techniques may be called morphological methods. This identification consists of comparing the form of particles captured with the morphology of particles of known composition. It goes without saying that morphological similarity is a necessary but not always sufficient condition for compositional identity. In spite of this problem this procedure is widely employed mainly in clean atmosphere, since even Aitken size particles can be identified morphologically (A. Mészáros and Vissy, 1974; Butor, 1976).

In the fourth type of identification the chemical composition of particles is studied *in situ*. By suitable chemical aerosol instruments the concentration and the size distribution of certain elements can be continuously monitored. The flame photometry of sodium containing particles (e.g. Hobbs, 1971) is a good example for such a method. Recently flame photometric detectors have also been developed to measure aerosol sulfur in the atmosphere (e.g. Kittelson *et al.*, 1978).

#### 4.4.2 Chemical composition of tropospheric aerosols

The chemical composition of aerosol particles in the troposphere results from the interaction of many formation and dynamic (e.g. coagulation) processes. For this reason particles are often composed of several materials and the composition varies

Table 19

The relative composition of aerosol particles expressed in percentage of total mass at two locations in California (Hidy *et al.*, 1975)

Components (Origin)	Pasadena	Pomona
	Total mass = 79 $\mu\text{g m}^{-3}$	Total mass = 178 $\mu\text{g m}^{-3}$
Organics	43	24
Sulfate	4	13
Nitrate	5	26
Natural (sea salt, soils)	11	8
Indust., cement dust	9	3
Transportation	12	6
Ammonium	?	10
Water	16	10
Total	100	100

as a function of time and location. The nature of the particulate matter is complicated in particular under locally polluted urban conditions. Table 19 gives the main aerosol components as measured at two sites during the California Aerosol Characterization Experiment (Hidy *et al.*, 1975). It is seen that carbon (organics), nitrogen and sulfur compounds<sup>10</sup> formed from gaseous precursors in the air constitute an important part of the particulate matter. This Experiment also has shown that the aerosol mass in the accumulation mode (see Fig. 27) is composed mostly of carbon, nitrogen and sulfur compounds. At the same time lead, vanadium and bromine can also be identified in the range of fine particles. However, particles in the coarse mode (giant particles) consist mainly of silicon, aluminium, iron, and titanium as well as of sea salt components (sodium, chloride etc.) in accordance with formation processes discussed in Section 4.2<sup>11</sup>.

The investigation of the composition of background aerosol started with the classical measurements of Junge (1963), who collected particles with a two-stage cascade impactor, the two stages corresponded respectively to the large and giant size ranges. Samples were washed off of the collecting surface with a small quantity of distilled water, and the ions dissolved were analyzed by microchemical methods (bulk analysis). The results of these early studies demonstrated that in the Federal Republic of Germany as well as at maritime locations of eastern U.S.A. (Round Hill and Florida) the majority of the water soluble fraction of large particles consists of ammonium sulfate. In the size range of giant particles the mass of sulfate and

<sup>10</sup> It is to be noted that nitrate ions are found in larger particles than sulfur and carbon species.

<sup>11</sup> Detailed discussion of the chemical composition of aerosol particles as a function of particle size in polluted atmosphere can be found in the review of Corn (1976).

ammonium ions was found to be smaller than in the large range, and an important part of the water soluble substances were composed of chloride.

Later Junge (1963) also studied the composition of water soluble particulate materials in Hawaii. Figures 31 and 32 show his results in the large and giant size ranges, respectively, as a function of geographical location. In these figures from left to right the environment becomes gradually less polluted. The first evidence emerging from Fig. 31 is that under continental conditions the concentrations of the ions measured are greater than in maritime environment.<sup>12</sup> This is caused essentially by the effect of anthropogenic gaseous sources. Furthermore, the chloride concentration is greater in Hawaii than in Florida which can be explained by the increasing mass concentration of sea salt particles.

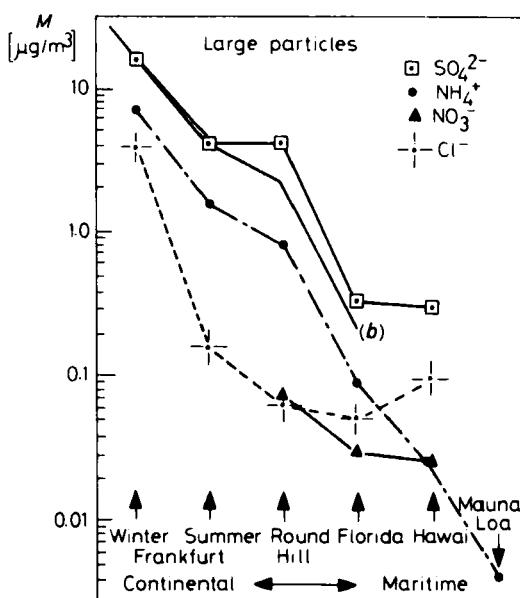


Fig. 31

Mass concentration ( $M$ ) of various soluble components in the large particle size range under different geographical conditions (Junge, 1963). Curve (b) gives sulfate concentrations calculated from ammonium concentrations and the stoichiometric ratio of  $\text{SO}_4^{2-}$  to  $\text{NH}_4^+$  in ammonium sulfate (By courtesy of Academic Press and the author)

<sup>12</sup> It can be also seen that the winter concentration of  $\text{SO}_4^{2-}$  is higher than the summer value. This seems to be in contradiction with findings reported in Subsection 3.6.4 indicating higher sulfate levels in spring or in summer. We have to emphasize that this latter fact is true only for the total concentration. In winter, due to higher relative humidities, an important part of Aitken size particles grows into the large range (E. Mészáros, 1970) showing an apparent seasonal variation in the sulfate concentration of large particles (see also Section 4.5).

The curve labelled *b* gives calculated sulfate quantities from measured  $\text{NH}_4^+$  concentrations and the stoichiometric ratio of  $\text{SO}_4^{2-}$  to  $\text{NH}_4^+$  in ammonium sulfate. In the large size range this practically coincides with the measured sulfate values indicating that the particles are composed of  $(\text{NH}_4)_2\text{SO}_4$ .

The most important difference between large and giant particles is that in the giant size range the chloride concentration steadily increases in the direction of more maritime environments. This finding indicates that an important fraction of the giant chloride particles is of maritime origin even over the continents. It also follows from this difference that the majority of the sea salt mass exists in particles with radius larger than 1  $\mu\text{m}$ , while chloride particles in the large size range may be of continental (anthropogenic) origin. Moreover, comparison of Figs 31 and 32 indicates that the mass of nitrate ions in giant particles is greater than in the large range (Round Hill, Florida and Hawaii). This finding can be explained by the interaction of gaseous  $\text{NO}_x$  and sea salt particles, as discussed in Subsection 3.5.4. Finally, we can see from Fig. 32 that Junge measured more sulfate in the giant size range than the quantities predicted on the basis of ammonium concentrations.

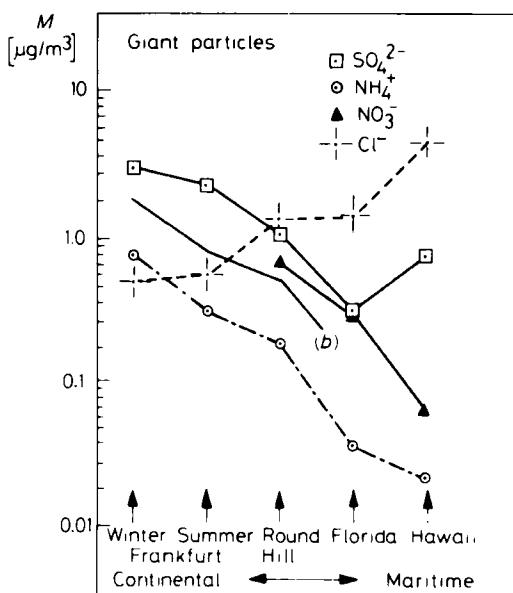


Fig. 32

Mass concentration (*M*) of various soluble components in the giant particle size range under different geographical conditions (Junge, 1963). Curve (*b*) gives sulfate concentrations calculated from ammonium concentrations and the stoichiometric ratio of  $\text{SO}_4^{2-}$  to  $\text{NH}_4^+$  in ammonium sulfate. (By courtesy of Academic Press and the author)

It should be mentioned that Junge (1963) also performed sodium, magnesium and nitrite analyses of his aerosol samples. No nitrite ion was found and the concentration of magnesium was also rather insignificant. In contrast, he identified a relatively large amount of sodium in the giant range when the air was of maritime origin.

Table 20

Size distribution of the mass of various ions in percentage of the total mass of the ion considered  
(E. Mészáros, 1968)

Size range	$\text{NH}_4^+$	$\text{SO}_4^{2-}$	$\text{Cl}^-$
Giant	8	12	33
Large	45	45	49
Aitken	47	43	18

The measurement technique of Junge was extended to Aitken particles in the sixties by several workers. In these studies cascade impactors were backed up by suitable filters to capture unimpacted small particles. Table 20 gives the results obtained in this way by E. Mészáros (1968) under moderately polluted continental conditions. In the table the values tabulated are expressed in percentage of the total mass. It can be seen from these data that approximately half of the mass of sulfate and ammonium ions may be found in the Aitken size range, which means that on *number basis* the great majority of sulfate particles have radii less than about  $0.1 \mu\text{m}$ . This is hardly surprising, considering the formation mechanism of secondary aerosol particles. It is to be noted that the mass median diameter of sulfate particles identified agrees well with the geometric mean of the accumulation mode, as discussed by Whitby (1978; see also Fig. 27). In contrast to sulfate and ammonium containing aerosol particles, only 20 % of chloride ions are detected in the Aitken-size range and in this case the fraction found on giant particles is also significant, in agreement with Junge's results discussed above. Mészáros' measurements also showed that the relative quantity of water soluble substances increases with decreasing particle size, which also suggests that the amount of particulate matter formed by mechanical disintegration is less significant in the range of smaller particles.

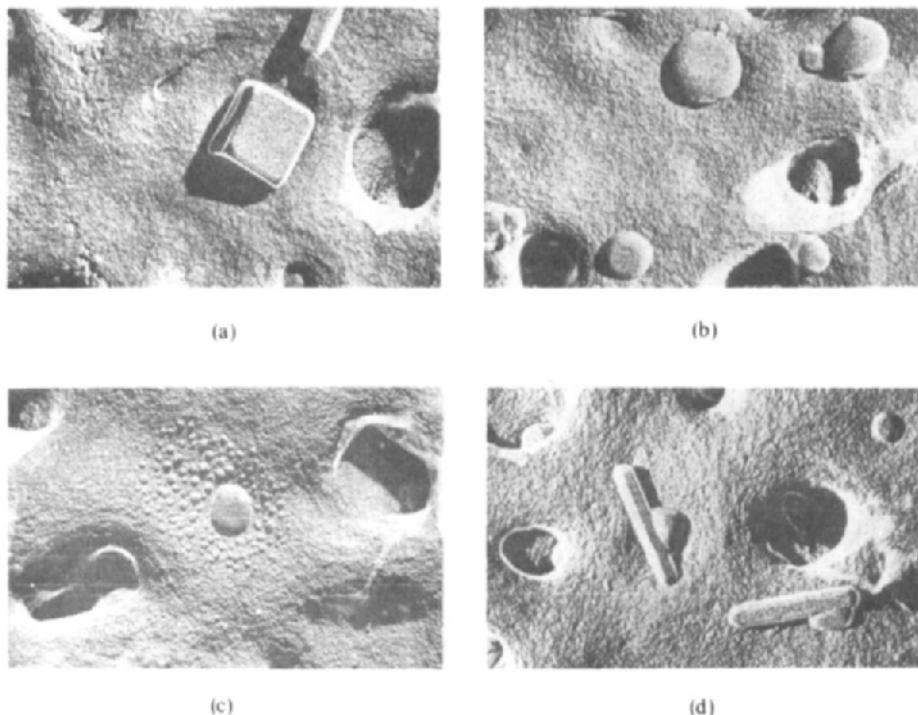
An important step in the understanding of the formation and composition of tropospheric background aerosol was provided by the work of Fenn *et al.* (1963) who demonstrated that in aerosol samples collected in Greenland<sup>13</sup>, 40 % of the large particles consisted of sulfate. This finding was confirmed by American authors

<sup>13</sup> In a more recent paper Flyger and Heidam (1978) report that Greenland aerosol consists mostly of soil-derived silicon ( $0.043 \mu\text{g m}^{-3}$ ) and sulfates ( $\sim 0.08 \mu\text{g m}^{-3}$ ). Note: sulfate was identified as sulfur.

(Cadle *et al.*, 1968) who showed by means of special microscopic techniques (e.g. morphological identification) that in Antarctic air the large particles are built from sulfates.

The composition of background aerosol particles, including a part of Aitken range, was investigated by morphological identification by A. Mészáros and Vissy (1974) on the basis of membrane filter samples collected in remote oceanic air in the Southern Hemisphere. They found that 75–95 % of the particles was composed of the following four substances (Fig. 33):

- (a) sea salt;
- (b) ammonium sulfate;
- (c) sulfuric acid;
- (d) mixture of sea salt and  $(\text{NH}_4)_2\text{SO}_4$ .



**Fig. 33.**

Electron micrographs of aerosol particles collected on membrane filters under remote maritime conditions (photo: A. Mészáros). (a) sea salt; (b) ammonium sulfate; (c) sulfuric acid; (d) mixed. The size of the field in the pictures is  $2.4 \times 3.6 \mu\text{m}$ . (By courtesy of *J. of Aerosol Science*)

In Table 21 the relative quantity of these substances, expressed in percentage of the number concentration of particles with  $r \geq 0.03 \mu\text{m}$ , is tabulated as a function of geographical position. It can be seen that the fraction which consists of these water soluble substances is the smallest in the vicinity of equator (75 %), owing to the fact that in these areas the number of insoluble particles with radii greater than  $0.5 \mu\text{m}$  was relatively significant.

Table 21

Chemical composition of atmospheric aerosol particles expressed in percentage of the number of particles with radius larger than  $0.03 \mu\text{m}$  (A. Mészáros and Vissz, 1974)

	Atlantic $0 \leq \varphi \leq 20$	Atlantic $40 \leq \varphi \leq 60$	Atlantic $\varphi > 60$	Indian Ocean
$(\text{NH}_4)_2\text{SO}_4$	69	38	33	18
NaCl	1.6	15	7.3	28
$\text{H}_2\text{SO}_4$	-	-	7.6	3.2
Mixed	4.9	42	36	31

Note: Collections were made in remote oceanic areas.  $\varphi$  is the geographical latitude in the Southern Hemisphere

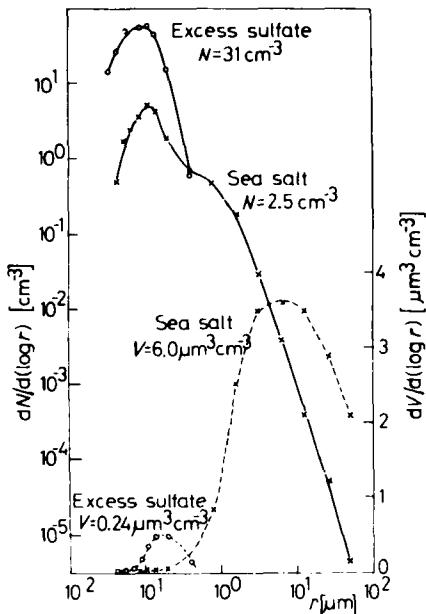


Fig. 34

Size distribution of the number ( $N$ ) and volume ( $V$ ) of excess (non sea salt) sulfate and sea salt particles with  $r \geq 0.03 \mu\text{m}$ . (Data of A. Mészáros)

Figure 34 represents the average size distribution of sulfate and sea salt particles as observed by A. Mészáros and Vissny (1974) over different parts of the South Atlantic. One can see that on a number basis (solid lines) sulfate particles with much smaller mean radii predominate, while the major proportion of the particle volume (dotted lines) is occupied by the sea salt fraction in the coarse size range. On the basis of the data plotted, only 4 % of the total volume of the particulate matter is composed of sulfates (that total volume is  $6.2 \mu\text{m}^3 \text{cm}^{-3}$ ). This means that the mass concentration of aerosol particles in remote oceanic areas is also controlled by sea salt.

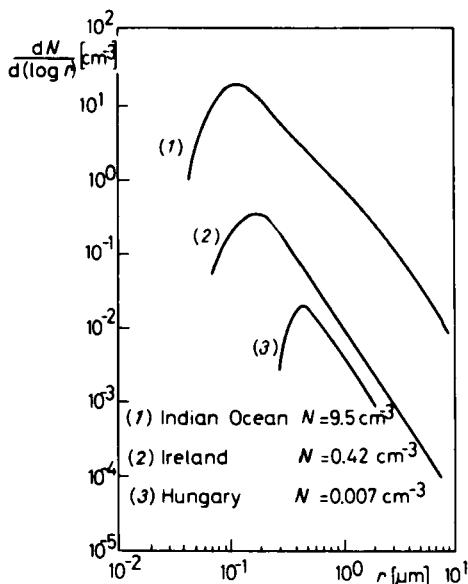


Fig. 35

Size distribution and concentration ( $N$ ) of sea salt particles from different geographical regions. (1): according to A. Mészáros and Vissny (1974) (by courtesy of *J. of Aerosol Science*); (2): according to Metnieks (1958) (by courtesy of School of Cosmic Physics); (3): according to E. Mészáros (1964) (by courtesy of *J. de Recherches Atmosphériques*)

The quantity of sea salt particles, identified as NaCl, was found to be particularly important over the Indian Ocean. This is explained by stormy weather conditions during the sampling period. Curve 1 in Fig. 35 gives the size distribution of sea salt particles measured over the Indian Ocean (the total number concentration,  $N$ , is also plotted). To represent the advection of sea salt particles over the continents, two other spectra are also shown. Curve 2 was measured by Metnieks (1958) in Ireland while distribution 3 was observed in the surface air in Hungary (E. Mészáros, 1964). These latter investigators used gelatin layers sensitized with silver nitrate to identify chloride particles. Figure 35 makes clear that the sea salt concentration is very small

in a continental environment. Furthermore, the maximum of the distribution is shifted in the direction of larger particles. However, even over the ocean very few sea salt particles have a radius smaller than  $0.1 \mu\text{m}$  ( $3.2 \text{ cm}^{-3}$  in our case) as compared to the total concentration of Aitken particles (Subsection 4.3.1). Finally, over the Indian Ocean practically all giant particles consisted of sea salt<sup>14</sup>.

It follows from Table 21 that the great majority of aerosol particles consist either of ammonium sulfate or from a mixture of ammonium sulfate and sea salt. Thus, if we disregard sea salt particles we can conclude that the particulate matter in tropospheric background air consists mainly of sulfur-containing species. This finding was more recently confirmed by Butor (1976) who made samplings over the North Atlantic and identified particles by electron microscopy. Moreover, the investigation of Mészáros and Vissz also shows that 70% of the number of ammonium sulfate particles are in the range of  $0.03 \leq r \leq 0.1 \mu\text{m}$  in agreement with the results of continental observations (see Table 20). It should be noted here that

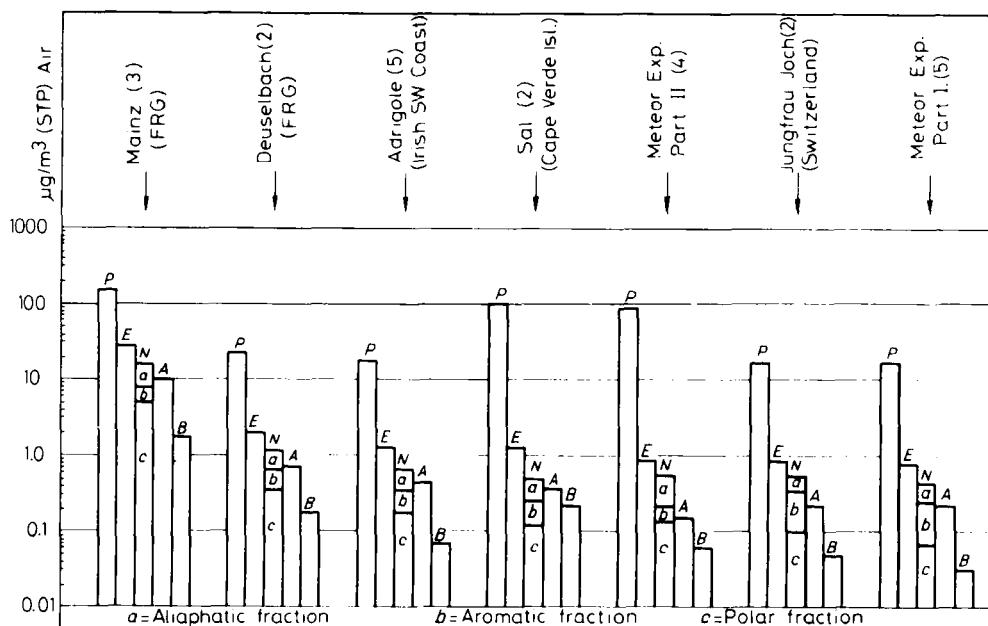


Fig. 36

Mass concentration of all aerosol particles (P) and of organic particles at different sampling sites according to Ketseridis *et al.* (1976). E: ether extractable organic material; N: neutral organic compounds; A: organic acids; B: organic bases. (By courtesy of *Atmospheric Environment*)

*Note:* The majority of the mass of all particles under marine conditions is sea salt (see Fig. 34). The numbers behind the names of the sampling locations give the number of samples analyzed

<sup>14</sup> Woodcock's classical studies demonstrated (Woodcock, 1953) that the number of giant sea salt particles decreases rapidly with increasing height over the ocean.

the direct chemical bulk analyses of Winkler (1975) also clearly indicate that the main component of the aerosol in the Aitken size range is sulfur under oceanic background conditions.

It is believed that this huge amount of smaller sulfur (sulfate) particles come into being by the chemical and physical transformations discussed in Subsections 3.6.3 and 4.2.2. This assumption is strongly indicated by the greater prevalence of ammonium sulfate particles near the equator, where conditions are very favourable for the initiation of photochemical and thermal reactions.

The organic fraction of atmospheric particulate matter was investigated by Ketseridis *et al.* (1976) at several locations, including remote oceanic areas. These authors collected particles on glass fiber filters and determined the total mass of suspended particles by weighing the filters before and after the sampling. They extracted ether soluble materials from the samples and were able to identify chemically organic acids and phenols, organic bases, aliphatic hydrocarbons, aromatic hydrocarbons and neutral compounds. The results obtained are summarized in Fig. 36. The data labelled 'Meteor' refer to samplings carried out on board the German research vessel Meteor in 1973 over the North Atlantic. It is to be noted that during Part II of this expedition as well as during sampling in Cape Verde an advection of Sahara dust was observed. One can see that, except in more polluted atmospheres, the concentration of organic material extractable in ether is practically constant at about  $1 \mu\text{g m}^{-3}$  STP. The fraction of different components is also independent of sampling location. At Jungfraujoch and over the Atlantic Ocean (without dust advection) about 5–10 % of the aerosol particle mass is composed of organics. Ketseridis *et al.* (1976) speculated that this constant concentration of organic particulate matter in tropospheric background is either due to particle advection from highly populated areas or to a constant production

Table 22

Chemical composition of aerosol particles in the upper troposphere over the Philippine Islands on November 19, 1969, from the aircraft measurements of Cadle (1973)

Latitude N	Longitude W	Height $10^{-3}$ feet	Concentration [ $\mu\text{g m}^{-3}$ ambient air]					
			$\text{SO}_4^2-$	Si	Na	Cl	$\text{NO}_3^-$	$\text{NH}_4^+$
35° 04'	139° 35'	26	0.041	—	—	—	0.020	0.0064
26° 21'	120° 40'	26	0.051	0.011	0.055	0.085	0.019	0
19° 32'	120° 40'	25	0.10	0.016	0.016	0.052	0.042	0.0013
16° 30'	117° 00'	25	0.15	0.022	<0.001	0.029	0.022	0.013
13° 00'	124° 00'	25	0.073	0.009	0.010	0.013	0.039	0.0033
21° 00'	127° 54'	25-39	—	0.014	0.019	0.018	—	—
11° 00'	119° 00'	39	0.16	0	0.019	0.018	—	—
11° 00'	122° 00'	39	0.23	0.007	0	0.057	—	0
16° 52'	117° 15'	39	0.068	0.003	0.016	0.052	0.026	0

Note: 1 foot = 30.48 cm

mechanism in clean tropospheric air. In a more recent study Ketseridis and Eichmann (1978) used an impactor to separate particles with radii smaller and larger than 1  $\mu\text{m}$ . They report on the basis of their measurements carried out in Ireland, that the majority of organics are in the smaller size range where these materials comprise 25 % of the aerosol mass. It is very probable that organic particles of these sizes are formed by gas-to-particle conversion (see Subsection 3.3.3).

In the upper troposphere the chemical composition of aerosol particles was widely studied by American research workers (Cadle, 1973). During aircraft flights, particles were collected on special filters, and the samples were subsequently analyzed by wet chemistry and neutron activation. The results obtained in the upper tropical troposphere near the Philippine Islands are tabulated in Table 22. These data show that the sulfate concentrations are much higher than those of silicon, chloride and sodium, showing that sea salt and mineral dust are unimportant at these altitudes. It is interesting that very small ammonium concentrations were found. This finding makes it likely that the majority of the sulfate consists of sulfuric acid droplets, which are less common near the Earth's surface (A. Mészáros and Vissy, 1974) owing to higher  $\text{NH}_3$  concentrations. Finally, it should be mentioned that Cadle argues that the relatively high nitrate concentrations are explained by the adsorption of  $\text{HNO}_3$  vapour by the filter material<sup>15</sup>.

Table 23

Vertical profile of the mass concentration of particulate sulfur according to Gillette and Blifford (1971)

Height [km]	Pacific Ocean [ $\mu\text{g m}^{-3}$ ]	Death Valley [ $\mu\text{g m}^{-3}$ ]
0.015	0.24 (3)	0.31 (5)
0.915	0.09 (4)	0.32 (5)
1.5	-	0.23 (1)
1.8	0.11 (6)	0.24 (5)
2.3	-	-
3.0	-	-
3.7	0.04 (6)	0.14 (5)
4.6	-	0.03 (1)
6.1	0.05 (5)	0.07 (6)
7.6	0.03 (5)	0.12 (6)
9.1	0.06 (4)	0.06 (5)

Note: Values in parentheses give the number of observations. Samples were collected in 1967.

<sup>15</sup> The results of Spicer and Schumacher (1977) suggest that alkaline sites on many filters collect gaseous nitric acid and cause it to be reported as particulate nitrate.

The vertical profile of different elements in particulate matter was investigated by Gillette and Blifford (1971) who used cascade impactors and filters to collect particles. The sulfur profiles obtained over the Pacific Ocean near California and over the American continent (Death Valley) are represented by the data given in Table 23. By re-calculating their concentrations in sulfate we can say that in the upper troposphere the sulfate level is  $0.1\text{--}0.2 \mu\text{g m}^{-3}$  which agrees reasonably well with figures in Table 22 as well as with the results of near surface measurements of Winkler (1975) and Flyger and Heidam (1978) carried out in remote areas. The X-ray fluorescence analyses of Gillette and Blifford (1971) also showed that 80–90 % of the sulfate (sulfur) found occurs in the Aitken size range.

On the basis of the foregoing discussion it is concluded that tropospheric background particles consist mainly of sulfur compounds. Sulfate particles contain hydrogen or ammonium ions as a function of the ammonia gas available. These mostly Aitken size particles are (externally or internally) mixed with some organic material at least near the Earth's surface.<sup>16</sup> More research is needed to know in more detail the chemistry of this aerosol.

#### 4.4.3 Stratospheric particles

At the end of the fifties a program was started in the U.S.A. to study stratospheric aerosol particles. The results of the program were analyzed by Junge and his associates (see Junge, 1963). The most important achievement of this study was the discovery of an aerosol layer between 15–20 km consisting mostly of large particles (see Subsection 4.3.3).

To investigate their chemical composition, stratospheric particles were collected by aircraft- and balloon-borne impactors. Elements with atomic numbers of 12–30 were identified in the samples by electron microprobe and X-ray fluorescence techniques. Table 24 summarizes the results obtained (Junge, 1963). In this table the sulfur is given as sulfate since further wet chemical analyses showed that the sulfur occurred as sulfate particles. It can be seen from the data tabulated that 89 % of the mass of the components identified is sulfate. Data also indicate that the quantity of  $\text{NH}_4^+$  is sufficient only to neutralize about one third of the sulfate ions. Further flights carried out over a wide range of latitudes ( $60^\circ \text{S}$ – $70^\circ \text{N}$ ) demonstrated that this sulfate layer can be observed everywhere in the stratosphere.

About ten years later a new stratospheric aerosol program was performed. In this case, particles were collected between 17 and 28 km by absolute filters having a collection efficiency of virtually 100 % in all size ranges. Table 25 gives the results of a sampling day when particles were collected at an altitude of 18 km. In the last column of the table the percentage of sulfate ions possibly neutralized by  $\text{NH}_4^+$  is also presented. It can be seen that the concentrations measured by this more recent

<sup>16</sup> According to Jaenicke (1978) in the Aitken size range 25 % of particles consists of organic materials under tropospheric background conditions.

program exceed by at least one order of magnitude the concentration found in the previous program (see Table 24). Furthermore, Lazarus and his co-workers (1971) found high sulfate mass concentrations even when the optical measurements designed to detect large particles did not indicate the presence of an aerosol layer.

**Table 24**  
Chemical composition of stratospheric aerosol  
particles (Junge, 1963)

Component	Number of observations	Concentration [ $10^{-3} \mu\text{g m}^{-3}$ ]	Relative composition
Mg	4	0.000	0.000
Al	4	0.43	0.056
Si	12	0.11	0.014
P	4	0.000	0.000
$\text{SO}_4$	11	6.82	0.89
Cl	4	0.01	0.0013
K	7	0.13	0.017
Ca	8	0.10	0.013
Ti	3	0.000	0.000
V	4	0.000	0.000
Cr	4	0.000	0.000
Mn	4	0.000	0.000
Fe	12	0.071	0.0093
Co	4	0.000	0.000
Ni	7	0.000	0.000
Cu	4	0.000	0.000
Zn	4	0.000	0.000
Total	12	7.68	1.00

These data strongly suggest that the difference between the results of the two programs is caused by the different sampling techniques used. More recent studies in which simultaneous impactor and filter samples were taken showed (Cadle *et al.*, 1973) that a sizable part of the sulfate was really in the Aitken size range. However, we cannot rule out the possibility that the concentration differences may be explained partly by an increase of stratospheric sulfate burden arising from the volcanic activity between 1960 and 1970.

The first stratospheric aerosol chemical analyses showed that only a small quantity of the aerosol particles in the lower stratosphere could be of meteoritic origin (e.g. no nickel was found in the samples, see Table 24). This problem was studied in detail by Shedlovsky and Paisly (1966) who found by means of neutron activation of aerosol particles collected on filters that the stratospheric Fe/Na ratio is close to that reported for the Earth's crust. They concluded that less than 10% of the iron and sodium identified at altitudes of 19–21 km come from meteorites. However, it is possible that between 30 and 50 km, where no such measurements were made, the meteoritic fraction of the aerosol is much more significant.

Junge (1963) speculated that the sulfate particles in the stratosphere are formed by chemical transformation of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  gases mixing into the stratosphere mostly over the tropics. It was also reported that sulfur gases are injected into the stratosphere by volcanic eruptions (SMIC, 1971). According to Cadle and Powers (1966) the chemical conversion of sulfur gases above the tropopause is promoted by the presence of atomic oxygen, while more recent studies (see Subsection 3.6.3) suggest that OH radicals play an important role in the transformation of sulfur gases at these altitudes. Furthermore, Crutzen (1976) recently argued that biogenic carbonyl sulfide may be at least partially responsible for the formation of stratospheric sulfate layer. The sulfuric acid vapour produced by chemical reactions can condense homogeneously to form acid droplets diluted with water. However, there is some indication that this condensation takes place on existing Aitken-size particles. Thus, Mossop (1965) found that stratospheric solution droplets frequently contain small insoluble particles. Theoretical work by Hamill *et al.* (1977) also indicates that heterogeneous condensation of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  vapours in the stratosphere is much more probable than a homogeneous phase transition.

Table 25

Mass concentration of sulfate and ammonium particles sampled at an altitude of 18 km on May 11, 1970 (Lazarus *et al.*, 1971)

Latitude	Longitude	$\text{SO}_4^2-$	$\text{NH}_4^+$	%
38° 10'	106° 50'	0.17	0.0030	5.0
42° 00'	106° 50'	0.22	0.0036	4.6
45° 36'	106° 52'	0.19	0.0030	4.5
49° 30'	106° 45'	0.16	0.0024	4.1
53° 02'	106° 56'	0.22	0.0030	3.9
54° 58'	106° 56'	0.24	0.0034	4.0
51° 15'	106° 57'	0.20	0.0043	5.9
48° 05'	106° 54'	0.15	0.0029	5.3
44° 30'	106° 53'	0.20	0.0038	5.2

Note: Values in last column give relative quantity of sulfate ions associated to ammonium. Concentrations are expressed in  $\mu\text{g m}^{-3}$

Martell (1966) concluded that large stratospheric sulfate particles are due to the coagulation of Aitken-size sulfate particles transported from the troposphere. This assumption is based among other things on the fact (at the time of the publication of Martell's paper this was only a hypothesis) that Aitken particles in the upper troposphere are composed of sulfates (see the last section). Ten years later Podzimek (1976) also reported evidence based on his particle counts that stratospheric Aitken particles are not produced in the lower stratosphere, but arise in the troposphere and are mixed upwards. He also states, however, that this process is negligible during strong volcanic eruptions which eject many gaseous and particulate materials to higher altitudes.

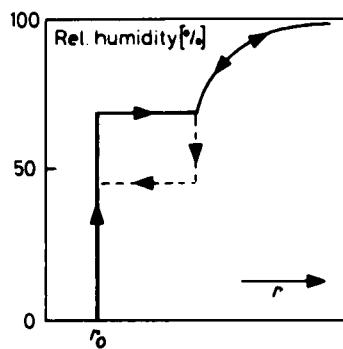
We can conclude that the origin of stratospheric particles is not well established. It is proposed, however, that volcanic activity is at least one of the most important factors governing the aerosol cycle in the stratosphere. It is obvious that much work remains to be done in measuring not only particulate, but also gaseous sulfur compounds in the stratosphere (see Georgii, 1978).

#### 4.5 Variation of the size of aerosol particles as a function of the relative humidity

##### 4.5.1 Theoretical considerations

The size distribution of aerosol particles was presented in Subsection 4.3.2. We have not discussed, however, the relation between the size distribution and the relative humidity of the air, since for such a discussion the knowledge of the chemical composition is necessary. The aim of this section is to summarize the problem with the presentation of some results of measurements. The interested reader is referred for further details to Hänel (1976).

The size distribution of aerosol particles varies as a function of the relative humidity because of the presence of water-soluble materials in the particulate matter. To understand the principle of this phenomenon let us consider a single water-soluble particle consisting of a given substance. The particle, with radius  $r_0$ , is in a dry state, that is, in an environment containing no water vapour. If the relative humidity of the particle's environment is increased the radius initially remains the same, disregarding the adsorption process which is of little importance (see Fig. 37). At a relative humidity determined by the nature of the substance (and also somewhat by the particle size) the radius of the particle suddenly changes to a larger value. This phenomenon is due to the fact that the particle has changed to a solution



**Fig. 37**

Schematic variation of the radius ( $r$ ) of a soluble particle as a function of relative humidity of the air.  $r_0$ : dry radius

droplet. The phase change takes place at the relative humidity at which a saturated solution of the substance considered is in vapour equilibrium with its environment.

It is known from physical chemistry that the equilibrium vapour pressure is smaller over solutions than over pure water. In the case of ideal solutions this vapour pressure decrease is proportional to  $x_0$ , the mole fraction of the solvent (Raoult's law). If the solution is real, the interaction of solvent and solute molecules cannot be neglected. For this reason a correction factor has to be applied to calculate the vapour pressure lowering. This correction factor is the so-called osmotic coefficient of water ( $g_v$ ). We also have to take into account that the soluble substance dissociates into ions, forming an electrolyte.

If we further raise the relative humidity after the phase change (see Fig. 37); the radius of the droplet increases and the solution becomes weaker and weaker. This means that at higher relative humidity a more dilute solution is in dynamic equilibrium with the vapour environment. It should be mentioned that the equilibrium radius is governed also by the curvature of the droplet. Since the relation between the curvature and droplet radius is given by the well-known Thomson equation, we may write (Dufour and Defay, 1963; E. Mészáros, 1969):

$$\ln \frac{p}{p^\infty} = \frac{2\sigma v_m}{kTr} + g_v \ln x_0 \quad [4.13]$$

where  $p$  and  $p^\infty$  are the real vapour pressure and the equilibrium vapour pressure relative to pure water, respectively,  $\sigma$  is the surface tension of the solution,  $v_m$  is the reciprocal of the number of water molecules in the solution, while  $k$  and  $T$  give the Boltzman constant and the absolute temperature, respectively.

After a simple mathematical transformation equation [4.13] yields

$$\frac{p}{p^\infty} \approx 1 + \frac{2\sigma v_m}{kTr} - g_v vx \quad [4.14]$$

since  $x_0 - 1 = -vx$ , where  $x$  is the mole fraction of the solute, while  $v$  the number of ions formed by the dissociation of one solute molecule. If we multiply [4.14] by 100, we obtain a relation between relative humidity and particle radius. The solid line of Fig. 37 represents schematically the results of calculations made using these equations. This curve was experimentally verified first by Dessens (1949) who used a microscope to study the change of radius of atmospheric particles (droplets) captured on spider web as the relative humidity was changed. He discovered that the phase change takes place at a lower relative humidity with decreasing than with increasing humidity (dotted line). This so-called hysteresis phenomenon was later confirmed by several other investigators (see Junge, 1963). It goes without saying that in the case of sulfuric acid solution droplets a sudden change in the particle radius is not observed. It was also more recently shown (Winkler and Junge, 1972)

that the curve is also smoothed if the particle is composed of a mixture of different salts.

Equations [4.13] and [4.14] are also supported by some atmospheric measurements. Thus, E. Mészáros (1970) measured the size distribution of the mass of atmospheric sulfate particles by means of a cascade impactor backed up by membrane filters. He found that the geometric mean radius of the distribution averaged by humidity intervals varies as a function of the relative humidity as shown by the points in Fig. 38. The solid line of this figure gives the theoretical relation calculated from equation [4.14] for an ammonium sulfate particle with a dry radius of  $0.14 \mu\text{m}$ , the value found for the geometric mean radius at low relative humidity. The line shows that the particle radius increases by a factor of two at a relative humidity of 80 %. Near 100 % the droplet radius is several times larger than the dry particle size. Comparison of the curve with the experimental points indicates that the behaviour of the atmospheric particle population is well approximated by the theory outlined. It cannot be excluded, however, that the real phase change is less sudden than the theory predicts.

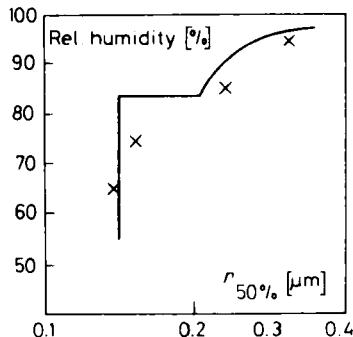


Fig. 38

Variation of geometric mean radius ( $r_{50\%}$ ) of sulfate particles as a function of relative humidity (crosses). Solid line represents the theoretical growth of an ammonium sulfate particle with  $r = 0.14 \mu\text{m}$  (E. Mészáros, 1970). (By courtesy of Tellus)

#### 4.5.2 Results of measurements

Variations of the size distribution of aerosol particles as a function of relative humidity can be observed *in situ* in the air. Changes in particle size distributions are detected by optical counters (Laktionov and Bogomolov, 1972), by nephelometers (Charlson *et al.*, 1969) or by diffusion channels (Sinclair *et al.*, 1974).

Another possibility is to capture particles, e.g. on impactor slides, and to study them after drying at different humidities under a microscope. Different relative humidities are generally created by different saturated salt solutions (isopiestic method). An investigation of this kind was carried out by A. Mészáros (1971) who

studied solid particles and solution droplets in the large and giant size ranges. Her results for particles from a continental environment (Hungary) are plotted in Fig. 39, where  $N_a$  is the number concentration of particles with radius larger than values on the abscissa. It can be seen that in summertime the number of droplets is very large even at low humidities. This finding is obviously caused by the presence of acid or supersaturated salt solution droplets in aerosol samples. This result confirms optical observations of Rozenberg (1967), who found that significant particle growth can be detected even around a relative humidity of 30 %.

From the results plotted in Fig. 39 the relative growth of a given particle size as a function of relative humidity can be calculated. The curves obtained in this way are shown for the winter and summer half-years in Fig. 40. It follows from this figure

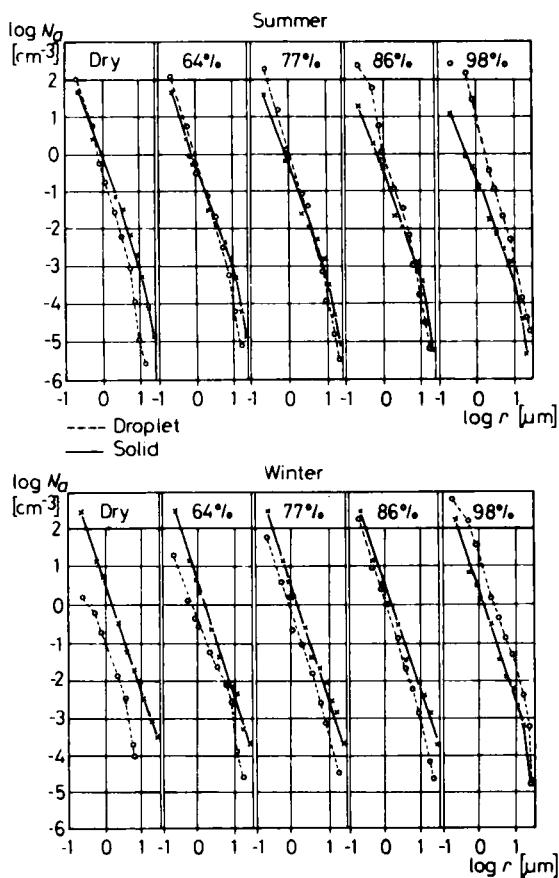
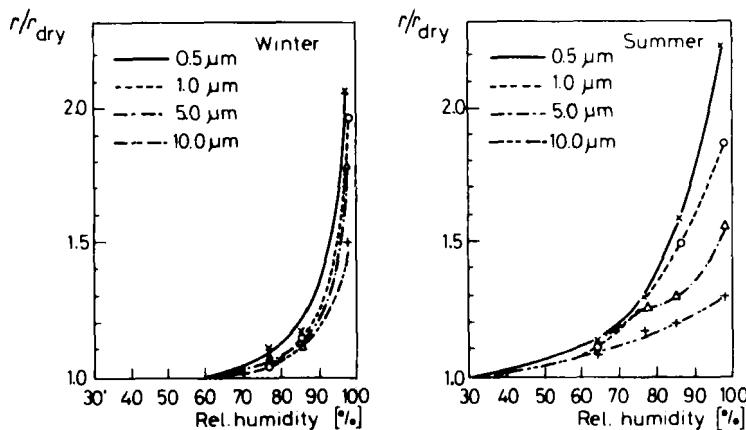


Fig. 39

Size distribution of large and giant particles as a function of relative humidity according to A. Mészáros (1971).  $N_a$ : concentration of particles with radius larger than the abscissa value. (By courtesy of Tellus)

that with increasing particle size the water soluble fraction of aerosol particles decreases, in accordance with direct chemical observations (E. Mészáros, 1968) and considerations on particle formation (Section 4.2). It should be also noted with respect to Fig. 40 that the results for 0.5  $\mu\text{m}$  radius particle, are in good agreement with Hänel's values (Hänel, 1970) derived from experimental data published by Winkler (1969).

Finally, we have to emphasize that the relationship between the relative humidity and particle growth is of importance for many atmospheric phenomena. Thus, the optical properties of the air and in consequence the atmospheric visibility vary as a function of relative humidity, owing to the variation of the scattering cross section of particles. This relation may be important even from the point of view of heat and radiation balance of the atmosphere, since tropospheric background particles consist mostly of water-soluble sulfate species.



**Fig. 40**

Relative growth of aerosol particles of different sizes as a function of relative humidity (A. Mészáros, 1971). (By courtesy of *Tellus*)

## **5. Removal of trace substances from the atmosphere**

### **5.1 Introduction**

The concentration of trace constituents in the atmosphere would rise quickly if sink mechanisms did not assure the cleansing of the atmosphere. Thus, Hales (1978) calculated from the sulfur source strength and the tropospheric volume that the average sulfur concentration would increase annually about  $70 \mu\text{g m}^{-3}$  without the action of removal processes. This means that within 1 year remote tropospheric air would become at least as polluted as dirty urban locations are today.

We have seen in Chapter 3 that in the case of several trace gases ( $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{O}_3$ ,  $\text{N}_2\text{O}$ ) these sink mechanisms are provided by chemical reactions producing components that are utilized by the biosphere. Another possibility for the removal of some gaseous species (sulfur, nitrogen and organic compounds) is their transformation into particulate matter (see Chapters 3 and 4).

The aim of this chapter is to present briefly our ideas on the removal of aerosol particles and water soluble gases (e.g.  $\text{SO}_2$ ,  $\text{NH}_3$ ,  $\text{NO}_2$ ), both during dry weather conditions (dry removal) and during periods with cloud and precipitation formation (wet removal). Because of wet removal, precipitation water contains many soluble (and insoluble) materials, as we will see at the end of this chapter.

### **5.2 Dry deposition**

#### **5.2.1 Dry deposition of aerosol particles**

The removal of aerosol particles under dry weather conditions is caused by turbulent diffusion and gravitational sedimentation, which transport particles to the Earth's surface, as well as by impaction on vegetation, buildings and other objects. Turbulent diffusion itself does not remove particles (Twomey, 1977). Soil and other surfaces are bordered by a thin laminar layer ( $\sim 1 \text{ mm}$  thick) across which particles must be transported by other processes (e.g. phoretic forces, molecular diffusion, sedimentation).

Disregarding impaction, dry removal of aerosol particles can be described formally by the following equation (e.g. Makhonyko, 1966):

$$\text{Dep.} = -k_z \frac{\delta N}{\delta z} + v_s N \quad [5.1]$$

where  $Dep.$  is the number (or mass) of particles deposited per unit surface per unit time,  $k_z$  is the turbulent diffusion coefficient,  $z$  is the height, while  $N$  and  $v_s$  are the particle concentration and sedimentation velocity, respectively. Under average conditions (see previous chapter) the concentration of aerosol particles decreases with increasing altitude. It should be mentioned, however, that this decrease is not necessarily observed near the surface (e.g. in the first 1–2 m). In this case turbulent diffusion may be an effective removal process, especially for smaller particles for which the second term at the right-hand side of equation [5.1] is negligible.

Impaction is a function of several variables. According to Ranz and Wong (1952) the impaction efficiency (defined in Subsection 4.1.2) depends on the parameter  $\psi$ :

$$\psi = \frac{A \rho_p v_h d_p^2}{18 \mu d_c} \quad [5.2]$$

where  $A$  is the Stokes–Cunningham correction factor (see Subsection 4.1.1),  $\rho_p$  is the particle density,  $d_p$  the particle diameter,  $v_h$  the horizontal wind speed,  $\mu$  the dynamic viscosity, and  $d_c$  is the characteristic size of the collector (e.g. the diameter of a cylindrical wooden branch). Since the impaction efficiency increases with increasing  $\psi$ , particle removal by impaction is more effective if the wind speed is high, the particle diameter is great and the collector size is small. We must stress, however, that  $v_h$  is the laminar flow speed. In a turbulent stream the impaction mechanism is obviously more complicated.

The dry deposition of aerosol particles ( $D'$ ) is generally measured by horizontal microscopic slide or so-called dustfall cans and jars. However, the results of such measurements, wide-spread in local pollution studies (Corn, 1976), have to be interpreted with caution because of the disturbance of the laminar and turbulent flow regime by the collector. Furthermore, the laminar layer covering the collector surface may be very different from that over soil and vegetation. In any case, if we also measure the particle concentration  $N$ , a parameter with the dimension of velocity can be defined (Junge, 1963):

$$v = \frac{D'}{N} \quad [5.3]$$

This parameter is termed the deposition velocity.

Concerning the estimation of different dry removal processes let us consider Fig. 41, reported by Hidy (1973), but due to Chamberlain (1960). Curve *A* in this figure refers to experimental deposition velocities, measured over flat surfaces roughened by grass. On the other hand, line *B* represents the sedimentation velocity calculated by equation [4.1]. It can be seen that curve *A* approximates line *B* in the range of very large particles with significant sedimentation velocities ( $d_p > 10 \mu\text{m}$ ). With decreasing particle size the deviation is more and more important. It is believed that this phenomenon is caused by turbulent diffusion. There is some indication that

curve A begins to increase with decreasing size in the range where Brownian motion becomes important.

To estimate the significance of impaction by trees we refer to the results of Neuburger and his co-workers (see Hidy, 1973), based on particle concentration measurements carried out inside and outside a forest area. Neuburger's data show that more than 80 % of pollen (coarse particles) is removed by trees while the corresponding value for Aitken particles is 34 %. Further research is needed, however, to confirm these results.

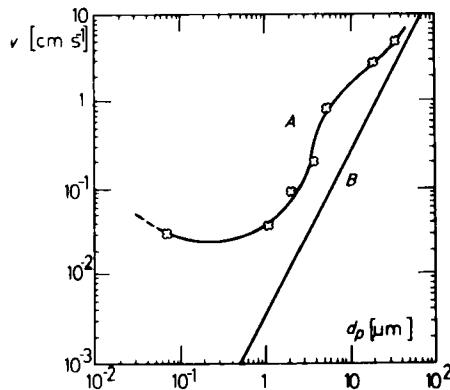


Fig. 41

Dry deposition velocity (A) and sedimentation velocity (B) of aerosol particles. Curve A refers to flow over grass (Hidy, 1973). (By courtesy of Plenum Press)

The deposition velocity defined in [5.3] makes possible the calculation of the "dry" residence time of particles (Junge, 1963):

$$\tau_t = \frac{H}{v} \quad [5.4]$$

where  $\tau_t$  is the tropospheric residence time, under dry weather conditions, while  $H$  is the scale height (see Subsection 3.6.4).

Equations [5.3] and [5.4] can be applied in the case of relatively simple and sensitive radioactivity measurements. The use of long-lived artificial fission products in intervals without nuclear tests seemed particularly suitable in the past since they have a relatively constant vertical distribution in the troposphere (e.g. Ishii, 1960) which facilitates the determination of  $H$ . In this way Small (1960), by using total  $\beta$ -activity measurements, calculated that the overall dry deposition velocity of aerosol particles over Norway is  $0.50 \text{ km day}^{-1}$ . On the other hand, Stewart found (see Small, 1960) a much smaller value in England. According to artificial  $\beta$ -activity measurements of E. Mészáros and Simon (1967), carried out near

Budapest, Hungary, the corresponding figure is  $0.17 \text{ km day}^{-1}$ , which is equivalent to  $0.2 \text{ cm s}^{-1}$ . This is a reasonable velocity in light of Fig. 41 if we consider that, in the sixties, 80 % of the artificial  $\beta$ -radioactivity was found to be on large particles (Gasiev *et al.*, 1966). If  $H$  is 10 km, it follows from this latter deposition velocity that without wet removal the residence time of aerosol particles would be as long as several months. Considering that the actual residence time of aerosol particles in the lower troposphere is estimated to be 3–4 days (Martell, 1966; E. Mészáros and Simon, 1967), the role of clouds and precipitation in particle removal is obvious.

We have previously seen that tropospheric background aerosol particles consist mainly of ammonium sulfate (Subsection 4.4.2). Bearing in mind that the radius of the majority of these particles is in the Aitken size range it seems to be reasonable to suppose on the basis of Fig. 41, that their dry deposition velocity cannot be greater than  $0.1 \text{ cm s}^{-1}$ . This figure is in good agreement with the recent estimate of Garland (1978) which gives the same value for the dry deposition of sulfate particles.

Finally, it is to be noted that in the foregoing discussion of dry removal we considered the total ensemble of particles. If size ranges are taken into account separately, additional sinks have to be mentioned. Thus, thermal coagulation of particles with very small size, as well as the condensation (below a relative humidity of 100 %) of vapours with low saturation vapour pressure provide effective removal for Aitken particles. It is believed (Hidy, 1973) that these processes are dominant in the removal of aerosol particles in the size range below  $0.1 \mu\text{m}$  radius.

### 5.2.2 Dry deposition of trace gases

In the dry removal of trace gases turbulent diffusion, followed by molecular diffusion in the laminar layer, plays an important role, provided that the soil, vegetation or water surface chemically adsorbs or absorbs the gas considered.

It follows from equation [5.1] that the dry deposition of trace gases ( $v_s = 0$ ) may be calculated by measuring their concentration gradient and the eddy (or molecular) diffusion coefficient. This procedure, called the gradient method, is widely used to determine the dry deposition velocity. Thus, Atkins and Garland (1974) studied the dry deposition of  $\text{SO}_2$  in this way. They determined the diffusion coefficient from wind profile observations. Using equation [5.3] these authors were able to calculate

**Table 26**

Dry deposition velocity of sulfur dioxide gas for different soil surfaces (Atkins and Garland, 1974)

Type of surface	Time of year	$v$ [ $\text{cm s}^{-1}$ ]
Short grass	March–June	0.14–2.0
Grass	November–January	0.20–1.3
Bare calcareous soil	February–March	0.50–2.2
Pine forest	June	<0.7

the deposition velocity. Their results obtained over different surfaces are tabulated in Table 26. Disregarding the data for pine forest, the deposition velocity lies between  $0.14\text{--}2.2\text{ cm s}^{-1}$ . As can be seen the highest deposition rates were measured over calcareous soils, which are very effective  $\text{SO}_2$  absorbers.

Recently, Garland (1978) has reviewed the results of measurements carried out to determine the dry deposition velocity of sulfur dioxide gas. He argues that the average removal velocity is around  $0.8\text{ cm s}^{-1}$ . It is to be noted here that the dry deposition velocity of  $^{131}\text{I}$  gas was also found to be in agreement with the data tabulated in Table 26. Thus, Chamberlain (1960) reports values between 0.3 and  $2.6\text{ cm s}^{-1}$  for this radioactive isotope.

Unfortunately, little information is available for other gaseous sulfur and nitrogen species. As we have mentioned in Chapter 3, Judeikis and Wren (1977) published values between  $0.015$  and  $0.28\text{ cm s}^{-1}$  for  $\text{H}_2\text{S}$  and DMS, on the basis of their model experiments. They also reported indications, however, that observed deposition velocities are due primarily to reversible physical adsorption. This means that real dry removal rate of these compounds may be much smaller.

Laboratory investigations by Bötger (1978; personal communication) indicate dry deposition velocity values for  $\text{NO}_2$  of the order of magnitude of  $0.01\text{ cm s}^{-1}$ . These experiments were carried out by measuring concentration loss in a plexiglass box which contained different water or soil surfaces. The results were corrected for a blank value obtained without any absorbing material. A particularly low velocity was found for ocean water ( $0.015\text{ cm s}^{-1}$ ), while the highest figure was obtained over wet sand:  $0.041\text{ cm s}^{-1}$ . It is questionable, however, how to extrapolate these results to natural soils covered by vegetation. Moreover, to the knowledge of the present author, no measured deposition velocities were published for atmospheric ammonia gas. It is obvious that much work remains to be done in this important field.

### 5.3 Wet deposition

#### 5.3.1 Rain-out of aerosol particles in clouds

The efficiency of wet removal of gases and particles is due to the fact that the falling speed of precipitation elements greatly exceeds the dry deposition velocity of trace constituents. In discussion of removal caused by clouds and precipitation it is reasonable to differentiate processes taking place in the clouds (rain-out) and beneath the cloud base (wash-out).

Rain-out of aerosol particles is begun at the moment of cloud formation, since at the supersaturations occurring in the atmosphere (<1 %, which is equivalent to a relative humidity of 101 %) condensation takes place on aerosol particles, called nuclei. To understand the principle of this phenomenon (see Mason, 1957; Fletcher, 1962) let us consider a cooling air parcel. Because of the cooling the relative humidity in the parcel increases. After reaching the saturation level, cloud drops begin to form on aerosol particles in the updraft. Each particle becomes active in the

cloud drop formation at a supersaturation (critical supersaturation) which is determined by the physical and chemical properties of the particle. It is obvious that condensation starts on particles having a low critical supersaturation. By further increase of the supersaturation more and more particles are involved in cloud formation by condensation. Owing to water vapour consumption the supersaturation begins to drop after a certain time. Only those particles can participate in the condensation whose critical supersaturation is equal to or less than the maximum supersaturation reached in the cloud.

Results of thermodynamic calculations show (e.g. Dufour and Defay, 1963; E. Mészáros, 1969) that the critical supersaturation of solution droplets formed on water soluble particles (see Subsection 4.5.1) is less than values for insoluble particles of the same size.<sup>1</sup> Furthermore, theory indicates that larger particles are more active in condensation processes than smaller nuclei. These theoretical considerations are in good agreement with experimental findings (e.g. Twomey 1971 and 1972) which suggests that the majority of active condensation nuclei are composed of water soluble ammonium sulfate particles with dry radii greater than 0.01–0.05 μm.

It follows from the foregoing discussion that, if the number of particles with low critical supersaturation is significant, a droplet population of high concentration and small average radius will be produced (providing that other factors, e.g. updraft speed, remain the same). In this case the concentration of the substances serving as condensation nuclei will be high in the cloud water. The number of active nuclei depends on the degree of pollution of the air as well as on the age of the aerosol present. Moreover, due to their mixing with the environment, the concentration of nuclei is larger near the edges of a given cloud. Thus, in a cloud parcel near the edge, the concentration of dissolved or suspended material in each drop is higher compared with drops in a parcel near middle of the cloud; this is also promoted by the smaller liquid water content caused by evaporation.

Because the mass of ammonium sulfate and sulfuric acid particles is mainly in the size range of active condensation nuclei, it is believed that this process provides a very effective removal mechanism for the tropospheric background aerosol. However, we have to emphasize that other processes are also operating in the cloud to remove small aerosol particles, of which the most important process is the coagulation of particles and cloud drops. As we have seen (Subsection 4.1.1), thermal coagulation is particularly effective in the range of very small particles inactive in condensation. To estimate this process, let us consider a cloud in which the number concentration of drops with radius  $r_c$  is  $N_c$ . If the number concentration

<sup>1</sup> The critical supersaturation of solution droplets may be calculated by equations [4.13] and [4.14] by using relative humidities greater than 100 %. The curves calculated in this way have a maximum at a certain supersaturation which gives the critical value (Fletcher, 1962). The critical supersaturation of insoluble particles is given by the Thompson formula, obtained by substituting  $x_0 = 1$  in equation [4.13].

of aerosol particles with radius  $r_p$  is designated by  $N_p$ , then the coagulation loss of particles per unit time may be written as follows (Greenfield, 1957):

$$-\frac{dN_p}{dt} = 2\pi(D_p + D_c)(r_p + r_c)N_p N_c \quad [5.5]$$

where  $D_p$  and  $D_c$  are the diffusion coefficient (see Subsection 4.1.1) of particles and cloud drops, respectively. Equation [5.5] may be transformed into the simpler form

$$-\frac{dN_p}{dt} = KN_p N_c \quad [5.6]$$

where  $K$  is equal to  $2\pi(D_p + D_c)(r_p + r_c)$ . In a turbulent cloud, coagulation due to the turbulent motion of particles and drops also has to be taken into account. In this case  $K = K' = K_B + K_T$ , where  $K_B$  represents the coagulation caused by the Brownian motion of particles, while  $K_T$  is the same parameter for turbulent coagulation. The value of this latter coefficient is given by equation [5.7]:

$$K_T = \frac{4}{3}\omega(r_p + r_c)^2 \quad [5.7]$$

where  $\omega$  is the gradient of the velocity (shear) perpendicular to the stream trajectories. When these points are taken into account, integration of equation [5.6] yields:

$$N_p(t) = N_p(0) \exp(-K'N_c t), \quad [5.8]$$

which means that the concentration of particles decreases exponentially with time, owing to their removal by coagulation with cloud elements. It should be mentioned that this removal mechanism is most effective at the cloud edges, where the mixing with the environment provides a constant particle input into the cloud.

By means of equation [5.8] Greenfield (1957) showed that particles with diameters smaller than  $0.01 \mu\text{m}$  are almost entirely removed from cloudy air under normal conditions.

Aerosol particles may also be removed in the clouds by the different phoretic forces, e.g. by diffusiophoresis. This phenomenon involves the motion of particles due to concentration gradient of condensing or evaporating vapour (Goldsmith *et al.*, 1963). In the case of condensation, particles displace towards the drop surface. According to Goldsmith *et al.* (1963), velocity caused by diffusiophoresis is

$$v_p = -1.9 \times 10^{-4} \frac{dp}{dx} \quad [5.9]$$

where  $dp/dx$  is the water vapour gradient expressed in millibar  $\text{cm}^{-1}$  (the dimension of  $v_p$  are  $\text{cm s}^{-1}$ ). Laboratory experiments and calculations show that the role of the

diffusiophoresis in liquid clouds is small compared to the effect of condensation and coagulation. However, in so-called mixed clouds, containing both liquid drops and ice crystals, relatively large numbers of particles can be removed by growing solid cloud elements (Vittori and Prodi, 1967).

The foregoing discussion can be summarized by a simple mathematical expression (Junge, 1963):

$$C_{1a} = \frac{E_a M_a}{w} \quad [5.10]$$

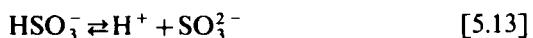
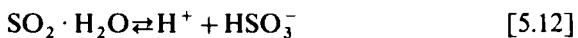
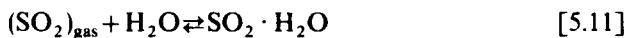
where  $C_{1a}$  is the concentration of trace constituents in precipitation due to aerosol particle removal,  $w$  is the liquid water content of the cloud, and  $E_a$  gives the removed fraction of the mass concentration of particles ( $M_a$ ). Junge (1963) estimated that under tropospheric background conditions  $E_a$  is equal to 0.9–1.0, which means that practically all particles are removed from the air during cloud formation.

### 5.3.2 Rain-out of trace gases

After cloud formation the sorption of soluble trace gases begins immediately. Rain-out is particularly important in those cases in which an absorbed gas reacts irreversibly in the liquid phase with another constituent. Examples of this type of transformation are provided by  $\text{SO}_2$ ,  $\text{NH}_3$ ,  $\text{NO}_2$  etc. In the following we will deal mostly with  $\text{SO}_2$  removal which is discussed in a considerable body of papers. However, the main points of the rain-out of  $\text{NH}_3$  and  $\text{NO}_2$  will also be mentioned.

The rain-out of reactive gases is determined by the transport of gas molecules to the droplet surface, their molecular diffusion into the liquid water, and by their rate of chemical transformation. It is shown (Beilke and Gravenhorst, 1978; Hales, 1978) that, in case of sulfur dioxide removal, the rate of this latter process is much smaller than that of diffusion, since the equilibrium between  $\text{SO}_2$  in the gas phase and sulfur(IV) in liquid water is reached within less than 1 s (in this form of notation, a Roman numeral in parentheses means the valence of the elements). For this reason the oxidation of sulfur(IV) in cloud drops is the rate-determining process in  $\text{SO}_2$  removal.

To understand this removal mechanism let us consider a heterogeneous system in which  $\text{SO}_2$  in the gas phase is in equilibrium with sulfur(IV) in liquid water. This equilibrium is represented by the following three equations:



In these equations sulfur (IV) in the aqueous phase is the sum of  $\text{SO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$ , while [5.11] describes a simple physical dissolution. Considering the foregoing discussion, the problem is to determine the nature and rate of the sulfur (IV) → sulfur (VI) transformation of bisulfite ( $\text{HSO}_3^-$ ) or sulfite ( $\text{SO}_3^{2-}$ ) ions (unfortunately there is no agreement among different authors as to whether the bisulfite ion, the sulfite ion, or both is the reactive species). It is well documented that the oxidation of sulfur (IV) to form sulfate ions can be proceeded by the following processes:

- (a) oxidation by  $\text{O}_2$  in the absence of catalysts;
- (b) oxidation by  $\text{O}_2$  in the presence of catalysts;
- (c) oxidation by strongly oxidizing agents ( $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ ).

The overall reaction of sulfite ions with absorbed oxygen is as follows:



Reaction [5.14] was studied in the absence of catalysts by several authors. It was found that the oxidation is zero order with respect to oxygen while the order is unity with respect to bisulfite ions. Unfortunately very different reaction rates ( $k$ ) were obtained by different research groups, as reviewed by Beilke and Gravenhorst (1978). There is agreement, however, that  $k$  depends on the pH of the solution. Thus Beilke *et al.* (1975) recently found that

$$k = 1.2 \times 10^4 [\text{H}^+]^{-0.16}$$

in a pH range of 3–6 and at a temperature of 25 °C. In this equation,  $k$  is expressed in  $\text{s}^{-1}$ , while the dimensions of the concentration of hydrogen ions ( $[\text{H}^+]$ ) are  $\text{mol l}^{-1}$ . Owing to this pH dependence some authors argued that ammonia gas, by raising the pH, plays an important part in this process. For example, using the model developed by Scott and Hobbs (1967), Georgii (1970) calculated that the rate of formation of sulfate ions in liquid water depends more strongly on the  $\text{NH}_3$  concentration than on the  $\text{SO}_2$  level, both in the air. However, new investigation by Drews and Hales (mentioned by Scott, 1978) shows that ammonia is much less soluble at atmospheric concentrations than previously thought. Furthermore, it is argued (Beilke and Gravenhorst, 1978) that the effect of acid droplets in the atmospheric particulate matter is not taken into account in the model of Scott and Hobbs (1967) giving generally rather high pH values. Thus, the most prevalent present opinion is that the major function of absorbed  $\text{NH}_3$  is to transform pre-existing sulfuric acid to ammonium sulfate, not to enhance sulfur (IV) oxidation. In any case this process provides an effective  $\text{NH}_3$  removal mechanism during the lifetime of the clouds.

Much more rapid transformation rates were obtained by using metal catalysts in the aqueous system (e.g. Junge and Ryan, 1958). Manganese and iron were found to be especially effective. Experiments also show (Hegg and Hobbs, 1978) that catalysis by certain "mixed" salts produces larger effects than one metal salt alone. On the basis of this finding Hegg and Hobbs (1978) argue that this process is of importance in clean rural air, while others (Beilke and Gravenhorst, 1978) speculate that this type of sulfur (IV) oxidation is significant only in urban fogs where the concentration of metal catalysts is high.

Sulfate formation by pathways (c) was studied by Penkett (1972) and Penkett and Garland (1974). Their laboratory experiment with bulk water and water drops demonstrated that  $O_3$  oxidizes bisulfite ions very rapidly and effectively. These authors found that at 10 °C, with an ozone concentration of 0.05 ppm, the sulfate formation rate is given by the following equation:

$$\frac{d[SO_4^{2-}]}{dt} = k'[HSO_3^-] \quad [5.15]$$

where  $k'$  is  $3.76 \times 10^{-4} \text{ s}^{-1}$ . Since bisulfite ion formation is determined by pH and the  $SO_2$  concentration in the air, these parameters also influence the sulfate production rate. In a more recent investigation Penkett and his co-workers also showed (see Beilke and Gravenhorst, 1978) that sulfate (IV) oxidation by  $H_2O_2$  in water samples is also very fast. However, the concentration of this species in the atmosphere is an open question.

The above discussion is summarized in Fig. 42. In this figure, due to Beilke and Gravenhorst (1978), three curves are represented. The dashed line shows the uncatalyzed sulfate formation rate as a function of pH as reported by Beilke *et al.* (1975) for 10 °C and for a  $SO_2$  concentration of 1 ppb. The solid line indicates the

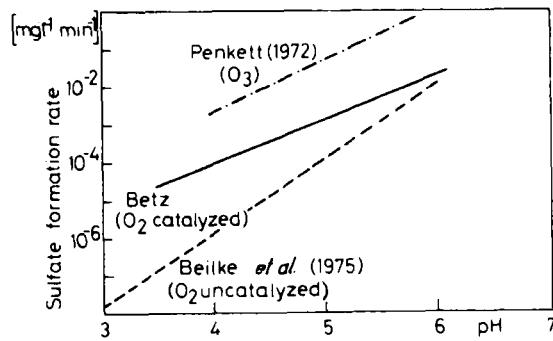


Fig. 42

Sulfate formation rate in the droplet phase as a function of pH of the liquid for three different  $SO_2$  oxidation mechanisms (Beilke and Gravenhorst, 1978). Conditions:  $SO_2$ ; 1 ppb;  $O_3$ : 40 ppb;  $T$  = 10 °C.  
(By courtesy of *Atmospheric Environment*)

results of Betz (see Beilke and Gravenhorst, 1978) obtained with natural rainwater containing manganese and iron in concentrations between  $10^{-7}$ - $10^{-6}$  and  $10^{-6}$ - $10^{-5}$  molar, respectively. The pH of the rainwater samples ranged from 3.2 to 5.2. Finally, the upper line is based on the experimental results of Penkett (1972) obtained with an ozone concentration of 40 ppb (the other parameters as above). This figure clearly suggests that oxidation by  $O_3$  is the dominant pathway for the fixation of sulfur dioxide in clouds. However, further research is certainly needed to confirm the generality of this conclusion<sup>2</sup>.

The majority of sulfur found in cloud and rainwater is sulfate (see later), while some sulfite (10–30 % of the total) has also been identified. It is believed that the quantity of sulfate ions found in rainwater samples at the surface is practically independent of reduced sulfur species (hydrogen sulfide, organic sulfides) because of their limited solubility. In other words this means that the wet removal of these compounds is expected to be unimportant (Hales, 1978).

It is well known that, after its absorption,  $NO_2$  forms nitric acid and nitrous acid in water. There is some indication that nitrite produced in this way is oxidized by dissolved  $O_3$  (Penkett, 1972). If neutralizing agents (ammonia, calcium carbonate etc.) are present, some nitrate salt is finally formed. It follows from this discussion that both  $SO_2$  and  $NO_2$  are oxidized in cloud water by atmospheric ozone. If this speculation is true a correlation should be found between the concentration of sulfate and nitrate ions in precipitation waters. Such a correlation was found in precipitation samples by Gambell and Fisher (1964) among others. However, correlations between any two species in rainwater must be considered with caution because the level of all ions is affected in a similar way by the precipitation intensity or quantity (see Subsection 5.4.1). Nevertheless the identical annual variations of the two ions in precipitation water (see Subsection 5.4.5) suggests that the two species are formed by some similar processes.

For the rain-out of trace gases, equation [5.10] can be applied. According to model experiments and calculations of Beilke and Georgii (1968)  $E_g$  ( $g$ : gas) ranges from 0.01 to 0.1 in the case of sulfur dioxide. On the other hand, Hales (1978) suggests that about 1 % of the airborne  $SO_2$  will dissolve in the aqueous phase at a liquid water content of  $1 \text{ g m}^{-3}$ ; this figure is equivalent to the lower limit proposed by the previous two authors.

### 5.3.3 Wash-out of trace constituents below the cloud base

Once a cloud is formed there are two possibilities concerning its future fate. One possibility is that the cloud partially or totally evaporates. In this case absorbed trace constituents again become airborne. However, a new aerosol spectrum is produced in this way compared to the size distribution before cloud formation, since

<sup>2</sup> It is to be noted that the laboratory experiments of Berry (see Beilke and Gravenhorst, 1978) do not clearly support this conclusion.

one drop generally captures several aerosol particles and some trace gases are transformed irreversibly in cloud water (see the previous paragraph) to acids or salts. Thus, the average size of airborne particles is markedly larger after cloud evaporation than it was before cloud formation, which promotes the further removal of particulate matter.

The other obvious possibility is that materials absorbed are carried by precipitation to the surface of the Earth, that is they are definitively removed from the air. There is no intention here to discuss the formation of precipitation. We only mention that it is believed (Fletcher, 1962) that, in winter layer clouds with small liquid water content, ice crystals play an important role in precipitation formation, while in summer convective clouds the coalescence of large drops with smaller ones is the dominant process. At the same time we have to emphasize that the wet removal of trace constituents is continued by falling precipitation elements (snow crystals, raindrops) below the cloud base. This removal mechanism is called wash-out.

Aerosol particles below the cloud base are captured by precipitation elements due to gravitational coagulation. This type of coagulation is caused by the difference between falling speeds of the aerosol particles and the raindrops or snow crystals. In other words, this means that precipitation elements "overtake" the particles. The air molecules go around the falling drops (or crystals) while large particles are impacted against the drops due to their inertia. For this reason precipitation elements are considered to be small impactors (see Subsection 4.1.2).

Let us suppose that the radius of raindrops is uniform and equal to  $R$ . One raindrop obviously sweeps out an air volume of  $R^2\pi h$  between the cloud base and the surface if the height of the cloud base is  $h$ . Let this air volume be filled with a monodisperse aerosol containing particles of unit density with radius  $r$  at a number concentration  $N(r)$ . Then the total mass of aerosol particles in the air volume swept out will be:

$$M_T = R^2\pi h \int \frac{4}{3} \pi r^3 N(r) dr \quad [5.16]$$

The raindrop will wash out a fraction  $\varepsilon M_T$  of this mass, where  $\varepsilon$  is the impaction efficiency as defined in Subsection 4.1.2 (for its numerical value see Mason, 1957). If the drop radius lies between 50–2000  $\mu\text{m}$  the impaction efficiency is 1 for  $10 \mu\text{m} \leq r < R$  and decreases with decreasing particle size. It ranges from 0.5 to 0.1 if the particle radius varies between 5  $\mu\text{m}$  and 2  $\mu\text{m}$ . This indicates that only giant particles in the coarse mode (Subsection 4.3.2) are significantly washed out below the clouds. Let us multiply the right-hand side of equation [5.16] by  $\varepsilon$  and divide the result by the volume of the raindrop. This yields the trace concentration in the drop ( $C_{2a}$ ) due to the capture of aerosol particles:

$$C_{2a} = \frac{\pi h}{R} \int \varepsilon r^3 N(r) dr \quad [5.17]$$

which is inversely proportional to drop radius.

The change of the mass concentration of aerosol particles ( $M$ ) caused by wash-out can also be calculated easily. Let us designate by  $v(R)$  the falling speed of the drops with number concentration  $N(R)$ . Suppose that this speed is much higher than the deposition velocity of the particles. Under these conditions the particle mass loss in the air per unit time is

$$-\frac{dM}{dt} = \varepsilon M R^2 \pi v(R) N(R) \quad [5.18]$$

or after integration:

$$M(t) = M(0) \exp[-\varepsilon R^2 \pi v(R) N(R)t] \quad [5.19]$$

where  $M(t)$  and  $M(0)$  are the mass concentrations at time  $t$  and at the beginning of the removal process, respectively. By the following substitution,

$$K'' = \varepsilon R^2 \pi v(R) N(R)$$

equation [5.19] yields:

$$M(t) = M(0) \exp(-K''t) \quad [5.20]$$

Physically, relation [5.20] means that the mass concentration of aerosol particles below the cloud base decreases exponentially due to wet removal.

Equation [5.20] was used by Greenfield (1957) among others. During his model investigation he utilized the results obtained by Best (1950) according to which the rainfall intensity unambiguously determines the drop characteristics. In this way he found that at a rainfall rate of  $2.5 \text{ mm hr}^{-1}$  75–80 % of particles with a radius of  $10 \mu\text{m}$  are removed during one hour. More recently the wash-out of sulfate particles below cloud base was modelled theoretically by Scott (1978). His calculations show that the wash-out of sulfate particles is of secondary importance compared to sulfate rain-out caused mainly by condensation. This result is not surprising when one considers the size distribution of sulfate particles (Subsection 4.4.2).

The absorption of trace gases below the cloud is controlled by the same laws as for the rain-out process. The wash-out of trace gases may be particularly significant if the concentration (partial pressure) of the gas considered increases with decreasing height, which is generally the case, especially in more polluted air.

Because of different rain-out and wash-out processes, the concentration of trace constituents,  $C$ , that can be measured in rainwater samples collected at the surface will be as follows (Junge, 1963):

$$C = f(C_{1a} + C_{1g}) + C_{2a} + C_{2g} \quad [5.21]$$

where  $f$  represents the effect of evaporation ( $f$  is equal to or greater than unity),

while indexes 1, 2, *a* and *g* refer to rain-out, wash-out, aerosol particles and gases, respectively.

The significance of the terms in equation [5.21] can be estimated by modelling in an appropriate way the wet removal of gaseous and particulate compounds. Table 27 gives the relative importance of the different terms, expressed in percentage of the surface concentration in rainwater for each sulfur species. All authors listed made model calculations using results of laboratory experiment and atmospheric observations. It can be seen that the relative influence of the wet removal of sulfate particles lies between 25 and 85 %. In a more recent paper, Scott (1978) speculates on the basis of his removal modelling that the sulfate mass measured at the surface in rainwater can be attributed totally to the rain-out and wash-out of airborne sulfate particles. This discrepancy in the models is obviously caused by the different assumptions used. It cannot be excluded, however, that this fraction really varies as a function of the degree of pollution of the atmosphere, or of other parameters.

**Table 27**  
Contribution of different scavenging processes to the total sulfate concentration  
in rain water (%)

	Beilke and Georgii (1968)			Miller and Pena (1972)			Varhelyi (1977)		
	SO <sub>2</sub>	SO <sub>4</sub> <sup>2-</sup>	Total	SO <sub>2</sub>	SO <sub>4</sub> <sup>2-</sup>	Total	SO <sub>2</sub>	SO <sub>4</sub> <sup>2-</sup>	Total
Rain-out	5	20	25	-	-	-	34	34	68
Wash-out	70	5	75	-	-	-	25	7	32
Total	75	25	100	15-20	80-85	100	59	41	100

### 5.3.4 The study of wet removal mechanisms by means of atmospheric measurements

For the investigation of the importance of the different wet removal processes, it is usual to compare the chemical composition of cloud and precipitation waters sampled simultaneously. This would appear to separate the effects of rain-out and wash-out. However, as we shall see, the results of such a comparison have to be considered with some caution.

The composition of cloud and precipitation water was investigated by Petrenchuk and Drozdova (1966), among others; they developed a special cloud water collector that worked at positive as well as at negative temperatures. Their results, obtained over the European parts of the U.S.S.R., are given in Table 28. It can be seen that over clean northern regions the difference between the sum of ions in cloud and precipitation elements is not great. In these areas the concentration of sulfate and nitrate ions is relatively small while the chloride content is great. This situation can be explained by maritime influences. In comparison, sulfate is the

predominant component over the south-western regions, and this is at least partly due to anthropogenic sources.

One of the most interesting (and disturbing) results of this investigation is the fact that in the case of some ions the concentrations are higher in cloud than in precipitation water, especially over the cleaner areas (north). In the case of chloride this unexpected difference was ubiquitous. Thus the  $\text{Cl}^-/\text{Na}^+$  ratio in clouds is greater than the corresponding value in sea water (equal to 1.8) while in precipitation it is smaller. It is very difficult to explain this finding. A partial explanation may be that the precipitation elements were formed from the more dilute part of the cloud water (i.e., the larger drops). Further, Petrenchuk and Drozdova speculated that gaseous chlorine could be liberated below cloud base due to chemical reactions of the sea salt components (see, e.g. Subsection 3.5.4).

Finally, the measurements of Petrenchuk and Drozdova (1966) also showed that in clouds with smaller drops the water contains more dissolved materials than in clouds with greater average drop size, in agreement with the previous theoretical considerations.

**Table 28**

Chemical composition of cloud and precipitation waters over the European part of the U.S.S.R.  
(Petrenchuk and Drozdova, 1966)

Territory	Sample	$\text{SO}_4^{2-}$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{NH}_4^+$	$\text{Na}^+$ [mg l <sup>-1</sup> ]	$\text{K}^+$	$\text{Mg}^+$	$\text{Ca}^{2+}$	pH	Conduct. [ $\mu\text{S cm}^{-1}$ ]	Total [mg l <sup>-1</sup> ]	$\text{Cl}/\text{Na}$
North	Precipitation	3.6	3.4	0.6	0.5	2.2	0.6	0.2	0.7	5.5	29	11.8	1.5
	Cloud	0.6	6.3	0.1	0.6	2.4	1.7	1.0	0.4	5.3	30	13.1	2.6
North-west	Precipitation	6.2	1.1	0.5	0.7	1.3	0.8	0.2	1.1	5.2	28	11.9	0.8
	Cloud	6.0	2.5	0.5	0.9	1.2	0.8	0.2	0.6	4.7	28	12.7	2.1
South-west	Precipitation	14.3	1.4	0.8	0.7	1.6	0.6	0.4	6.0	6.1	62	25.8	0.9
	Cloud	8.9	2.1	0.8	1.8	0.7	0.6	0.5	1.0	4.8	40	16.4	3.0

More recently, Fricke *et al.* (1978) reported the results of a similar investigation. In this study, carried out over Bavaria, F.R.G., the composition of cloud water collected at the cloud base was compared with the composition of rainwater sampled at the surface. It was found that the concentration of heavy metals at cloud base was about twice the value at ground level in rainwater, in agreement with some of the results of Petrenchuk and Drozdova (1966). Fricke's study also indicated that the total sulfur content (sulfate +  $\text{SO}_2$  + sulfite; about 30 % of the total was  $\text{SO}_2$  and sulfite) was doubled between the cloud base and the surface, probably due to  $\text{SO}_2$  wash-out.

The understanding of wet removal of trace constituents is further facilitated by sampling at several altitudes above and below the cloud base. Such an investigation was done by Georgii (1965) in the Alps. He collected rainwater samples at four levels. The altitude difference between the highest and lowest station was 1800 m (the horizontal distance was 6.5 km). At the two higher sampling points, which were

generally in the cloud, the cloud water was also sampled. The mean results for electrolytic conductivity (measure of the total ion content) obtained in 1963–1964 are plotted in Fig. 43. The abscissa gives values expressed in percentage of the conductivity observed at the lowest level (Innsbruck), while for the cloud and rainwater collected inside the clouds the absolute values are also given. One can see from this figure that the electrical conductivity of cloud water was found to be practically the same as that of rainwater in Innsbruck. On the basis of this finding, in the absence of other information, we should say that the wash-out was negligible during this study. However, the quantity of ions in precipitation collected above the cloud base was found to be significantly smaller than the same parameter in cloud water. This is consistent with the hypothesis that precipitation forms from more diluted part of cloud water, as mentioned above.

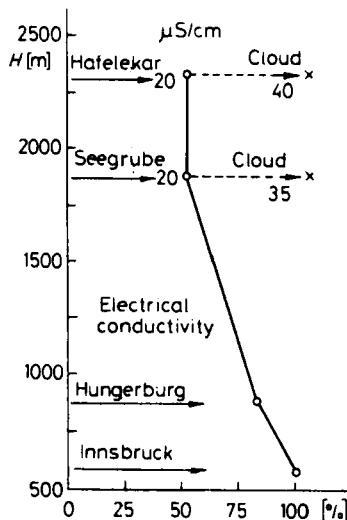


Fig. 43

Variation of the electrical conductivity of cloud and precipitation as a function of altitude according to Georgii (1965). The solid line corresponds to rain water and is expressed in percent of conductivity measured in Innsbruck. (By courtesy of Deutscher Wetterdienst)

It also follows from Fig. 43 that the composition of cloud and precipitation water, at least in the lower part of the cloud, does not depend very much upon the altitude. On the other hand, below the cloud base, which was generally between Hungerburg and Seegrube, the electrical conductivity increases by a factor of two, which means that rain-out and wash-out processes contribute about equally to the final concentration of salts in precipitation water measured at the surface.

Wet removal processes can also be studied by measuring the variation of the chemical composition during individual rainfalls. Figure 44 gives the results of such a study (unpublished work by the present author; samples taken near Budapest). The part (a) of this figure refers to calcium ions, which come only from particulate matter, while part (b) represents the concentration variation in case of ammonium ions, which are due both to ammonium containing particles and to gaseous ammonia in the air. In Fig. 44 the change of rainfall rate during precipitation is also given (dotted lines). It is to be noted that concentrations in rainwater (ordinate) are expressed in units of the average for total rainfall, while the abscissa gives the time in percentage of the duration of precipitation. One can see from Fig. 44 that calcium and ammonium concentrations in rainwater decreased to a constant value in the middle of the rainfall period, when the precipitation intensity is at a maximum. At the end of the rainy interval the calcium concentration begins to rise, but it does not reach the starting values. This phenomenon is not observed in the case of ammonium ions. It can also be seen that at the beginning of the rainfall calcium concentration increases slightly.

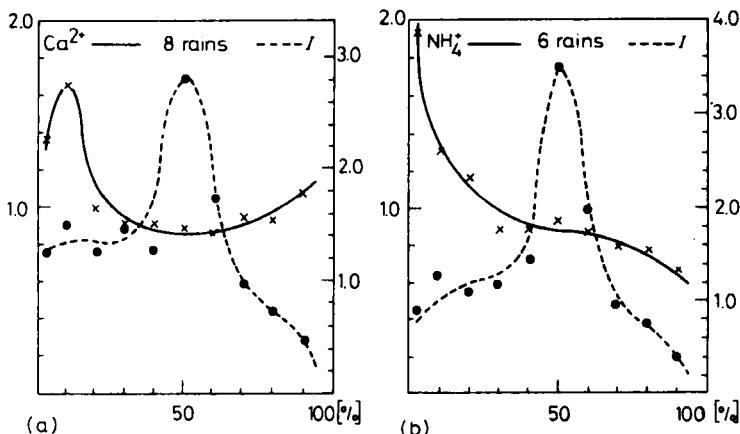


Fig. 44

Average variation of calcium and ammonium concentration in precipitation samples (solid lines) as a function of the duration (expressed in %) of rainfall. Dashed line is the precipitation intensity

On the basis of our foregoing discussion, the pattern represented by Fig. 44 may be explained as follows. Let us consider a cloud with precipitation which moves over our sampling site. At the beginning, precipitation elements fall from the frontal part of the cloud. In this part, near the edge of the cloud, the liquid water content is low and consequently the water is more concentrated. Since there is a direct relation between liquid water content in the cloud and precipitation intensity at the surface the rainfall rate is also low at this time. The light rain falls in an "unwashed" polluted atmosphere which is frequently unsaturated with water vapour. Both circumstances

promote the formation of higher concentrations in rainwater. Some larger, more dilute drops reach the surface faster than smaller ones (see the curve for calcium) because of their higher falling speed. In the middle of the rain period precipitation elements arrive from the centre of the cloud where the liquid water content is higher and the water is less contaminated. Also, in this period the air below the cloud base is cleaner and already saturated. At the end of the precipitation the drops fall from the rear part of the clouds where liquid water is again small. However, the air is much cleaner then before the rainfall due to the wet removal. Hence the concentration increase is not large enough to reach the initial values (calcium); it may not occur at all (ammonium).

It follows implicitly from this discussion that smaller precipitation elements are generally more concentrated than larger ones since rain of low intensity is composed of smaller drops (Best, 1950). This relation was experimentally proved by Georgii and Wötzl (1967) who constructed a special rainwater collector that classified rain drops according to their size. In this way they demonstrated that the concentration increased with decreasing drop size.

We can expect that the level of trace constituents in the air decreases during rainfall. However, variations of surface air concentration of atmospheric substances are not representative of the wet removal taking place at higher tropospheric levels. It is very difficult to make a separation between effects caused by wash-out and those which are due to air mass exchanges. With these problems in mind the data obtained by Georgii (1960) in Frankfurt am Main are presented in Table 29. In this table the concentration of different gaseous and particulate constituents are given, measured before and after precipitation. It can be seen that the decrease may be as great as 73 % (nitrate particles).

Table 29

Concentrations of trace constituents in the air before and after rainfall in Frankfurt am Main between June 1956 and May 1957  
(Georgii, 1960)

Conc. [ $\mu\text{g m}^{-3}$ ]	Aerosol particles			Gases		
	$\text{NH}_4^+$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{NH}_3$	$\text{NO}_2$	$\text{SO}_2$
Before rain	6.7	6.0	16.7	21.6	11.9	328
After rain	4.7	1.6	9.7	11.0	9.1	212
Difference [%]	30	73	42	48	24	36

This discussion indicates that atmospheric observations at least qualitatively support the wet removal theory outlined in the previous paragraphs. Further research is needed, however, to determine reliable quantitative relationships between the concentration level of a substance in the air and in precipitation water as a function of atmospheric conditions.

## 5.4 Chemical composition of precipitation

### 5.4.1 Introduction

Precipitation water has been generally sampled for subsequent chemical analysis in one of the following two ways. The first procedure consists of collecting the precipitation in an open rain gauge. In this case the samples also contain a part of the dry deposition. The second is the use of so-called automatic collectors, which are closed in dry periods and open only during rainfall. The second sampling method is obviously better. In spite of this fact, open samplers are frequently used because of their simplicity. The results of precipitation analysis<sup>3</sup> are generally expressed in  $\text{mg l}^{-1}$  or  $\text{ppmm}$  which are numerically equivalent.

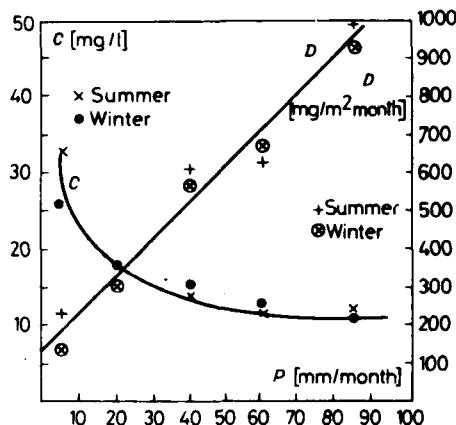


Fig. 45

Wet deposition ( $D$ : ordinate at right) and concentration ( $C$ : ordinate at left) of sulfate ions in precipitation as a function of precipitation quantity ( $P$ )

On average, the data show an inverse relation between the concentration ( $C$ ) of different components and the precipitation quantity ( $P$ ) during the sampling time. This fact is illustrated by curve  $C$  of Fig. 45, constructed on the basis of sulfate ion analyses of monthly precipitation samples collected in Hungary (Kozák and Mészáros, 1971). The relation between  $C$  and  $P$  was calculated separately for the summer and winter half-years. However, results for the two half-years do not differ significantly. A more detailed analysis of the data showed that the *minimum* concentration values in a given precipitation quantity interval are independent of  $P$ , which means that the character of the curve is determined by the relation between *maximum* concentrations and precipitation amount. This means that with increasing precipitation amount the scatter of the data decreases. This phenomenon was first demonstrated by Georgii and Weber (see Junge, 1963). Junge (1963)

<sup>3</sup> Concerning details of chemical analyses the interested reader is referred to the original papers cited.

speculates that the greater data scatter in the case of smaller precipitation amounts is caused by differences in wash-out and evaporation below the cloud base. On the other hand, the composition of precipitation water in the case of greater precipitation quantity is determined by rain-out processes taking place inside the clouds.

Precipitation amount is normally reported in millimeters. One millimeter of precipitation means that 1 liter of water fell on 1 m<sup>2</sup> of horizontal surface. Thus, if we multiply the concentration, expressed in mg l<sup>-1</sup>, by the precipitation quantity in mm, we obtain the mass of trace constituents in mg deposited on 1 m<sup>2</sup> of the ground during the sampling time. The value of this parameter, termed the wet deposition, increases linearly with increasing precipitation quantity (see curve D in Fig. 45).

The study of the chemical composition of precipitation is of interest for the evaluation of many scientific and practical problems. Thus, a knowledge of the chemical composition makes it possible to evaluate the degree of air pollution, the sink terms in the atmospheric cycle of aerosol particles and water soluble gases, the corrosiveness of atmospheric waters and the effect of precipitation on the material balance of soils, waters and vegetation. For these reasons, many precipitation analyses have been done, mostly in the last three decades. In this book only those works are mentioned in which an extensive network were (or are) operated, as in the American, Swedish and Soviet programs.

We have seen that the trace constituents of precipitation are principally soluble acids and salts. Furthermore, it has been pointed out that, under tropospheric background conditions, water-soluble components are predominant in the particulate matter. For this reason we shall restrict our discussion to the ions found in precipitation water, including hydrogen ion.

#### 5.4.2 American measurements

The first network to collect precipitation samples for subsequent chemical analyses all over the United States of America was organized by Junge and Werby (1958). More recently researchers at the National Center for Atmospheric Research<sup>4</sup> have published a compilation of data obtained between 1960 and 1966 by means of a network consisting of 33 stations (Lodge *et al.*, 1968). At the stations, situated mostly in locally non-polluted rural environments, automatic rain gauges were used.

The aim of this program has been:

- (a) to determine the spatial distribution of the composition over the country;
- (b) to study the trend of concentrations during a longer time;
- (c) to reveal the source distribution of trace constituents on the basis of precipitation chemistry data.

<sup>4</sup> The National Center for Atmospheric Research is sponsored by the National Science Foundation, U.S.A.

The spatial distribution of the concentration of sulfate ions is reproduced in Fig. 46. One can see that the concentrations are higher over industrialized north-east territories as well as over arid areas of west and mid-west. It is speculated

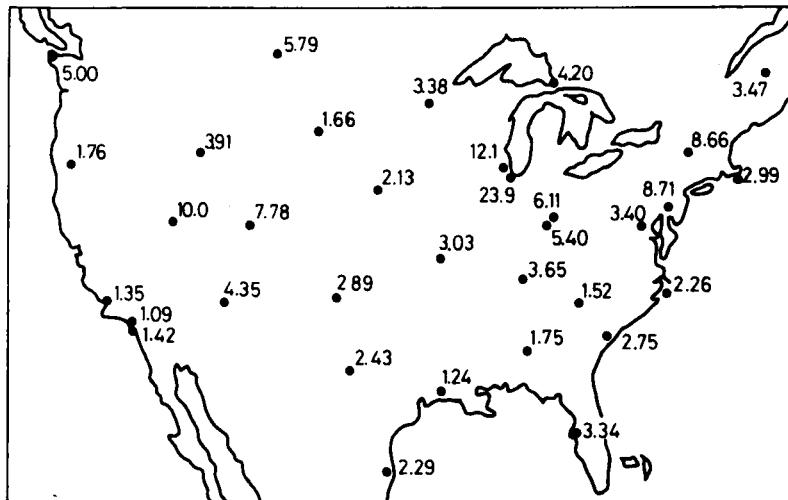


Fig. 46

Average concentration of sulfate in precipitation over the U.S.A. according to Lodge *et al.* (1968). Values are expressed in ppmm. (By courtesy of the National Center for Atmospheric Research)

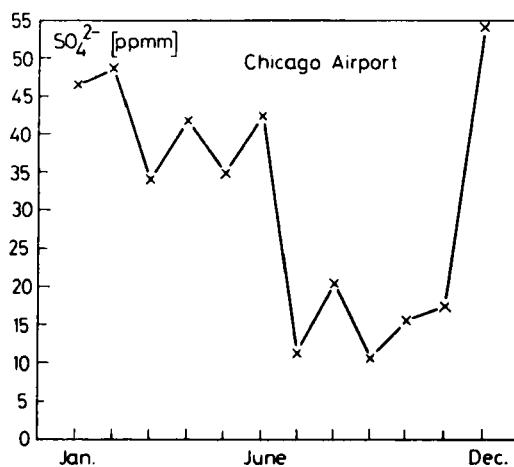


Fig. 47

Annual variation of sulfate concentration in precipitation at Chicago-Airport (Lodge *et al.*, 1968). (By courtesy of the National Center for Atmospheric Research)

(Lodge *et al.* 1968) that the greater sulfate content of precipitation water in an arid environment is due to mineral dust particles and to the effect of evaporation below the cloud base. Soils in these areas contain calcium carbonate and calcium sulfate in significant proportions. Calcium carbonate particles in the air are transformed into calcium sulfate by reacting with sulfur dioxide. The process is an interesting interaction of natural and man-made trace constituents.

The high concentrations over the north-eastern part of the U.S.A. are explained by the effect of man's activities. This is further illustrated by annual variations in the sulfate concentration in precipitation water collected at Chicago airport, as shown in Fig. 47. We can see that at this station near Chicago the concentrations are highest in the winter, when fuel consumption is significant. The curve plotted also shows that during spring and early summer a secondary maximum can be observed in the concentration. This is in a good agreement with the annual change of the sulfate content of precipitation water in cleaner environments (see Subsection 5.4.5).

Finally, it is to be noted that the data analyses of Nisbet (see Hales, 1978) demonstrated that in North America the sulfate concentration in precipitation increased until 1965 by a rate of 60–65 % every decade. Although a levelling off occurred after 1966, the concentration has an upward trend, even at present.

#### 5.4.3 The "Swedish" network

The first major precipitation chemistry program was initiated by Swedish scientists (see Egnér and Eriksson, 1955). The network was extended to the northern and western parts of Europe and for some time chemical data were published in the scientific journal *Tellus*. At the beginning of the sixties more than one hundred stations were involved in the network. This network is still in operation, and it is now called the European Atmospheric Chemistry Network (Granat, 1978), since not only precipitation chemistry is measured in this program (see Egnér *et al.*, 1955). The number of stations at present is about 50. Monthly precipitations samples are collected by open rain gauges.

Figure 48 illustrates the spatial distribution of chloride ions measured by the Swedish network in 1957 and 1958 (Junge, 1963). In this figure the results of a Czechoslovakian program performed during the International Geophysical Year (Macků *et al.*, 1959) are also included. One can see that the isolines practically follow the contour of the continent which makes evident that in locally unpolluted air the atmospheric chloride is of maritime origin. In Scandinavia the concentration initially decreases exponentially with distance from the ocean and reaches a rather constant value.

Concerning possible damage caused by atmospheric precipitation to other media of our environment (e.g. lakes, soil, vegetation), the acidity or pH of precipitation water is of crucial interest. It should be noted here that the neutral point of atmospheric waters is lowered by the presence of CO<sub>2</sub> in the air. Thus, it can be calculated (Junge, 1963) that the neutral point is at pH = 5.6 at a temperature of

10 °C. This hydrogen ion concentration is then altered by different trace constituents.

The spatial and temporal distribution of pH in precipitation over Scandinavia was first studied by Barrett and Brodin (1955). According to their data, in South Sweden and in seaside areas, the pH is between 4 and 5 in the majority of cases. In a more continental environment the pH reaches the value of 6. The above authors

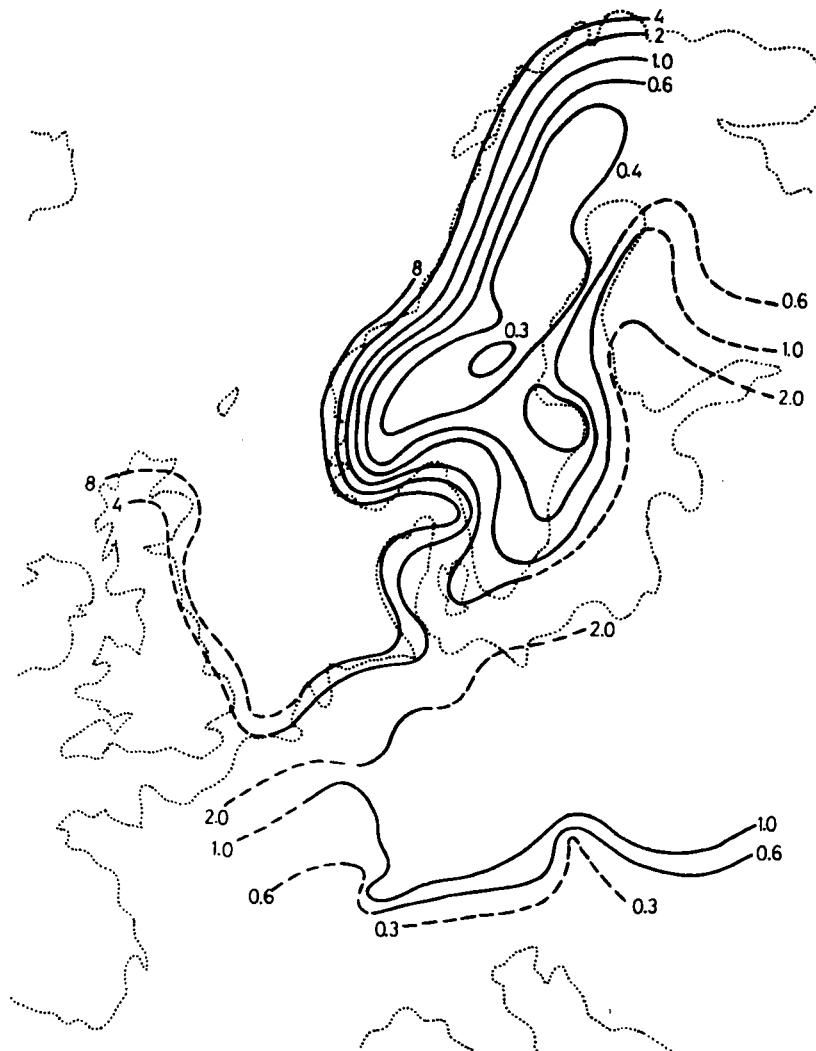
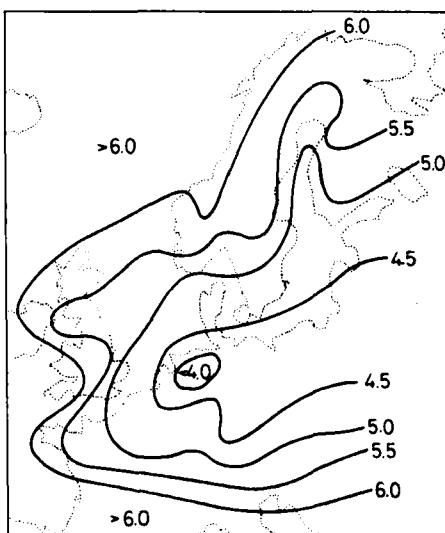


Fig. 48

Distribution of chloride concentration of precipitation water over North and North-West Europe (Junge, 1963). (By courtesy of Academic Press and the author)

attributed this spatial distribution to the advection of polluted air from West and Central Europe. The concept of anthropogenic effects was also confirmed by the annual variations of pH, which showed a clear winter minimum. The low values found in Norway near seaside were explained by the influence of H<sub>2</sub>S of maritime origin.

The pH distribution in precipitation over North-West Europe was studied by Odén. Figure 49 is taken from Odén's work, as published by Butcher and Charlson (1972). This distribution is believed to be caused by the anthropogenic SO<sub>2</sub> emission, the maximum intensity of which approximately coincides with areas of lowest pH values.



**Fig. 49**

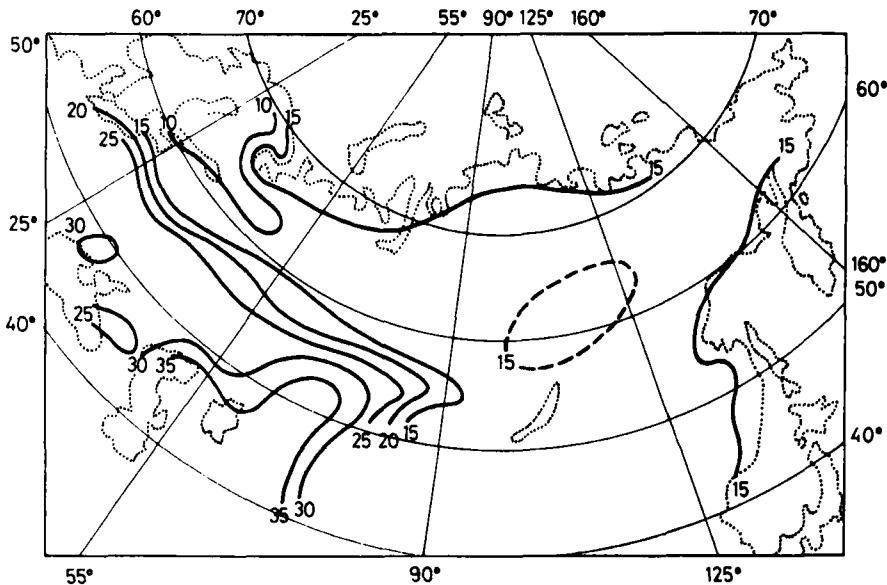
Spatial distribution of pH of precipitation according to Odén (see Butcher and Charlson, 1972). (By courtesy of Academic Press and the authors)

Recently Granat (1978) has analyzed data on sulfur concentration in precipitation and sulfur wet deposition obtained in European Atmospheric Chemistry Network. According to his paper the deposition has been constant during the last ten years over North-West Europe. It is postulated that sulfur emitted in this area is transported and deposited over other areas, probably in an eastward direction (see Subsection 3.6.6). However, using the nitrate data of the same network, Söderlund (1977) reports an overall increase of 50–100 % in the nitrate wet deposition at many stations during the 20 years ending in 1973.

#### 5.4.4 Chemical composition of precipitation waters over the Soviet Union

The study of the chemical composition of precipitation in the U.S.S.R. by means of an extensive network was started in the International Geophysical Year under the auspices of the Main Geophysical Observatory, Leningrad. Stations were initially operated over the European part of the Soviet Union with collectors covered during dry periods. The network was later extended to the Asian part of the country. The results of analyses of daily and monthly precipitation samples collected at 13 European stations in 1958–1961 are summarized by Drozdova *et al.* (1964). Some of their data are reproduced in Table 28. The data tabulated clearly show that rather high concentrations of contaminants can be found in the southwest. In these areas the concentration of sulfate ions is particularly significant. Soviet workers attribute this finding to the effects of anthropogenic sources. However, dispersed soil components may also play a certain role in the control of the composition of precipitation (see Subsection 5.4.2).

This assumption is also supported by the spatial distribution of the sums of the concentrations of all ions measured over the whole of Soviet Union as shown in Fig. 50 (Petrenchuk and Selezneva, 1970). This figure indicates that very high concentrations are measured in the south over arid areas. One can also see from Fig. 50 that minimal concentrations are detected over the northern territories and over



**Fig. 50**

Distribution of the sum of the masses of ions in precipitation ( $\text{mg l}^{-1}$ ) over the U.S.S.R. (Petrenchuk and Selezneva, 1970). (By courtesy of the American Geophysical Union and the authors)

Siberia. It is possible that the Siberian value of  $15 \text{ mg l}^{-1}$  represents the continental background of Europe and Asia.

Petrenchuk and Selezneva (1970) made model calculations to evaluate the removal both in the cloud and beneath the cloud. They found that, in a clean tropospheric environment, 55 % of the trace constituents found in precipitation collected at the ground level is due the rain-out processes, in agreement with Georgii's results discussed in Subsection 5.3.4.

Soviet data also demonstrate that the sum of the concentrations of the different ions is independent of sampling location in the case of frontal precipitation systems, and is equal to about  $6 \text{ mg l}^{-1}$  over the whole of the Soviet Union. The pattern shown in Fig. 50 is thus mostly produced by local precipitation systems, which are much more sensitive to local pollution. Petrenchuk and Selezneva (1970) argue that in frontal systems the rain-out of aerosol particles by condensation is the dominant mechanism in the control of precipitation water composition.

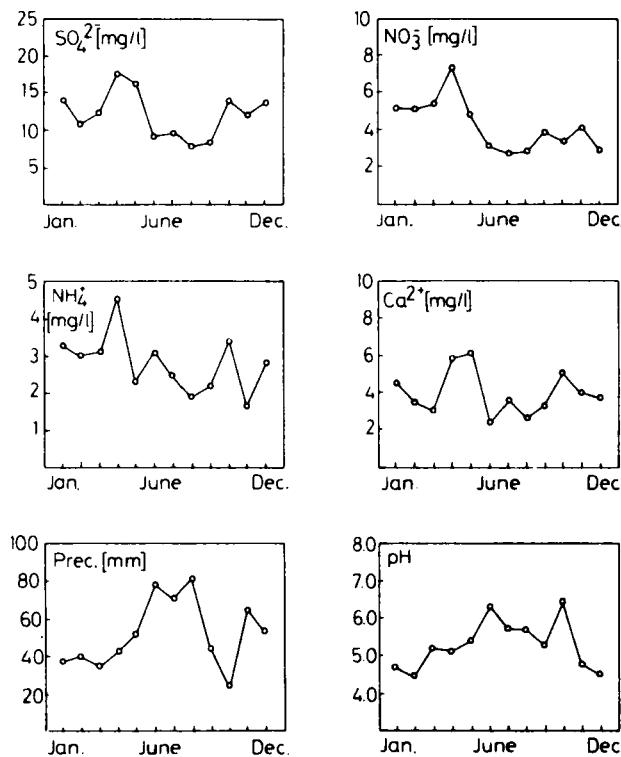
On the basis of precipitation chemistry data, Selezneva (1972) was also able to estimate that, over rural areas of the Soviet Union 30–40 % of the contamination found in precipitation is due to the background level of trace constituents, while 60–70 % of the concentration reflects the effects of local sources. About half of this latter fraction is provided by pollutants. In this important work she also showed that about 20–30 % of the quantity of ions is anthropogenic even over such clean areas as Siberia.

#### 5.4.5 Annual variations of the chemical composition

In the discussion of Fig. 45 it was stated that no differences are detected in the precipitation composition in the summer (April–September) as compared with the winter (October–March) half-years. However, if the more detailed annual variation of the concentration of different ions is studied by means of monthly averages, an interesting spring maximum can be identified. Figure 51 shows the average annual variation of the concentration of several parameters of precipitation water collected at four rural stations in Hungary (E. Mészáros, 1974a). In the figure the average precipitation amount is also plotted. One can see that the concentrations of all components except pH have a maximum in March or April. The presence of a late summer or early fall minimum is also obvious. In the winter months, in the case of all the ions studied, a secondary maximum emerges, while ammonium and calcium distributions also show a small summer peak. It is evident that the secondary winter maximum is caused by anthropogenic effects. Furthermore, the small summer peaks are obviously explained by the influence of natural sources. The exception is the pH, the monthly values of which vary as a function of the difference between the sum of calcium and ammonium and the sum of nitrate and sulfate ions. Its annual variation is similar to that found in Scandinavia by Barrett and Brodin (1955).

In Subsection 5.4.1 it was shown that there is an inverse relation between the concentration of chemical components and precipitation amount. However, the

spring maximum cannot be attributed to this effect since in the spring months the quantity of monthly precipitation increases. Only the October peak in the distribution of chemical parameters can be interpreted by this relationship.



**Fig. 51**  
Annual variation of chemical composition and precipitation quantity (Prec.) over Hungary (E. Mészáros, 1974a). (By courtesy of *Tellus*)

We can thus conclude that the spring maximum cannot be explained either by the annual variation of source intensity at the Earth's surface or by the variation of the quantity of precipitation. It has been postulated (E. Mészáros, 1974a) that this maximum is due to the oxidation effects of tropospheric ozone, the concentration of which also has a maximum during the spring (see Fig. 13). Ozone oxidizes  $\text{SO}_2$  and  $\text{NO}_2$  in atmospheric liquid water (see Subsection 5.3.2) which leads to the lowering of the pH. The increase in the concentration of hydrogen ions promotes the absorption of ammonia gas from the air, as well as the transformation of insoluble mineral components (e.g. calcium carbonate) into water-soluble materials. If this speculation is correct, this process provides a non-negligible ozone sink in the

troposphere (Subsection 3.4.5) and plays an important role in the cleansing of the lower atmospheric layers from anthropogenic pollutants.

The existence of the spring maximum was also illustrated by Soviet and Swedish precipitation chemistry data (E. Mészáros, 1974a). Furthermore, Granat (1978) has demonstrated more recently, on the basis of a large amount of data gained in the European Atmospheric Chemistry Network, that the sulfur concentration in precipitation has a maximum in March. Further evidence is needed, however, before the acceptance of the above hypothesis

#### 5.4.6 The future of precipitation chemistry measurements

It becomes more and more obvious that anthropogenic effects can modify (and will modify considerably in the future) the chemical composition of the atmosphere, even on a global scale (see Chapter 3). Since these modifications may lead to inadvertent climatic modification (see Chapter 6), there is an increasing need to monitor the trends in large scale atmospheric composition. Since, on the one hand, sampling of precipitation water is rather easy and, on the other hand, the precipitation composition is a good indirect indicator of the pollution of a large part of the troposphere, the World Meteorological Organization decided to include the measurement of the chemical composition of precipitation in its background air pollution monitoring program. Considering that the density of this network is adequate at present only in Europe and in North America, further efforts have to be made so that this program becomes really world-wide. The standardization of sampling and chemical analysis procedure is also an obvious need.

Furthermore, in all international programs intended to determine the long-range transport of sulfur and nitrogen containing pollutants (e.g. across national boundaries) one has to organize a dense precipitation chemistry network to follow the wet deposition of these components. Such studies (e.g. the present program of the Economic Commission for Europe) seem to be indispensable in order to understand the atmospheric pathways of trace constituents on a continental scale in a more reliable way and to make international air quality management possible.

## **6. Connection of variations of the climate with the chemical composition of the atmosphere**

### **6.1 Introduction**

The Earth's climate depends among other parameters (see later) on the chemical composition of the atmosphere. Thus, any variation in the composition raises the possibility of climatic change. First of all, the chemical composition regulates the radiation balance of the Earth-atmosphere system. However, since differences in radiation balance in various geographical regions control the atmospheric circulation, there is also a relationship between composition and dynamic processes. In this chapter we shall deal mainly with the effects of compositional variations on the radiation balance. Moreover, the significance of so-called feedback mechanisms will also be stressed.

In the last decades the study of climatic change has become one of the most important problems of atmospheric science because of the possible variation of the climate due to the effects of anthropogenic pollution on our environment.<sup>1</sup> Since it is evident that we cannot evaluate the importance of the present variations without the understanding of past climates, independent of human influences, this interest has also given an impetus to the investigation of the Earth's climate during geological times. The problem of climatic change was discussed in detail by an international group of experts in 1971 in Sweden. The main aim of this study was to evaluate the role of man in the present climatic variations. The conclusions of their discussion were published in an excellent report (SMIC, 1971)<sup>2</sup> which was summarized in a shorter form by Schneider and Kellogg (1973). This chapter is also based in many respects on that report.

The history of the Earth dates back nearly 5 billion years. We have reliable information, however, concerning only the last 500 million years or so. This information has been obtained mostly from studies of minerals and oceanic sediments, as well as from studies of the forms of mountains and the ocean floor. The understanding of the climate of more recent eras was facilitated by the investigation

<sup>1</sup> Human activities can also influence the climate in other ways: modification of the surface, energy production, etc. We shall limit our discussion, however, to the effects of air pollution in view of the scope of this book.

<sup>2</sup> SMIC: Study of Man's Impact on Climate.

of ice layers in Greenland and Antarctica, but important results were provided also by biological studies.

This research, together with other studies, demonstrated that for 90 % of the time from the beginning of the Cambrian period (500–600 million years ago) the poles of the Earth were free of ice. The first important glaciation began at the end of the Paleozoic era (250–300 million years ago), which was followed by a warmer era in the Triassic era. Approximately 150 million years ago the temperature started to drop. Thus, according to studies made by Knauth and Epstein (1976) on hydrogen and oxygen isotope ratios in nodular and bedded cherts in the western and central parts of North America, the average temperature decreased from about 34 to 20 °C through the Paleozoic period, increased to 35–40 °C in the Triassic period and then decreased again to its Tertiary period value (~17 °C). The glaciation of Antarctica began about 5 million years ago; the corresponding date for Greenland is 2 million years.

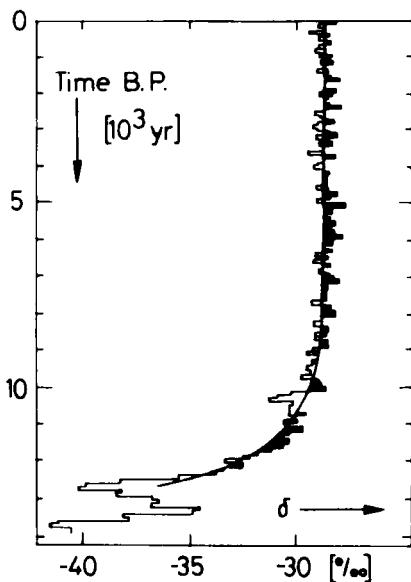


Fig. 52  
Variation of  $^{18}\text{O}/^{16}\text{O}$  ratio ( $\delta$ ) as a function of time B. P. according to Dansgaard *et al.* (see SMIC, 1971).  
(By courtesy of Massachusetts Institute of Technology)

In the Pleistocene era, warmer and cooler intervals alternated. There is some indication that each glaciation built up over a period of about 90 000 years and terminated in a shorter time of about 10 000 years. The last "ice age" reached its

maximum about 20 000 years ago and had largely disappeared 10 000 years later. We have much reliable information on the average temperature for the last 14 000 years as a result of the  $^{18}\text{O}/^{16}\text{O}$  isotopic studies made in ice layers deposited in Greenland in different epochs. An increase in this ratio indicates a warmer temperature in the time of ice and snow deposition. Figure 52 represents the results of such an investigation, carried out by Dansgaard and his co-workers (see SMIC, 1971). Blackened parts on the right-hand side of the smoothed curve refer to warmer periods, while white parts to the left indicate cooler intervals. The amplitude of the variations is around 1–2 °C. It can be seen that, in spite of these fluctuations, the temperature in the last 8000 years has been practically constant. Since the beginning of our era, a short cold period was noted after 1200 and between 1550–1700 ("little ice age").

Different authors attribute the above climatic variations to the following causes:

- (1) variations in solar activity;
- (2) fluctuations in the Earth's orbit;
- (3) fluctuations of the quantity of  $\text{CO}_2$  or volcanic dust in the atmosphere;
- (4) changes of the position and size of the continents;
- (5) variations in oceanic circulation;
- (6) intransitivity of the Earth-atmosphere system (see later).

Among these causes only those mentioned in point 3 are within the scope of this book. We shall discuss them in some detail in Section 6.5 in connection with present climatic variations. Of the other factors we shall clarify here only point 6, which is probably less known than the others. If in our climatic model (see later) the random modification of initial conditions results in a nonzero probability that the climate remains unchanged, then the climate is called stable. If the system has only one single stable climate (and possibly many unstable ones) it is said to be transitive (see more detail in SMIC, 1971). Otherwise, it is said to be intransitive. According to Lorenz (1968) the climate of the Earth is intransitive. This means that climate can go from one stable state to another without the modification of external or initial conditions, that is, variations are due to the "internal" fluctuations of the system.

The above list of possible causes of climatic changes starts with the most deterministic explanation, according to which the variations are totally due to an external factor, namely fluctuations of solar activity. The list ends with the least deterministic theory predicting that climatic variations are caused by internal random fluctuation of the Earth-atmosphere system.

After this discussion the reader is surely curious to know which factor is the most important in the control of climatic variations. Unfortunately the experts are not able to make such a choice at present. Furthermore, it cannot be excluded that the interaction of several factors produced past climatic variations.

## 6.2 Radiation balance of the Earth-atmosphere system

The Earth-atmosphere system consists of the ensemble of the atmosphere, ocean, continents and ice cover. The climate of this system is controlled by the orbit and rotation of the Earth, the physical state and chemical composition of the surface (including liquid water and ice), and by the density and composition of the atmosphere. This last parameter participates mainly in the control of the radiation balance. For this reason our knowledge of the radiation balance of the Earth-atmosphere system will be summarized briefly in this section. The interested reader is referred to Paltridge and Platt (1976) for further details.

The Sun can be considered as a black body, the temperature of which is around 5800 K. In accordance with this temperature, 90 % of the energy radiated is composed of radiation with wavelength ranging from 0.4 to 4.0  $\mu\text{m}$ . The intensity maximum is in the visible range around 0.5  $\mu\text{m}$ .

Of the radiation energy coming from the Sun, 30 % is reflected by the Earth-atmosphere system. This fraction is termed the planetary albedo. The planetary albedo is regulated in a significant way by the clouds in the atmosphere. It is estimated that 20–25 % of the incoming radiation is reflected by clouds. This part of the albedo obviously varies as a function of the nature and the dimensions of the cloud cover. The rest of the planetary albedo is due to reflection from the surface and scattering by gas molecules and aerosol particles. Another 25–30 % of the incoming radiation is absorbed by gases, aerosol particles and cloud elements, while the balance of the radiation reaches the surface and is absorbed there.

Among atmospheric gases,  $\text{O}_2$ ,  $\text{O}_3$  and water vapour molecules are the most effective absorbers. Above 100 km, radiation with wavelength shorter than 0.18  $\mu\text{m}$  is absorbed by molecular oxygen, which leads to the heating of this air of low density (thermosphere). A very small part of the energy absorbed is used for chemical dissociation and ionization. Radiation of wavelengths in the range of 0.18–0.29  $\mu\text{m}$  is absorbed in the stratosphere, and to a lesser extent in the mesosphere, by  $\text{O}_2$  and  $\text{O}_3$  molecules. The relatively high temperature around the stratopause (see Section 1.2) is caused by this process. In the lower part of the atmosphere (troposphere), absorption by water vapour molecules is the most important.

The Earth-atmosphere system radiates energy back into space in a quantity equal to the incoming energy. The Earth's surface, like all radiating bodies, emits radiation according to its temperature. Because of the inverse relationship between temperature and the wavelength of the emitted radiation, the surface radiates in the infrared range (4–400  $\mu\text{m}$ ). If the total quantity of the energy emitted at the surface left the atmosphere, the temperature of our planet would be around  $-20^\circ\text{C}$  (effective radiation temperature). However, the atmosphere absorbs a significant part of the infrared radiation. As a result the average global temperature of surface air is  $14^\circ\text{C}$ .

The infrared radiation is absorbed by atmospheric gases like water vapour, carbon dioxide and, to a lesser extent, ozone. Furthermore, in this wavelength band,

clouds are nearly perfect absorbers, while it is believed that the effect of aerosol particles is less important. Cloud elements and gas molecules absorbing the infrared radiation from the Earth are also radiation emitters. A certain part of these radiations are directed back toward the surface, which reduces the heat loss of the lower layers. Since the atmospheric emitters are cooler than the surface, they emit less energy than they absorb. The energy leaving the Earth-atmosphere system is thus less than that emitted by the surface. The Earth's surface provides a heat source for the lower atmosphere in this way. With distance away from this heat source the temperature decreases, which results in the formation of the troposphere.

It has been mentioned above that the energy leaving the Earth-atmosphere system is equal to the incoming energy. It should be emphasized, however, that this is true only for the whole of the system on a long time scale. Locally, at a given location on the Earth, the deviation from the equilibrium can be very significant. Thus, in the equatorial belt between latitudes 30 °N and 30 °S, the quantity of the energy received considerably exceeds the quantity emitted. In other words this means that the radiation balance of these areas is positive. At midlatitudes equilibrium conditions are nearly satisfied, while in polar areas the balance is negative (there is an energy deficit). This latter fact is explained by the low intensity of incoming radiation as well as by the high albedo of these areas covered by snow and ice. The latitudinal distribution of the sign and value of the radiation balance is the cause of the atmospheric circulation modified considerably by the rotation of the Earth, while horizontal and vertical motions in the atmosphere, in turn, regulate the global distribution of clouds and precipitations (subject to the availability of water vapour and condensation nuclei).

Atmospheric circulation transports heat from areas of positive radiation balance to areas where there is an energy deficit. A significant characteristic of this circulation is that a portion of the heat is transported in latent form, which means that the heat is delivered by the condensation of water vapour in the moving air. It is estimated that about one-third of the energy crossing latitude of 30° of both hemispheres is in the form of latent heat. Another one-third of the energy transport takes place in the ocean. Thus only 30 % of the heat is transported directly by the atmosphere.

The surface temperature of the ocean, controlled by the mixing in the upper layers of the water, plays an important role in regulating the heat exchange between the atmosphere and ocean. Unfortunately, these exchange processes are not sufficiently known to determine quantitatively the role of the ocean in the global heat transport. Thus, further work remains to be done to clarify this point which is of great importance for climate research.

### 6.3 The theory of climate and climate modeling

The influence of atmospheric composition (and other factors) on climate can be studied by determining physical principles governing the climate and by constructing appropriate mathematical equations on the basis of these principles. As we have seen, the climate (radiation balance, temperature, circulation, etc.) is determined by the interaction of several processes. The parameters controlling these processes can be included in statistical or physico-mathematical equation systems which are called climate models. The solutions of these model equations provide the so-called climate theories. With the aid of these models, if they are formulated correctly, we can calculate theoretically the consequence of a given change in the parameters (e.g. an increase of CO<sub>2</sub> level). Furthermore, it is also possible to include the effects of human activity in the models as supplementary mathematical relations.

More precisely, climate modeling consists in the simulation of large-scale atmospheric processes by applying the basic physical principles and the correct initial conditions in a consistent way (Smagorinsky, 1974). An important part of climate modeling is the consideration of the interaction of macro-processes with phenomena taking place on the micro-scale (radiative transfer, turbulence, and processes of cloud physics and air chemistry). In the equations, the horizontal scale of variations is at least 100 km, while the vertical scale lies between 10 m and 100 km. The volume of air taken into account is a measure of the resolution of the calculation. Phenomena of smaller scale can be included in the model by appropriate statistical methods. This procedure is termed the parameterization.

If surface effects and extraterrestrial factors (e.g. the intensity of incoming solar radiation) are assumed to be known, then atmospheric processes are described by the following laws (SMIC, 1971):

- (1) Newton's second law concerning the conservation of momentum;
- (2) the principle of conservation of mass;
- (3) the first law of thermodynamics relating the work done by the system and its temperature to the heat received or emitted;
- (4) the laws of radiative transfer, relating heat emission and absorption to the molecular structure and composition of the atmosphere;
- (5) the principles of diffusion and the thermodynamics of water vapour.

The mathematical formulation of these principles gives a closed system of equations governing the model. Without going into detail we have to mention that, in accordance of our foregoing discussion, small scale processes also have to be included in the model. In the governing equations the following parameters can be found: horizontal and vertical components of the wind (also the random turbulent components after parameterization), the atmospheric pressure, temperature and density as well as the mass fraction of different chemical substances.

Climate models can be divided in four categories:

- (1) Global-average models, in which the parameters determining the climate are independent of location and are averages for the whole of the atmosphere (Earth).
- (2) "Statistical" models, in which the variables depend only on geographical latitude and time. In these models large scale atmospheric motions are taken into account statistically.
- (3) Semiempirical climate models, in which partially empirical relations are included on the basis of atmospheric observations.
- (4) Large-scale dynamic models, in which large-scale atmospheric processes are taken into account in an explicit way and all important physical effects can be modelled in a parameterized form.

The discussion of the details of these models is not within the scope of this book. We mention here only the following. It is evident that models of the first type are the simplest one, while large-scale dynamic models simulate reality most closely. However, the differential equations in these complicated models can only be integrated numerically which involves serious computer problems. Furthermore, in simulating climate (minimum time scale is one week) the interaction of atmosphere and ocean also has to be considered. That is, the model must contain equations which relate changes in the state of the ocean to atmospheric parameters. Unfortunately the variations of the state of the ocean as a function of time are not well understood; as a result the parameterization of the effect of the ocean is particularly difficult.

Finally, in this section some words must be said about feedback mechanisms, which complicate considerably the simulation of atmospheric phenomena. Modifications in atmospheric composition can produce deviations from the present radiation balance. These changes in radiation balance bring about further effects which can accentuate (positive feedback) or suppress (negative feedback) initial variations.

One of the best-known feedback mechanisms is the radiation-temperature coupling. The principle of this coupling is as follows. If the radiant heat received by a body is increased then the temperature of the body increases. Since higher temperature involves the emission of more energy, the increased radiation emission of the body limits the temperature changes. This is the classical example of the negative feedback.

An obvious positive feedback mechanism is provided by the interrelation between the temperature of the atmosphere and the extent of polar ice. When the temperature decreases, the extent of the ice cover increases. Since the albedo of ice is much higher than that of other surfaces, this change leads to a further temperature drop; that is, the process is accentuated. In the case of temperature increase the inverse phenomenon is produced. Thus, positive feedback mechanisms are particularly serious from the point of view of climate variation, since small initial effects can lead to significant irreversible changes.

Unfortunately, the incorporation of feedback mechanisms into climate models is not easily done. Thus, we are sure that changes of the radiation balance (due e.g. to the rise of CO<sub>2</sub> level) produce modifications in the atmospheric circulation, but we do not know the nature of these modifications. We have also no doubt that variations in cloud cover (due, e.g., to anthropogenic alteration of the aerosol burden) can substantially influence the radiation balance, but we are not able to predict the direction of this effect in a reliable way since clouds control the transfer of incoming shortwave radiation as well as of outgoing infrared radiation.

It is obvious from this discussion that much work remains to be done to construct acceptable climate models. This work seems to be indispensable, however, to understand the relation between human activity and the atmospheric environment.

#### 6.4 Present climatic variations

In the following, the word "present" refers to the last hundred years during which industrial activity has considerably increased and the scale of human activity has become large enough that an impact on climate is credible. For this time period we have fairly satisfactory data obtained by routine meteorological observations, which means that a description of climatic variation during that period is an easy task. It must be emphasized that, while the climatic impact of man is most striking in large cities, these local effects will not be discussed here. Our aim is to evaluate only global modification caused by large-scale atmospheric pollution.

During the last hundred years the temperature of the Earth's atmosphere has varied significantly. The most important feature of this variation is the nearly steady temperature increase from the eighties of the last century until about 1945. The mean annual temperature increase was 0.008 °C. From 1945 the temperature

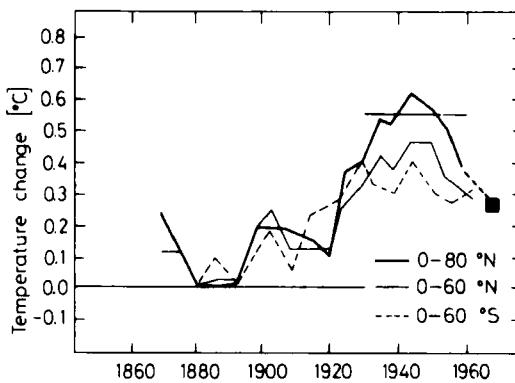
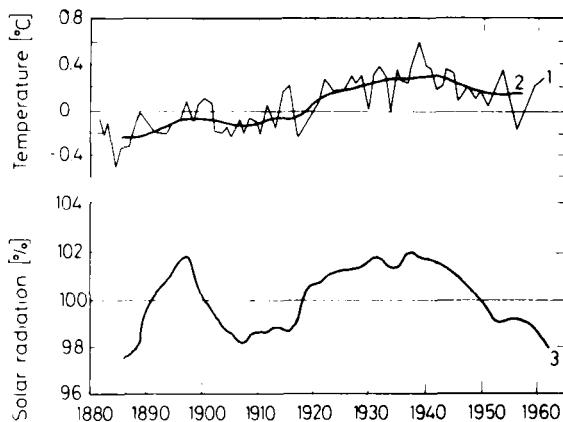


Fig. 53

Changes in temperature of surface air compared to the value observed in 1880 according to Mitchell (see SMIC, 1971). (By courtesy of Massachusetts Institute of Technology)

decreased with a higher rate than the above value. Figure 53 represents these variations as a function of latitude belts according to Mitchell (see SMIC, 1971; Schneider and Kellogg, 1973). The horizontal line plotted in this figure gives the mean temperature of the surface air calculated from observations carried out between 1931 and 1960. The dotted line is Mitchell's prediction. The predicted trend was later confirmed by measurement (black square). The plotted curves show that the amplitude of variation increases with increasing latitude. This is an important finding, since temperature fluctuations at higher latitudes have a much larger influence on man than fluctuations at lower latitudes.



**Fig. 54**

Variation of temperature (1, 2) and solar radiation intensity (3) according to Budyko (1969). 1: annual mean; 2: ten year mean. (By courtesy of *Tellus*)

It is obvious that there is a direct relationship between radiation intensity and temperature in the atmosphere. In Fig. 54 the trend of average temperature and radiation flux measured in surface air is plotted according to Budyko (1969). Data referring to midlatitudes of the Northern Hemisphere are expressed in absolute (temperature) and relative (radiation) deviations from the average values. One can see from this figure that the two parameters have varied together since the beginning of this century. For this reason Budyko speculates that temperature variations are determined either by changes in turbidity (extinction caused by aerosol particles) of the air or by fluctuations in the intensity of solar radiation reaching the upper layers of the atmosphere.

Budyko (1969) argues that the study of present climatic variations is particularly important since the thermal state of the Earth-atmosphere system as well as the present ice cover are in unstable equilibrium (during 90 % of the Earth's history from the beginning of the Paleozoic era our planet was free of ice, see Section 6.1). A relatively small change in temperature would lead to irreversible change (positive feedback, see previous section).

During the last hundred years the parameters characterizing the circulation also underwent significant fluctuations. Lamb demonstrated (see SMIC, 1971) that the number of days with westerly winds over the British islands increased until the middle of twenties while it decreased until about 1960. Lamb speculated but did not prove that these variations in the circulation pattern are connected with changes in temperature and precipitation fields.

## 6.5 Possible explanation for present climatic variations. Connection of climatic variations with the air pollution

### 6.5.1 Variations in the chemical composition of the stratosphere

The aim of this section is to discuss the modifications of the atmospheric composition which can be related to the variations of the radiation balance and temperature observed in this century. We shall first deal with the relation between short-range modifications of atmospheric (stratospheric and tropospheric) composition and the transfer of incoming radiation. After this discussion, atmospheric factors influencing the absorption of infrared radiation emitted by the Earth's surface will be presented briefly.

From the foregoing parts of this book it is clear that solar radiation in the stratosphere is primarily attenuated by ozone (see Subsection 3.4.3) and at a lesser extent by the stratospheric sulfate aerosol layer (see Subsection 4.4.3). This means that any change in the stratospheric  $O_3$  burden or aerosol concentration involves modification of radiative transfer in this atmospheric domain. We should remember that the residence time of trace constituents above the tropopause is rather long because of the thermal structure and the absence of wet removal. Furthermore at these altitudes the density of the air is low as compared to that of lower layers. For this reason even an insignificant quantity of pollutants can produce relatively long and significant effects.

The study of the possible modification of the stratospheric ozone "shield" seems to be particularly important since ozone absorbs radiation dangerous to living species. Furthermore, this substance plays an important role in the control of the heat balance of the stratosphere.

One possible agent of inadvertent stratospheric modification is  $NO_x$  emitted by supersonic transport aircraft. As discussed in Subsection 3.4.3  $NO_x$  takes part in photochemical processes in the stratosphere in such a way that it catalyzes the reaction of  $O$  and  $O_3$  molecules (see also Fig. 9). That this reaction occurs was confirmed in individual cases by measuring the vertical profile of  $O_3$  over an area (Berlin) where supersonic transport is heavy (Grasnick, 1974). It is much more difficult, however, to assess long-range global effects. One estimate (Rowland, 1976) states that if 100 supersonic aircraft of models available at present were operated, the increase in ultra-violet radiation erythemally effective would be 0.04 % at the

Earth's surface, which is equivalent to an ozone decrease of 0.02 % (there is a factor of two between the two parameters, see WMO, 1976). Another calculation (Rowland, 1976) suggests that a 500-plane fleet of Boeing supersonic aircraft would result in an ozone depletion of 16 % in the Northern and 18 % in the Southern Hemisphere. However, "currently planned supersonic transport aircraft, due to their lower flight altitudes of 17 km and their limited numbers (30–50 projected) are not predicted to have an effect that would be significant or that could be distinguished from natural variations" (WMO, 1976). More recent calculations suggest that the previous models may have erred with regard to the sign of the effect. Nevertheless studies in this area must continue, and international agreements on flight altitudes, numbers of flights and NO<sub>x</sub> emission standards may yet become necessary.

According to various estimates the effect of halogenated hydrocarbons on the stratospheric ozone layer may exceed that of nitrogen oxides. As we have seen (Subsection 3.3.3), these anthropogenic species are emitted into the atmosphere at the surface but they reach the stratosphere by mixing. There they photolyze, forming chlorine, which may reduce the ozone quantity (see Subsection 3.4.3). Figure 55, published by Wofsy *et al.* (1975), reproduces the results of model

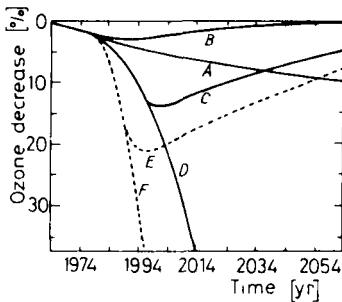


Fig. 55

Calculated effects of fluorocarbons on global ozone according to Wofsy *et al.* (1975). A: production held constant at present rate; B: production ceases in 1978; C: production increases by 10 % per year, ceases in 1995; D: production increases by 10 % per year; E: production increases by 22 % per year, ceases in 1987; F: production increases by 22 % per year. (Copyright 6.2. 1979 by the American Association for the Advancement of Science)

calculations aimed at estimating the chemical effects of fluorocarbons in the stratosphere. Curve A gives the computed ozone depletion in percentage if production remains constant at the present rate (see Subsection 3.3.3). One can see that according to this prediction the ozone decrease would reach 10 % in less than hundred years. This would result in an increase of 20 % of the intensity of UV radiation at the surface and in a decrease of about 10 °C of the temperature of the upper stratosphere (WMO, 1976). Furthermore, Curve B represents ozone depletion values if production of fluorocarbons had ceased in 1978. Even in this case

around 1990 the ozone reduction would be several percent. Further curves in this figure give different combinations of production rate and cessation time (see the caption of the figure). This figure preceded the evidence (see Subsection 3.4.3) that the interaction of chlorine and nitrogen species can considerably limit the effect of halogenated hydrocarbons on stratospheric ozone. The chlorine nitrate chemistry (and some new rate constants) were recently considered by Miller *et al.* (1978). They also took into account the multiple scattering of solar radiation by different molecules. By using a one-dimensional model these workers obtained the results given in Fig. 56. The figure represents two cases in which fluorocarbon production is stopped at the end of 1976 and 1978, respectively. The maximum ozone depletion is 0.62 % and 0.77 %, respectively. Miller *et al.* (1978) also calculated that the ozone depletion in the indefinite future (in several hundred years) with a steady state release at the 1975 level is 5.1 %. However, it should be noted that other model calculations carried out recently give a higher ozone depletion. Thus, in discussing new US reports on this problem and averaging the results of different estimates Rowland (1979) showed that the steady state ozone depletion is around 20 % due to the increase of the rate constant of the reaction [3.30]. Should further study confirm such a high value, the cessation of the anthropogenic production of halocarbons may become necessary.

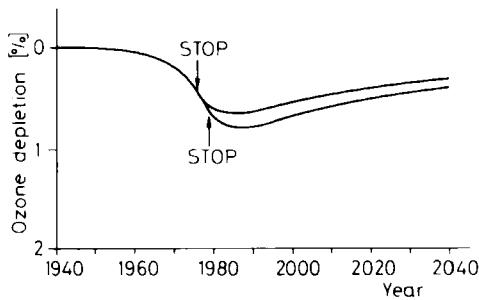


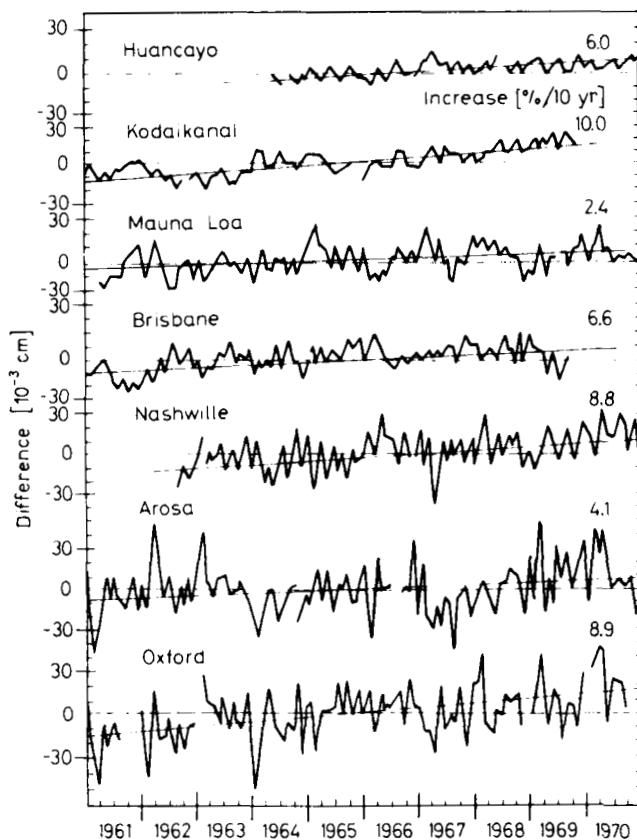
Fig. 56

Calculated ozone depletion as a function of time for two cases of stopping fluorocarbon production at the end of 1976 and at the end of 1978 (Miller *et al.* 1978). (By courtesy of *Atmospheric Environment*)

It follows from this discussion that the inadvertent ozone depletion in the past and at present is not expected to be measurable. This conclusion is supported by observational data on total ozone showing a net increase during recent years. This is confirmed by observations carried out at various places on the Earth's surface. Thus, according to Komhyr *et al.* (1971) between 1958 and 1970 the rate of this increase has been as large as several percent per decade (see Fig. 57). It is to be noted in this respect that Mastenbroek (1971) found that the stratospheric water vapour burden over the U.S.A. also increased significantly in recent years and this was attributed to the water vapour emission of supersonic aircraft. In Subsection 3.4.3 we mentioned that free radicals formed from water vapour can play a certain role in

ozone photochemistry. However, the temporal rise of total ozone cannot be explained by this effect, which is considered to be negligible (see Fig. 9). Furthermore, Birrer (1974) demonstrated that the value of the ozone trend decreases with an increasing period of observation. On the basis of data obtained beginning in 1926 in Arosa, Switzerland, this author was able to show that in the past, when the possibility of man-made effects was excluded, total ozone underwent through much more significant variations than since 1960. He also found a periodicity of 42 months in the ozone data. It follows from this finding that we have to be cautious in estimating possible anthropogenic modifications in stratospheric photochemistry.

It was mentioned above that the modifications of the stratospheric aerosol layer can also induce climatic variations. For this reason the following part of this



**Fig. 57**

Temporal variation of total ozone in the atmosphere over different stations according to Komhyr *et al.* (1971). Values are expressed in units of difference from the mean. (By courtesy of *Nature* and the authors)

subsection is devoted to the discussion of this problem. We have to emphasize that solar energy absorbed by stratospheric particles is not so important quantitatively. However, the radiation equilibrium of these atmospheric layers is so delicate that the appearance of some new absorbers results in significant alterations. Since we believe that volcanic gases and particles play an important role in the control of the stratospheric aerosol burden (Subsection 4.4.3) it is suggested that variations of volcanic activity are related to changes of stratospheric heat balance. Furthermore, some authors speculate (e.g. Budyko, 1969) that climatic variations in the past and at present can be explained by the effect of volcanic materials on the radiation and heat balance of the Earth-atmosphere system. This idea seems to be confirmed by the fact that in the first part of this century, when the average global temperature increased, the volcanic activity index, which is proportional to the mass of volcanic gases and particles injected into the stratosphere, was relatively low (SMIC, 1971). Volcanic eruptions with higher intensity were observed, however, after the beginning of the forties when the temperature started to drop. The mass of material emitted by Agung volcano in the equatorial zone in 1963 was considerably significant. However, it must be stressed that this situation may be due to a simple coincidence, because we have no real proof to explain climatic variations by volcanic activity, although the possibility of such an explanation cannot be entirely ruled out.

We have seen in Subsection 3.6.2 that a significant amount of anthropogenic sulfur dioxide is emitted into the troposphere by energy production from fossil fuels. In spite of the fact that the removal of this species in the lower layers of the atmosphere is rather fast, we cannot exclude the possibility that a certain fraction of this sulfur gas reaches the stratosphere. However, it is estimated (SMIC, 1971) that this  $\text{SO}_2$  quantity is negligible compared to that due to the volcanic activity.

Finally, it should be mentioned that supersonic aircraft also emits soot particles and carbon dioxide gas. Although these soot particles can increase the stratospheric temperature in some cases, the effect of carbon dioxide emitted in this way is considered to be negligible (Schneider and Kellogg, 1973).

#### 6.5.2 Effects of tropospheric aerosol particles on the radiation balance

It was mentioned in Chapter 4 that aerosol particles scatter and absorb solar radiation. These processes depend upon the concentration, size distribution, form, refractive index and absorption coefficient of the particles, as well as upon the wavelength of the radiation. In the case of water-soluble particles the extinction is also controlled by relative humidity (see Section 4.5). The energy absorbed by particles leads to an increase of temperature, while backscattering produces an energy loss for the system. Since this energy loss may be characterized by the albedo, it is proposed to examine first the relation between albedo and temperature in surface air.

Budyko (1969) determined the following empirical relation between the temperature ( $T$ ) and the radiation intensity emitted ( $I$ ):

$$I = c_1 + b_1 T - (c_2 + b_2 T)n \quad [6.1]$$

where  $n$  is the cloud cover expressed in tenths of the sky, while  $b_1, b_2, c_1$  and  $c_2$  are empirical constants. Furthermore, for the whole of the Earth we can write that

$$Q(1 - \alpha_E) = I \quad [6.2]$$

where  $Q$  is the incoming solar radiation intensity, while  $\alpha_E$  is the albedo. By combining [6.1] and [6.2] an equation can be obtained relating the temperature to the intensity of incoming radiation, extent of cloud cover and albedo. A simple calculation shows that a change of 1 % in average albedo produces an average temperature variation of 2.3 °C.

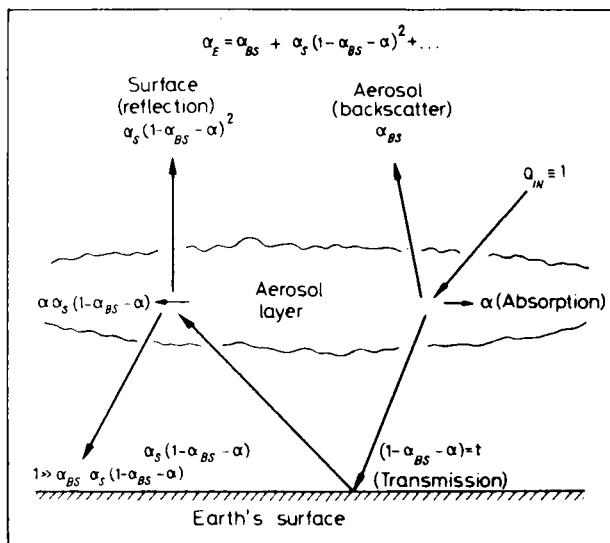


Fig. 58

Schematic diagram showing the effect of aerosol particles on incoming solar radiation ( $Q_{IN}$ ) according to Schneider and Kellogg (1973). (By courtesy of Plenum Press)

Let us consider in more detail the relation between albedo and atmospheric aerosol particles in the case of one aerosol layer in the lower atmosphere (see Fig. 58; Schneider and Kellogg, 1973). In this figure  $Q_{IN}$  is the intensity of incoming radiation, taken as unity. Furthermore,  $\alpha_{BS}$  is the albedo of the aerosol layer while  $\alpha$  gives the absorption by particles. Owing to scattering and absorption by the layer,

the radiation intensity at the surface will be  $(1 - \alpha_{BS} - \alpha)$ . This quantity is termed the transmission. If the albedo of the surface is equal to  $\alpha_s$ , then the radiation intensity reflected by the surface will be  $\alpha_s(1 - \alpha_{BS} - \alpha)$ . A certain part of this radiation is scattered back in the direction of the incoming radiation, while an other part is absorbed by the particles. If we subtract these fractions from the intensity reflected by the surface the so-called surface reflection is obtained. The total albedo,  $\alpha_t$ , is obviously given by the sum of aerosol backscatter and surface reflection.<sup>3</sup> Let us suppose that  $\alpha_{BS} = \alpha = 0.05$  and  $\alpha_s = 0.1$ , which seem to be acceptable values. Under these conditions  $\alpha_t$  (0.131) is greater than the albedo without the aerosol layer ( $\alpha_t = \alpha_s = 0.1$ ). An increase of 3.1 % in albedo implies a significant temperature decrease in the surface air according to the above hypothesis of Budyko (1969).

Calculations made by this global-average model further indicate that the presence of an aerosol layer leads to a decrease in the value of total albedo if the surface albedo is greater than about 0.5. In other words this means that the aerosol layer causes an increase in the surface air temperature over a surface covered by ice. Furthermore, since the albedo of dense clouds is also high, the effect of an aerosol depends on its position relative to the clouds. If the particles are below the cloud cover they produce cooling, while above the clouds their presence tends to raise the surface air temperature. It is thus concluded that the effect of an increase in the concentration of aerosol particles is a function of the albedo of the Earth's surface below.

In Chapter 4 it was stated that tropospheric background particles are mainly composed of sulfates. On the basis of the data given in Fig. 19 we can speculate that 72 % ( $30 \times 10^6 \text{ t yr}^{-1}$ ) of the  $\text{SO}_2$  transformed into sulfates in the troposphere comes from anthropogenic sources, assuming that anthropogenic and natural (formed from  $\text{H}_2\text{S}$ ) sulfur gases are removed in the same ratio as they are produced. Approximately the same figure is obtained for the strength of the sulfate source provided by natural gases ( $20 \times 10^6 \text{ t yr}^{-1} + 12 \times 10^6 \text{ t yr}^{-1}$ ). This means that on a global scale about one half of the sulfate particles are due to human activity, in agreement with the estimate of Granat *et al.* (1976). However, we have to stress (see Subsection 3.6.6) that the major portion of anthropogenic sulfur is emitted over a rather restricted area of the Northern Hemisphere (mainly U.S.A. and Europe). Thus, Bolin and Charlson (1976), considering the physical and chemical properties of sulfate particles, calculated that over the eastern United States and Western Europe sulfate particles, predominantly of man-made origin, scatter solar radiation to produce a temperature drop of several degrees. It is to be noted that ventilation was not taken into account in their model, and the authors assumed a cloudless atmosphere. Distributing this effect over the whole Northern Hemisphere, Bolin and Charlson (1976) were able to deduce that the change of hemispheric albedo

<sup>3</sup> The ellipsis in the formula at the top of the figure indicates that the fraction of the radiation intensity scattered downward by the aerosol layer is again reflected by the surface and this phenomenon continues *ad infinitum*. However, the significance of these supplementary terms is small.

caused by American and European sulfur emission corresponds to a temperature drop of 0.03–0.06 °C.

In Section 6.4 of this book evidence is presented showing that the temperature of the atmosphere dropped after the middle of the forties. At first sight it would seem reasonable to attribute this temperature drop to the increase of the concentration of anthropogenic aerosol particles. In Chapter 4 we saw that electrical measurements indicate an increase of the aerosol over the Northern Hemisphere which can be probably explained by the increase of the emission of gaseous sulfur compounds. However, in the Southern Hemisphere no such increase was found, but the temperature also decreased during this time period. Furthermore, the calculation of Bolin and Charlson (1976) indicate smaller changes than those observed. Finally, the temperature drop has been the greatest over the regions where we could expect a temperature increase due to the high albedo of the surface (see above). We have to conclude that the temperature decrease measured after 1940 cannot be attributed directly to anthropogenic particle pollution.

However, the problem is more complicated than the foregoing discussion shows. By acting as condensation nuclei, aerosol particles can also modify the average cloud distribution, which determines the albedo in a very significant way. We remind the reader of Subsection 5.3.1 in which it is argued that an increase of condensation nuclei produces clouds with many small drops. These clouds are rather stable systems (Fletcher, 1962) since the probability of precipitation formation is rather low in clouds with small drops. Thus, an increase in the concentration of aerosol particles tends to increase the lifetime of clouds.

**Table 30**

Formation rate of anthropogenic and natural condensation nuclei according to Squires (1966)

Area	Natural ( $N$ ) $\text{cm}^{-2} \text{s}^{-1}$	Anthropogenic ( $A$ ) $\text{cm}^{-2} \text{s}^{-1}$	$A/N$ [%]
U.S.A.	500	68	14
Northern Hemisphere	200	9	5

The formation rate of natural and anthropogenic condensation nuclei active at a supersaturation of 0.5 % was determined by Squires (1966). His results with respect to the U.S.A. and to the Northern Hemisphere are tabulated in Table 30. One can see from these estimates that the anthropogenic fraction provides 14 % of the condensation nuclei of natural origin over the U.S.A. The corresponding percentage value for the whole of the Northern Hemisphere is estimated to be 5 %. This means that on a global scale the formation of clouds is not yet significantly modified by the activity of mankind. However, over more industrialized areas like Western Europe the number of natural and anthropogenic nuclei is estimated to be comparable (Pruppacher, 1973).

According to Twomey (1977) an increase of cloud droplet concentration involves an increase of the albedo if other factors (liquid water content, thickness of cloud) remain constant. Thus, for a cloud thickness of 0.1 km (liquid water content  $0.3 \text{ g m}^{-3}$ ) the albedo is raised from 0.25 to 0.43 when the drop concentration is increased by a factor of eight. For a cloud with a thickness of 1 km the corresponding albedo increase is from 0.82 to 0.90. However, an increase in the optical thickness of a cloud also leads to a higher absorption of the infrared radiation emitted by the Earth's surface.

The effect of an increase in the extent of cloud cover on the atmospheric heat balance was numerically studied by Schneider (1972). He took into account the variation of the planetary albedo as well as the decrease of the infrared radiation loss. Schneider found that a more extensive cloud cover produces a temperature drop at low and midlatitudes if the height, thickness and albedo of the clouds remain unchanged. In contrast, over polar regions, where the intensity of incoming solar radiation is low and the surface albedo is great, an increase in the extent of cloud cover leads to a temperature rise in the surface air.

A small but important class of atmospheric aerosol particles are the ice nuclei. These nuclei promote the freezing of water drops in clouds (see Fletcher, 1962). In this way they play a definite role in the formation of precipitation in mixed clouds containing both water drops and ice crystals. This kind of precipitation formation is due to the fact that the saturation vapour pressure over ice is smaller than over liquid water. In this way ice crystals grow by condensation while drops tend to evaporate. Thus, if human activity emits ice nuclei to the atmosphere the precipitation distribution can be modified. Results of measurements show that in the vicinity of steel works and aluminum foundries the concentration of ice nuclei active at a temperature of  $-20^\circ\text{C}$  is unusually high. It is believed that this is caused by the presence of some metal oxides in the air (Pruppacher, 1973). More recent studies on ice nuclei also showed that lead compounds (e.g.  $\text{PbI}_2$ ) in exhaust gases of vehicles also have ice nucleating ability. It is believed, however, that anthropogenic ice nuclei cannot play an important role, except in local scale processes (see Pruppacher, 1973).

Finally, it should be mentioned that cirrus clouds formed in the upper troposphere can also control the radiation balance of the atmosphere. On occasion these clouds are certainly caused by the growth of condensation trails from high-flying aircraft. This problem is important from the point of view of anthropogenic modification of the atmospheric composition since a significant quantity of water vapour (and ice nuclei?) is emitted in aircraft exhaust. Hence it is not surprising that in recent years the quantity of cirrus clouds has increased. It is estimated by experts (see SMIC, 1971) that in day-time the albedo increase caused by these clouds generally exceeds the effects of absorption of infrared radiation by ice crystals. This means that cirrus clouds cool the troposphere in day-time. At night, however, cirrus clouds produce the inverse effect on the tropospheric temperature in the majority of cases.

### 6.5.3 Effects of carbon dioxide on the radiation balance

In the last subsection the relation between short-wave radiative transfer and tropospheric composition changes has been presented. The aim of this subsection is to discuss the interaction between infrared radiation emitted by the Earth's surface and variations in the chemical composition of the troposphere. Since the influence of aerosol particles on infrared radiative transfer is not clear and is sometimes neglected,<sup>4</sup> this paragraph is devoted to the effects of the carbon dioxide increase, which seems to be a very important environmental factor.

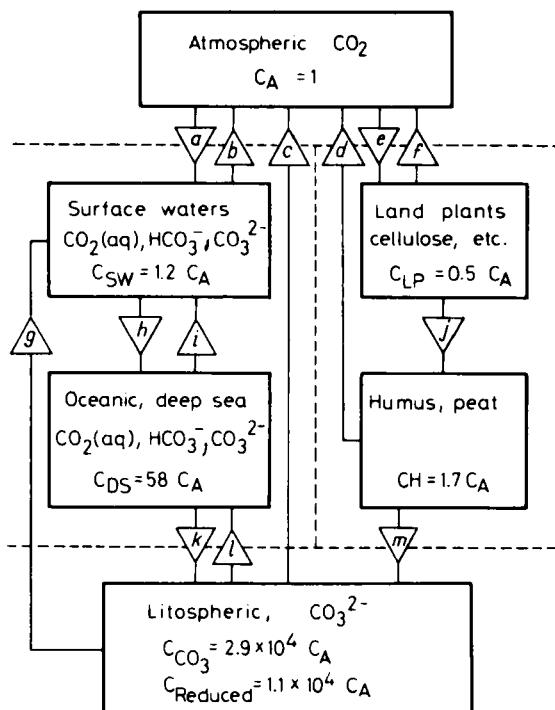


Fig. 59

The global carbon cycle in nature according to Butcher and Charlson (1972). The amount of carbon in each reservoir (rectangle) is shown relative to that in the atmosphere ( $C_A$ ). The exchange processes are shown as triangles. (a): air-sea sorption; (b): water-air desorption; (c): combustion; (d): oxidation of dead plants; (e): photosynthetic  $\text{CO}_2$  consumption; (f): respiration; (g): rock weathering; (h): ocean surface-deep sea exchange; (i): deep sea-ocean surface exchange; (j): decay of plant material; (k): oceanic bottom deposition; (l): dissolution of marine deposits; (m): metamorphosis. (By courtesy of Academic Press and the authors)

<sup>4</sup> The effect of other anthropogenic gases ( $\text{H}_2\text{O}$ , halocarbons, etc.) on infrared radiative transfer can also be neglected compared to that of  $\text{CO}_2$  (Kellogg, 1977).

In this book we have restricted our discussion to the atmospheric pathways of constituents. However, before discussing the climatic effects of the carbon dioxide increase, it seems useful to study briefly the global cycle of carbon in nature, including all terrestrial reservoirs. Figure 59 gives the cycle of the carbon in nature according to Butcher and Charlson (1972). The carbon quantity of different reservoirs is expressed in multiples of the atmospheric burden. Triangles in the figure represent various exchange processes the reliable modeling of which is not always an easy task since they depend upon many variables. One can see from this figure that the pathways of carbon in nature are complex. A perturbation of a given part of the cycle may directly or indirectly produce changes in any other part of the system. It can also be seen that the atmosphere is particularly sensitive to variations in other reservoirs, since only a small quantity of natural carbon is found in the atmosphere.

The reader is reminded here of Fig. 4, showing that the carbon dioxide level in the atmosphere has increased significantly from the end of the last century until about 1958. Since this date an increase of 16 ppm has occurred (Bolin, 1977b), which means that the total increase is about 18 %. Butcher and Charlson speculate on the basis of Fig. 59 that this increase may be due theoretically to the following factors:

- (1) a decrease of CO<sub>2</sub> quantity in surface layers of the ocean, e.g. owing to the temperature increase of the water;
- (2) an increase in the oxidation of dead plants;
- (3) a decrease in photosynthetic activity, or an increase in respiration;
- (4) an increase in the anthropogenic combustion of reduced carbon.

Many authors state that the increase of the CO<sub>2</sub> level of the atmosphere is solely due to factor 4. Thus, even at the turn of the century Arrhenius pointed out (see Bolin, 1977b) that the rise of the combustion of coal and oil might cause an increase in the concentration of carbon dioxide in the atmosphere. In the thirties, Callender (1938) formulated the same hypothesis in a more direct way. These early ideas were confirmed by the finding that the <sup>12</sup>CO<sub>2</sub>/<sup>14</sup>CO<sub>2</sub> ratio in the atmosphere was increasing (Revelle and Suess, 1957). This also strongly suggests that anthropogenic combustion plays an important role, since fossil fuels do not contain <sup>14</sup>C. However, more recently Bolin (1977a) has drawn attention to the possibility that man's reduction of forests and cultivation of fields for agricultural purposes also may be an important factor. Stuiver (1978) speculates from measurements of the <sup>13</sup>C content of tree rings that between 1850 and 1950 two-thirds of the CO<sub>2</sub> added to the atmosphere was due to biospheric sources caused by deforestation and only one-third was emitted by fossil fuel combustion. He also argues that at present this latter factor is the dominant one, since net biological fluxes have become negligible. There is no intent here to discuss this problem in further details. We conclude that although the past CO<sub>2</sub> increase in the atmosphere may be due to several activities of mankind, the CO<sub>2</sub> rise in the future will be determined by fossil fuel combustion.

The effects of the increase of the atmospheric CO<sub>2</sub> level on climate can be estimated by appropriate model calculations. Such a calculation was made by Manabe and Wetherald (1967) who assumed that the increase of CO<sub>2</sub> level does not change the albedo of the Earth-atmosphere system. They also supposed that the temperature of the atmosphere will increase to reach a new equilibrium value because of the increase of the absorption of infrared radiation by carbon dioxide molecules. During this time the average temperature gradient and the relative humidity at different altitude remain unchanged. By using this "convective-radiation" model these authors calculated that an increase of 20–25 % in CO<sub>2</sub> level corresponds to a global-average temperature increase of 0.5 °C.

This result shows that the average temperature change (about +0.5 °C) observed prior to the middle of this century cannot be explained by the increase of CO<sub>2</sub> alone since this latter has been below 10 % before 1940 (see also Fig. 4). Recently Manabe and Wetherald (1975) with the aid of a statistical model calculated the two-dimensional variation of temperature caused by a CO<sub>2</sub> increase. In this new model Manabe and Wetherald also took into account the effects of changes in the extent of the polar ice. Their results obtained by doubling the amount of carbon dioxide in the atmosphere are reproduced in Fig. 60 as a function of latitude and elevation. It is estimated (Kellogg, 1977) that a doubling of the atmospheric CO<sub>2</sub> level will be reached in about 2050. One can see from Fig. 60 that, according to this prediction, the average surface temperature at midlatitudes in 2050 will be greater by 2–3 °C than the present value. Furthermore, the temperature rise at the poles will be even more significant. Bolin (1977b) estimates that these results may be uncertain by a factor of two or three in either direction. Even assuming that the temperature rise will be one-third of that predicted by this model, major heating at the poles will be produced by the CO<sub>2</sub> increase. At the same time a significant temperature decrease is expected in the stratosphere.<sup>5</sup>

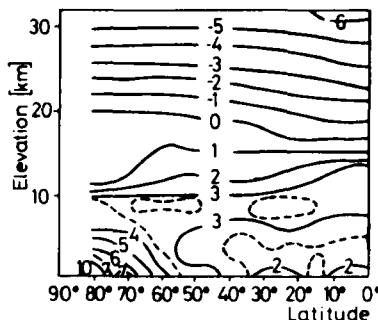


Fig. 60

Computed changes in the mean temperature of the atmosphere as a function of geographical position and height that would result from a doubling of the atmospheric carbon dioxide burden (Manabe and Wetherald, 1975). (By courtesy of American Meteorological Society)

<sup>5</sup> This stratospheric temperature decrease can modify, among other things, the ozone cycle.

It is very difficult to propose a means of avoiding this inadvertent and possibly major climatic disturbance since human need for energy production is continually increasing. However, Bolin (1977b) states that "The long-term environmental effects, particularly the possibility of a change of the global climate, should determine the degree to which fossil fuels may be used as an energy source, not the magnitude of available resources of oil and coal."<sup>6</sup> This statement indicates a necessity to look for other energy sources that can be used without polluting our environment.

#### 6.5.4 Summary

Our discussion about the relationship between anthropogenic global air pollution and climatic variations can be summarized as follows. It is improbable that the variations observed from the end of the last century to date have been caused by human activity. It cannot be entirely excluded, however, that air pollution has produced marginal effects. However, in the future, with the augmentation of the use of fossil fuels, more significant influences are foreseen.

It follows from the foregoing discussion that the problem of climatic variations is very complex and not well understood. For this reason we must beware of hasty opinions concerning the relationship between air pollution and climate. However, on the basis of the material discussed, we may risk the following prediction. Owing to the heating effect of carbon dioxide the temperature in the lower atmosphere will rise. Anthropogenic aerosol particles at lower latitudes will cool, and at higher latitudes will heat, the surface air. If these effects are not compensated by natural factors a small, but steady, heating may be predicted. In addition, the resulting decrease in temperature difference between the poles and the equator may lead to a loss in the driving force for the atmospheric "heat engine". Such changes can lead through various feedback mechanisms (e.g. variations in atmospheric circulation, decrease in the extent of polar ice) to major irreversible consequences.

We may thus conclude that it is necessary to protect the atmosphere from pollution as far as possible since the very existence of mankind is dependent on the present atmospheric composition and climate. Beyond this, a deeper understanding of the interrelation between human activity and our atmospheric environment is a challenge for all responsible scientists.

<sup>6</sup> It is estimated that, if all the economically recoverable fossil fuel were burned, the CO<sub>2</sub> burden of the atmosphere would rise to five to eight times its value in the last century (Kellogg, 1977).

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