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Heterogeneous processes in the Earth's atmosphere and their ecological consequences†

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ABSTRACT. The principal information about the heterogeneous reactions involving ozone and other minor constituents of the atmosphere is described. The influence of the simplest heterogeneous reactions on the gas composition of the atmosphere in the middle latitudes and on tropospheric stratospheric coupling is examined on the basis of model estimates. The real situations and certain scenarios for an appreciable improvement of the gas composition of the atmosphere as a result of heterogeneous reactions are analysed. The oxidation of sulphate ions in cloud droplets is considered.

The bibliography includes 105 references.

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I. Introduction

The heterogenous chemical processes in the atmosphere have been attracting an increasing amount of attention.[1] The interest in this field of chemistry has intensified especially during recent years in connection with the appearance of ideas about the effective influence of heterogeneous reactions on the decomposition of the ozone layer in the Antarctic during spring.

For ecology, three problems associated with heterogeneous chemical phenomena in the atmosphere are of greatest importance; (1) the change in the gas composition under the influence of heterogeneous processes; (2) dissolution and reactions in drops leading to acid rain; (3) chemical formation and growth of aerosols. Attention will be concentrated on the first two problems in this review. We shall endeavour to base the review on specific examples, concentrating attention on the problem of the content of ozone and hydroxyl radicals in the atmosphere and the problem of acid rain. The results of laboratory studies on the interaction of atmospheric gases with the surfaces of solids and liquids whose compositions are similar to those of atmospheric aerosols are also represented although without a detailed analysis.

† The five articles at the beginning of this issue are a continuation of issue No. 10 devoted to the "chemistry of the atmosphere".

The problem of the influence of changes in the radiation balance and in the intensity of the solar radiation passing through the atmosphere on the composition of the latter are outside the scope of this review. As a rule, we shall consider the situations in which the chemical action of aerosol particles on the gas composition of the atmosphere is more effective than the optical or thermochemical influences.

II. Brief information about atmospheric aerosols

1. Chemical composition

Primary aerosol particles appear in the atmosphere as a result of soil erosion, while in the layer near the water over the oceans there are salt particles. Anthropogenic sources also make an appreciable and increasing contribution. Secondary aerosols are formed in the atmosphere itself as a result of the chemical reactions of gases of natural and anthropogenic origin. The commonest of these are sulphuric acid particles — the principal aerosols of the stratosphere. It is believed that sulphuric acid is formed as a result of the photochemical transformation of carbon oxide sulphide COS into sulphur dioxide and the subsequent oxidation of the latter to H_2SO_4.[2,3] The chemical homogeneity and a single-peaked distribution of the particles with respect to size throughout the middle latitudes may serve as confirmation of a unique mechanism for the formation of the stratospheric sulphuric acid aerosol. In the troposphere, where COS is not photolysed and does not react with atomic oxygen, the formation of sulphuric acid particles is due to the chemical reactions of the SO_2 molecules arriving from the earth. Review information about the mechanisms of the formation of secondary aerosols is available in monographs.[2–5]

In the aerosol model of photochemical reactions, it is postulated that under normal (background) conditions the particles of the troposphere have the following composition[6]: up to a height of 3 km — 50% of sulphates (the main form is ammonium sulphate), 35% of soil particles, and 15% of sea salt (NaCl); above 3 km — 60% of sulphates and 40% of soil particles. According to this model, the soil particles consist of 53% SiO_2, 17% Al_2O_3, 7% of Fe_2O_3, and 23% of other compounds. The chemical composition of the aerosols in industrial regions may be different. For example, the aerosol over Houston (USA) consists of sulphuric acid to the extent of 30%[7], and in certain cases the H_2SO_4 content in aerosol over cities may reach 50%[2]. In city aerosols the fraction of SiO_2 may be 30%, while the contribution of aluminium oxide is up to 10% and that of iron oxides is several per cent[2]. In extreme situations (large amounts of industrial waste, forest fires, volcanic eruptions, nuclear explosions), the composition and concentration of aerosol particles

may change significantly. More detailed information about the physicochemical properties of aerosols is available in other publications [1,2,8].

As already stated, the stratospheric aerosol in the middle latitudes consists under background conditions mainly of sulphuric acid particles (the Junge layer, height $Z = 18-20$ km). Immediately after volcanic eruptions, a large amount of sulphur compounds and particles of volcanic ash penetrate into the lower layers of the stratosphere. These have the following approximate composition: 60% SiO_2, 20% Al_2O_3, 3% Fe_2O_3, 2% MgO, 5% CaO, 5% Na_2O. The primary volcanic stratospheric aerosol particles are apparently to a large extent coated by sulphuric acid and water. As a result of chemical reactions involving the sulphur compounds H_2S and SO_2, ejected in volcanic eruptions to a height of 25–30 km, aqueous sulphuric acid aerosols, containing between 60 and 80% of H_2SO_4, are produced. They then fall downwards and concentrate in the lower part of the stratosphere at a height of 18–20 km.

The composition of the stratospheric polar clouds, formed during the winter in the Arctic and the Antarctic, is more homogeneous. These are mainly ice particles with dissolved nitric and hydrochloric acid molecules [9,10]. The ice particles and water drops are the natural constituents of the stratospheric and tropospheric aerosols.

2. The size, distribution with respect to height and the number concentration of particles

Tropospheric aerosols can be subdivided according to particle size into three characteristic ranges (modes) [2,11,12]. The first mode consists of condensation nuclei which are particles with a radius less than 0.2 μm, the second mode comprises growing particles with a radius of 0.2–1 μm, and the third mode includes particles with a radius from 1 to 10 μm. The concentration of the solid non-hydrated particles constituting the first mode in the troposphere is highest and the main bulk of the surface of the solid particles per unit volume (the specific surface A) actually corresponds to them. The average particle radius which contributes most A is 0.13 μm [2]. The growing particles of the second mode are as a rule non-uniform in composition and appreciable amounts of water may be present on their surfaces. Large particles ($r > 1$ μm) are mainly highly hydrated forms or water drops.

The distribution of the concentration of solid particles in the troposphere with respect to height can be conveniently represented in an exponential form:

$$N_Z = N_0 e^{-Z/Z_0}. \quad (1)$$

The concentration N_0 at the Earth's surface and the characteristic height Z_0 depend on specific conditions (region, temperature, humidity). The following model is available for the distribution of aerosol particles of the troposphere with respect to height [2]: first mode—$N_0 = 10^3-10^5$ cm^{-3}, $Z_0 = 2-3$ km; second mode—$N_0 = 5-300$ cm^{-3}, $Z_0 = 1.5-2$ km; third mode—$N_0 = 10^{-2}-10^{-4}$ cm^{-3}, $Z_0 = 0.5-1$ km. The stratospheric aerosol in the middle latitudes is located at a height of 16–22 km (the Junge layer). The concentration of sulphuric acid particles is a maximum at a height of 18–20 km and their average radius is 0.05–0.1 μm. During volcanic eruptions, the concentration of aerosol particles in the stratosphere increases by a factor of 20–30, approaching the background concentration of aerosols near the Earth's surface ($\sim 10^3$ cm^{-3}).

The specific aerosol surface A in the troposhere near the Earth's surface under normal conditions, in volcanic clouds [13], and also in cold polar stratospheric clouds [9,10,14] is approximately the same and amounts to 10–50 μm^2 and cm^{-3} or $(1-5) \times 10^{-7}$ cm^{-1}. The polar stratospheric clouds are concentrated in regions with a temperature below −85 °C [15]. In the cold Antarctic stratosphere, the maximum density of aerosol particles is attained at a height of 16–18 km and there are several sharp concentration peaks in this region.[16]

3. The rate constant for a heterogeneous reaction

The interaction of molecules with the surface includes a series of stages: adsorption and desorption, diffusion within the liquid aerosol and evaporation, and reactions of the adsorbed molecules with one another and with the molecules of the adsorbent or the molecules incident from the gas phase. The probability of the reactions γ depends both on the parameters of the atmosphere (temperature, pressure, humidity) and on its gas composition. Furthermore, the chemical composition of the aerosols themselves is a function of the state of the atmosphere. This gives rise to considerable complications as regards a self-consistent description of the composition of the atmosphere taking into account its multiphase nature and the presence of definite relations between the heterogeneous and homogeneous phases (see, for example, Carmichael et al.[17]). In view of the complexity of the problem, the heterogeneous fraction is parametrised by specifying the average particle size r, the concentration of aerosol particles N, and the reaction probability γ or by introducing the specific surface A and γ. The parameters r, N, and A are determined from the results of experiments under natural conditions and the values of γ are based on laboratory data.

The rate of consumption of gases in a reaction involving spherical atmospheric particles is described by the equation for a unimolecular first-order process with an effective rate constant [18] given by

$$K_{het} = \frac{4\pi r N D}{1 + \lambda l/r}, \quad (2)$$

where D is the molecular diffusion coefficient, l the length of the free path in the gas, and

$$\lambda(\gamma) = \lambda_{\gamma=1} + \frac{4(1-\gamma)}{3\gamma}. \quad (3)$$

Here $\lambda_{(\gamma=1)} \simeq 1$ is a function weakly dependent on the Knudsen number $K_n = l/r$. The value of the function varies from 0.71 to 1.3 as l/r varies from 0 to ∞. At atmospheric pressure, $l \simeq 0.1$ μm, which is close to the radius of the solid tropospheric particles making the main contribution to the specific surface and the parameter $\gamma l/r$ almost always exceeds unity. Only a small region of the atmosphere near the Earth's surface, where $\lambda l/r$ is close to unity for $\gamma \simeq 1$, is an exception. Therefore, under atmospheric conditions, the limiting case of the destruction of molecules on solid particles in the kinetic region, where $\lambda l r \gg 1$, occurs most widely. In this case, the heterogeneous consumption constant is

$$K_{het} \simeq \frac{c\gamma}{4} A, \quad (4)$$

where c is the average thermal velocity of the molecules (it is assumed that $D = lc/3$. Eqn. (4) yields the number of active collisions of the molecules with the surface, per unit volume, in 1 s. The approximate form of the dependences of A on the height [8,19] is illustrated in Fig. 1. The values of A in the background atmosphere near the Earth's surface (~ 100 μm^3 cm^{-3}) and in volcanic and polar clouds (10–50 μm^2 cm^{-3}) are approximately the same. In urbanised regions, A at the Earth's surface is higher by two orders of

magnitude than the background value, while in the Junge layer under background conditions $A \simeq 1$ μm^2 cm^{-3}. The values of γ required for the calculation of K_{het} are presented below.

III. The influence of heterogeneous reactions on the concentrations of ozone and other minor constituents of the atmosphere

1. Model estimates for the atmosphere in the middle latitudes

Together with oxygen and nitrogen, the atmosphere contains many other constitutes at a low concentration (the so called minor constituents). These comprise primarily the gases H_2O, CH_4, N_2O, NO_x, etc. ariving from the Earth and entering into various reactions, the reservoir gases H_2O_2, N_2O_5, HNO_3, HCl, HOCl, $ClONO_2$, HO_2NO_2, etc. formed in photochemical reactions, as well as the radicals H, OH, HO_2, $O(^3P)$, $O(^1D)$, NO, NO_2, Cl, ClO, etc. In the modelling of the minor constituents, all the gases are divided into families[3]. The oxygen family includes $O(^1D)$, $O(^3P)$, and O_3. The active odd hydrogen family comprises the H, OH, and HO_2 radical species. The OH and HO_2 radicals play a decisive role in establishing the gas composition of the stratosphere and especially the troposphere. Their concentration depends to a large extent on the content of hydrogen peroxide, which is the principal reservoir of the hydrogen family and supplies OH radicals by its photolysis. The odd nitrogen family $NO_x = NO + NO_2$ is closely related to the NO_y family, which incorporates the reservoir gases N_2O_5, HNO_3, $ClONO_2$, and HO_2NO_2, whose photolysis leads to the formation of NO_2. The calculated and experimental concentrations of many gas constituents have been published in monogrphs[3,4] and in a review[8]. The heterogeneous decomposition of long-lived components of the atmosphere, whose chemical reactions are slower than their vertical transport, must be taken into account for $\tau_{het} \lesssim 10\tau_D$, where $\tau_{het} = K_{het}^{-1}$ and $\tau_D = H^2/K$ are respectively the characteristic heterogeneous decomposition and vertical transport times. The height of the uniform atmosphere $H = 5-7$ km and the turbulent transport (eddy diffusion) coefficient $K \simeq (10^4-10^5)$ cm^2 s^{-1}. The contribution of heterogeneous decomposition is appreciable if

$$\gamma > \frac{0.4K}{cH^2A} \simeq \frac{(10^{-12}-10^{-13})}{A} \text{ cm}^{-1}. \quad (5)$$

A specific surface $A \simeq 10^{-7}-10^{-6}$ cm^{-1} is characteristic of the background troposphere near the Earth's surface and stratospheric clouds (see Fig. 1) and heterogeneous processes must therefore be taken into account if

$$\gamma_1 > 10^{-7}-10^{-5}. \quad (6)$$

Over highly polluted cities, A reaches $10^{-4}-10^{-5}$ cm^{-1} and heterogeneous reactions may prove to be significant already when

$$\gamma_2 > 10^{-9}-10^{-7}. \quad (7)$$

The long-lived components of the atmosphere include methane, N_2O, and fully substituted chlorofluorocarbons (Freons). Generally speaking, low values of γ such as $10^{-9}-10^{-7}$ may be entirely realistic characteristics of the catalytic oxidation of methane, for example, on the surfaces of the oxides Al_2O_3 and Fe_2O_3, or of the heterogeneous decomposition of N_2O. However, there is apparently no direct evidence for the occurrence of heterogeneous-catalytic reactions in the atmosphere.

It is more difficult to select a criterion of the need to include heterogeneous reactions when one is dealing with chemically reactive gases whose lifetime is shorter than the vertical or horizontal transport time. This applies primarily to radicals. For example, the rate of the heterogeneous destruction of the OH or HO_2 radicals must be compared with the rate of descent of these radicals and reservoir gases, in which they are "stored". In particular, the main radical destruction processes of the radicals of the hydrogen family, OH and HO_2, in the troposphere are the reaction $\dot{O}H + H_2O_2 \rightarrow H_2O$ and $H\dot{O}_2$ and the heterogeneous elution of hydrogen peroxide. Their overall rate at the surface of the Earth is $W \simeq 10^5$ cm^{-3} s^{-1} [8,20-22]. With increase in height, the rate of destruction falls.

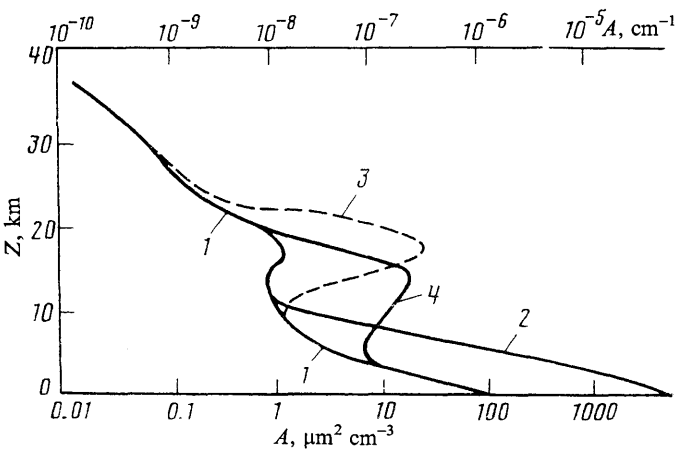


Figure 1. An approximate illustration of the distribution of the specific aerosol surface[19,20]: *1*, background atmosphere; *2*, urbanised regions; *3*, stratospheric volcanic clouds; *4*, polar stratospheric clouds.

The aerosol decomposition of OH or HO_2 must be taken into account when

$$W_A = K_{het}[R] > 0.1W \quad (8)$$

or

$$\gamma \geq \frac{0.4W}{c[R]}. \quad (9)$$

Here $[R]$ is the concentration of radicals. At the Earth's surface, [OH] $\simeq 10^6$ cm^{-3}, [HO_2] $\simeq 10^8$ cm^{-3} [8,22], and condition (9) assumes the form

$$\gamma_{OH} > \frac{10^{-6} \text{ cm}^{-1}}{A} \text{ and } \gamma_{HO_2} > \frac{10^{-8} \text{ cm}^{-1}}{A}. \quad (10)$$

Fig. 1 makes it possible to trace the range of values of γ for which it is necessary to take into account the heterogeneous destruction of OH and HO_2. Under background conditions, $\gamma_{OH} \simeq 0.3-1$ and $\gamma_{HO_2} \gtrsim 10^{-2}$. For polluted cities, the estimates are displaced by two orders of magnitude: $\gamma_{OH} \gtrsim 10^{-2}$ and $\gamma_{HO_2} \gtrsim 10^{-4}$.

Probable estimates for heterogeneous O_3, NO_x, and HO_x decomposition processes on aerosols, carried out in accordance with different models, have been published in a review.[8] In the

calculations based on the one-dimensional model, use was made of the average specific surface of the aerosol (20 μm^{-2} cm^{-3}), which does not vary along the height and corresponds to the particle content in the background atmosphere and also in the stratospheric volcanic and polar clouds. The hypothesis that the specific surface profile is constant as a function of height makes it possible to estimate the sensitivity of the atmosphere to the aerosol decomposition of various compounds in the troposphere and the stratosphere. Direct heterogeneous decomposition of ozone affects its content and the concentrations of other minor constituents (NO_x, HO_x) for $\gamma_{O_3} \gtrsim 10^{-4}$ and the process is most significant at a height of 18–20 km, i.e. at the height corresponding to the stratification of volcanic clouds. The direct decomposition of ozone leads to concomitant changes in the concentrations of other minor constitutents. In the stratosphere, where the homogeneous decomposition of O_3 is mainly caused by the reactions of the nitrogen cycle

$$\begin{aligned} &NO + O_3 \rightarrow NO_2 + O_2 \ , \\ &\underline{NO_2 + O \rightarrow NO + O_2} \ , \\ &O + O_3 \rightarrow 2O_2 \ , \end{aligned}$$

the decrease in $[O_3]$ leads to an increase in the NO and NO_2 concentrations, while in the troposphere, where the destruction of ozone is associated with the reactions of the hydrogen cycle

$$\begin{aligned} &OH + O_3 \rightarrow HO_2 + O_2 \ , \\ &\underline{HO_2 + O_3 \rightarrow OH + 2O_2} \ , \\ &2O_3 \rightarrow 3O_2 \ , \end{aligned}$$

the concentration of gases of the given family increases.

The critical value of γ_{NO_x}, beyond which the gas composition diminishes owing to the capture of NO and NO_2 by the aerosol surface, is 10^{-5}. However, for $\gamma_{NO_x} \simeq 10^{-5}$, large changes in concentration occur only in the upper stratosphere ($Z > 30$ km), where the specific surface of the aerosols apparently never reaches the value 20 μm^2 cm^{-3} adopted in the model under consideration. It is of interest that the presence of the stratospheric-tropospheric coupling leads to an increase in the amount of NO_x in the troposphere even if there is an additional heterogeneous NO_x sink. This is associated with the fact that the additional destruction of NO_x in the stratosphere induces a marked increase in the content of stratospheric ozone and a decrease in the intensity of the radiation penetrating the troposphere. This diminishes the rate of photodissociation of O_3 $[O_3 + h\nu \rightarrow O(^1D) + O_2]$ and the rate of the main OH radical formation reaction in the troposphere $O(^1D) + H_2O \rightarrow 2OH$. The decrease in the concentration of the tropospheric hydroxyls as a result of the heterogeneous destruction of NO_x in the stratosphere decreases the rate of removal of NO_x via the principal homogeneous reaction $\dot{O}H + NO_2 + M \rightarrow HNO_3 + M$. The contribution of this process, which exceeds the contribution of the direct heterogeneous destruction of NO_x in the troposphere, becomes increasingly significant with increase in γ_{NO_x}.

The critical values of γ_{OH} and γ_{HO_2} under the conditions near the Earth's surface were given above. For a uniform distribution of the aerosol with $A = 20$ μm^2 cm^{-3}, the contribution of the heterogeneous OH destruction to the change in the composition of the atmosphere should be higher than for the background distribution.

The influences of the heterogeneous destruction of the hydrogen family radicals OH and HO_2 on the content of tropospheric and stratospheric ozone are qualitatively different. In the troposphere, where O_3 is decomposed mainly in the hydrogen cycle, the additional decrease in the OH and HO_2 concentrations entails an increase in the ozone content, while in the stratosphere an increase in the NO_x concentration as a result of the diminution of the OH concentration (the rate of the reaction $\dot{O}H + NO_x + M \rightarrow HONO_x + M$ falls) leads to additional decomposition of O_3 in the nitrogen cycle. The results of modern calculations performed for $\gamma_{OH} = 0.1$ [8] have shown that a decrease in the OH concentration is accompanied by an increase in the NO_x content at all heights. On the other hand, the ozone concentrations in the troposphere and the stratosphere vary in different ways.

2. Laboratory studies on the heterogeneous decomposition of ozone and the $\dot{O}H$ and $H\dot{O}_2$ radicals

The first systematic studies on the heterogeneous interaction of the gases distributed in the atmosphere with substances whose compositions are close to those of the aerosols were carried out in 1979.[23] The interaction of the carbon particles and sulphuric acid drops characteristic of the polluted atmosphere of cities was considered. The reactions on the H_2SO_4 surface at 300 K were studied most thoroughly. For the majority of gases, including O_3, NO, NO_2, alkenes, alkanes, CF_4, CCl_2F_2, and atomic O and N, $\gamma < 10^{-6}$. The results of measurements for other gases, more reactive in relation to H_2SO_4, are presented below:

Molecule	H_2O	NH_3	H_2O_2	OH	HNO_3	N_2O_5	HO_2NO_2	$ClONO_2$
γ	$\sim 2\cdot10^{-3}$	$>10^{-3}$	$7.8\cdot10^{-4}$	$4.9\cdot10^{-4}$	>2 $4\cdot10^{-4}$	$3.8\cdot10^{-5}$	$2.7\cdot10^{-5}$	10^{-5}

The authors[23] reached the important conclusion that the tropospheric sulphuric acid aerosol can alter the gas composition of the atmosphere in polluted cities. However, a quantitative estimate was not made.

Numerous studies have been devoted to the heterogeneous decomposition of ozone. In this respect, the stratospheric aerosols are naturally of principal interest.

The interaction of ozone with various surfaces [ice, HNO_3, SiO_2, soot, NH_4NO_3, $(NH_4)_2SO_4$, NaCl, H_2SO_4] was studied in greater detail recently and fairly numerous measurements of the values of γ_{O_3} were made.[24] For the majority of materials investigated, $\gamma_{O_3} < 10^{-6}$ and, under the conditions of the stratosphere in the middle latitudes, including volcanic clouds, ozone is therefore only slightly subjected to heterogeneous decomposition. Values of γ greater than or approximately equal to 10^{-5} were obtained for the Al_2O_3 [25,26] and soot[24] surfaces. Such surfaces can influence the concentration of stratospheric ozone in certain extreme situations. For example, the scenario of a nuclear explosion in mines, whereupon large amounts of soil basalt can enter the atmosphere, has been considered.[27] When the amount of Al_2O_3 ejected reaches 17%, the column of ozone will diminish as a result of direct heterogeneous decomposition to the extent of 30–40%.

It follows from literature data[24,28,29] that the probability of the heterogeneous decomposition of O_3 on the liquid acid depends greatly on a series of factors difficult to take into account, such as the ratio of H_2SO_4 and H_2O, the presence of impurity Fe^{2+} ions,[29] and the duration of the action of O_3 on the surface. Nevertheless, in all cases the values of γ_{O_3} for H_2SO_4 do not exceed 10^{-6}.

The vigorous investigation of the heterogeneous destruction of $\dot{O}H$ and $H\dot{O}_2$ radicals has been promoted in recent years by the development of highly sensitive methods for their detection. The first study of the destruction of OH radicals on the surface of one of the tropospheric aerosols (carbon) was performed in 1975 [30]. The value

$\gamma_{OH} = 5 \times 10^{-2}$ obtained is sufficiently large for the heterogeneous destruction of OH to be taken into account in the modelling of the composition of the atmosphere in polluted cities. The heterogeneous destruction of $\dot{O}H$ [31,32] and $H\dot{O}_2$ [33–35] in the atmosphere was investigated. Table 1 shows that, in the case of typical atmospheric salt aerosols, γ_{OH} is fairly large, amounting to between 8.5×10^{-3} and 0.24 [31]. High values of γ_{OH} are also characeristic of silicon and metal oxides and especially of ice and sulphuric acid.[32] The value $\gamma_{OH} \simeq 1$ obtained for sulphuric acid[32] differs greatly from the value of 4.9×10^{-4} found in another study[23]. Although in both cases concentrated sulphuric acid was used, the surfaces themselves were apparently different. Gershenzon et al.[32] generated a liquid film on a quartz rod by immersing it in liquid sulphuric acid. Baldwin and Golden[23] poured concentrated sulphuric acid onto the bottom of a chamber directing a stream of radicals onto it. In contrast to the study of Baldwin and Golden[23], where the OH recombination products on the surface (most probably water) together with the unreacted OH radicals were directed to a mass spectrometer in which particles with an atomic weight of 17 were detected, Gershenzon et al.[32] used the direct EPR method for the detection of $\dot{O}H$ radicals. It will be shown below that information about the value of γ_{OH} for interaction with a volcanic sulphuric acid aerosol is of fundamental importance for the understanding of the effect of a decrease in ozone concentration after powerful volcanic eruptions.

Table 1. Probabilities of the heterogeneous destruction of $\dot{O}H$ radicals on aerosol-like surfaces.

Surface	γ	T, K	Refs	Surface	γ	T, K	Refs.
$Pb(NO_3)_2$	0.24 ± 0.12	300	[31]	NH_4NO_3	0.01 ± 0.002	300	[31]
NH_4Cl	0.13 ± 0.03	300	[31]	$(NH_4)_2SO_4$	$(8.5\pm1.7)\cdot10^{-3}$	300	[31]
$Fe(NO_3)_3$–FeO_x	0.4 ± 0.08	300	[31]	H_2SO_4	1	300	[32]
$FeSO_4\cdot H_2O$	0.12 ± 0.03	300	[31]	Ice	0.4	250	[32]
$Zn(NO_3)_2$	0.045 ± 0.02	300	[31]	Fe oxide	0.12 ± 0.08	250–350	[32]
$NaNO_3$	0.036 ± 0.018	300	[31]	Al oxide	0.04 ± 0.02	250–350	[32]
Na_2SO_4	0.018 ± 0.01	300	[31]	SiO_2	$(5.6\pm2)\cdot10^{-3}$	250–350	[32]

Table 2. Probabilities of the heterogeneous destruction of $H\dot{O}_2$ radicals on aerosol-like surfaces.

Surface	SiO_2	NaCl	Ag oxide	Fe oxide	Ni oxide	H_2O
γ	$(1-8)\cdot10^{-3}$	$7.5\cdot10^{-3}$	$1.2\cdot10^{-2}$	$1.7\cdot10^{-2}$	$<10^{-3}$	0.2
Refs.	[33–35]	[34, 35]	[33]	[33]	[33]	[36]

For the vast majority of aerosol materials, the values of γ_{OH} are comparatively high and are in the range from 0.1 to 1, although $\gamma_{OH} \simeq 10^{-2}$ for a series of salts and SiO_2 (Table 1).

Although fairly numerous studies on the destruction of $H\dot{O}_2$ radicals on various surfaces have been carried out in recent years, aerosol surfaces have been investigated comparatively little. It follows from Table 2 that the values of $\gamma_{HO_2} \times 10^{-2}$ may be regarded as typical for tropospheric aerosols. It has been noted[33–35] that γ_{HO_2} depends on the presence of water vapour and hydrocarbons in the gas. However, the main factor determining the value of γ_{HO_2} is nevertheless the material of the surface. The temperature dependence of γ_{HO_2} is as a rule negative[34].

The probability of the mass accommodation of HO_2 on finely dispersed water drops saturated with $LiNO_3$ or NH_4HSO_4 has been measured[36]. The apparatus made it possible to model the behaviour of HO_2 in cloud formations, although the size of the aerosol drops in the experiment (0.05–0.1 μm) was appreciably smaller than the size of the cloud drops. The value $\gamma_{HO_2} = 0.2$ obtained is fairly high, which can influence appreciably our ideas about both the composition of the gas in clouds and mist and about the oxidation processes occurring in the water drops (see Section IV).

There is as yet insufficient information about the heterogeneous OH and HO_2 destruction processes. In particular, it is essential to measure γ_{HO_2} for ice, sulphuric acid, and salts of nitric and sulphuric acids [NH_4NO_3, $(NH_4)_2SO_4$, etc.]. Nevertheless, as suggested in a study by one of the authors[37], it is possible to adopt on the basis of the data in Tables 1 and 2 the typical values $\gamma_{OH} \simeq 0.1-1$ and $\gamma_{HO_2} \simeq 10^{-2}$ for all tropospheric aerosols.

3. The influence of heterogeneous processes on the gas composition of the troposphere and on the tropospheric-stratospheric coupling

In the modern molecular models of the atmosphere, account is taken as a rule of only two heterogeneous processes occurring in the troposphere and on the surface of the Earth. The first is associated with the elution of soluble gases or gases reacting with water ("moist elution") and the second involves the precipitation and decomposition of molecules on a supporting surface ("dry deposition").

(a) Dry deposition, moist elution, and the scattering of sunlight by the cloud cover. Dry deposition occurs when gases are adsorbed on the surfaces of the oceans and dry land, after which the adsorbed gases decompose. The destruction of gases at the boundary of the atmosphere as a result of heterogeneous reactions leads to the appearance of a diffusional flux towards the surface. In the chemistry of the atmosphere, this phenomenon is regarded as the deposition of the entire column of gas at a rate V_{de}. The characteristic rate of deposition of O_3 is 0.02 cm s^{-1} on the snow cover and 0.6 cm s^{-1} on soil[8]. In the solution of the problem of the transfer of the SO_2 impurity, the value $V_{de}^{SO_2} = 0.8$ cm s^{-1} was used[38]. The characteristic time of the vertical deposition of the column of gases

$$\tau_{de} = H/V_{de}' \simeq 10^6 - 10^7 \text{ s}$$

is comparable to the time of the turbulent transport in a homogeneous atmosphere to a height $H = 5-7$ km. Model calculations for the summer and winter deposition of ozone[8] have shown that, with decrease in V_{de} by a factor of 30 (from 0.6 to 0.2 cm s^{-1}), the concentration of O_3 at the surface of the Earth increases during the winter by a factor of approximately two. On the

other hand, at a height of 3–5 km the gas composition of the atmosphere virtually no longer depends on the rate of deposition of O_3.

The moist elution of gases readily soluble in water (with a Henry constant greater than 10^3 mol litre^{-1} atm^{-1}) is usually regarded as a first-order process. The distribution of the rate constants for this process with respect to height is consistent with the results of measurements of the content of the minor constitutents carried out in nature. The rate constants for the elution of many gases with different solubilities (H_2O_2, CH_2O, CH_3OOH, HNO_3, etc.) are believed to be the same. This is apparently a fairly rough approximation. According to Logan[22], the elution constants at different heights are

$$K_z = 2.3 \times 10^{-6} \exp[1.6 - 0.4Z] \text{ s}^{-1} \text{ for } Z < 4 \text{ km},$$

$$K_z = 2.3 \times 10^{-6} \text{ s}^{-1} \text{ for } Z > 4 \text{ km}. \quad (11)$$

The H_2O_2 moist elution process is decisive in the balance within the hydrogen family in the troposphere. As already pointed out, the loss of this family occurs principally as a result of the elution of hydrogen peroxide[8]. The results of model calculations[39] of the dependence of the concentrations of the minor constituents on the elution constant have been analysed in a review[8]. Variation of K_Z in the range from 10^{-6} to 10^{-5} alters the calculated values of $[HNO_3]$, $[NO_x]$, and $[HO_x]$ by tens and hundreds per cent. The concentrations of the OH and HO_2 radicals undergo a particularly marked change. Thus, with increase in K_Z from 1.15×10^{-6} to 5×10^{-6} s^{-1}, the concentration of radicals at different heights falls by a factor of 1.5–2. Together with the heterogeneous-chemical factors examined above, the gas composition of the troposphere is also affected by the scattering of the solar radiation by cloud drops.

Radicals of the hydrogen family are generated in the troposphere mainly as a result of the reaction $O(^1D) + H_2O \rightarrow 2OH$ and the photolysis of formaldehyde $H_2CO + h\nu \rightarrow H + HCO$. The $O(^1D)$ atoms in the troposphere also appear as a result of photolysis: $O_3 + h\nu \rightarrow O(^1D) + O_2$. The rate of generation of HO_x radicals in the lower troposphere therefore depends markedly on the cloud cover, which scatters solar radiation.

(b) The influence of the heterogeneous destruction of the OH and HO_2 radicals on aerosols on the concentration of tropospheric hydroxyl radicals and other minor constituents of the atmosphere. Under background conditions, one cannot expect appreciable variations in the concentration of hydroxyl radicals as a result of the heterogeneous destruction of OH or HO_2. The destruction of OH and HO_2 radicals on aerosols becomes the main cause of the loss of gases of the hydrogen family in urbanised regions, while the specific aerosol surface increases by more than two orders of magnitude compared with the background value. The gas composition of air over polluted cities has been modelled[38]. The results of one of the calculations of the deviations of the height profiles of the O_3, CO, NO_x, $\dot{O}H$, $H\dot{O}_2$, and H_2O_2 concentrations are presented in Fig. 2. The calculations were performed for $\gamma_{OH} = 1$ and the height profile of the distribution of the aerosol concentration was specified by Eqn. (1), where $N_0 = 10^4$ cm^{-3} and $Z_0 = 1$ km. The average radius of the aerosol particles was assumed to be 0.1 μm. According to theoretical calculations[40] and experimental measurements,[32] the diffusion coefficient of the OH radicals is

$$D_{OH} = \frac{1.41 \cdot 10^{-2} T^{1.72}}{p} \text{ cm}^2 \text{ s}^{-1}, \quad (12)$$

the pressure p being expressed in mmHg.

Fig. 2 illustrates the percentage deviations of the concentrations of various substituents according to the aerosol model from the concentrations calculated in accordance with the molecular model:

$$\alpha = \frac{[n]_A - [n]_M}{[n]_M}. \quad (13)$$

Fig. 2 shows that the gas composition of the atmosphere in the presence of the aerosol is appreciably modified: the calculated content of the NO_x, CO, and O_3 gases, which are harmful to animals and plants, increases. Furthermore, the content of hydroxyl and perhydroxyl radicals falls by a factor of approximately 4–5. The effect becomes even greater if account is taken of the heterogeneous destruction of HO_2 radicals. For $\gamma_{HO_2} \simeq 10^{-2}$, the concentration of OH radicals near the Earth's surface by a factor of approximately five and that of HO_2 diminishes by a factor greater than 10.

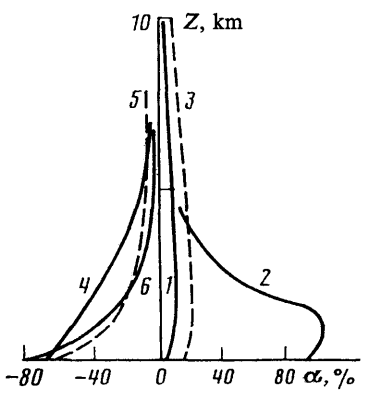


Figure 2. The height profiles of the deviations of the concentration of minor constituents in urbanised regions[38]: *1*, O_3; *2*, NO_2; *3*, CO; *4*, H_2O_2; *5*, $\dot{O}H$; *6*, $H\dot{O}_2$.

(c) The influence of tropospheric heterogeneous processes on the concentration of stratospheric ozone and the oxidation of Freons. OH radicals are known to be the "cleaners" of the atmosphere, ensuring the oxidation of the impurities arriving from the Earth. The self-cleaning of the atmosphere takes place mainly in the lower part of the troposphere, because the temperature and hence the rate of the reactions of OH with impurities decrease with increase in height. We saw above that a number of heterogeneous processes affect the concentration of OH radicals: (1) the scattering of radiation by the cloud cover; (2) dry deposition of O_3; (3) moist elution of H_2O_2; (4) heterogeneous destruction of OH and HO_2 radicals on aerosols. Incomplete allowance for these factors leads to considerable uncertainty in the determination of the concentration of OH radicals. We shall consider in that way this can affect predictions concerning the ozone layer of the atmosphere. The

desruptive effect of Freons is associated with the fact that they do not react with the tropospheric radicals but penetrate freely into the stratosphere. The photodissociation of Freons in the stratosphere leads to the formation of Cl and the decomposition of O_3 in the chlorine cycle:

$$\begin{aligned} &Cl + O_3 \rightarrow ClO + O_2 \ , \\ &\underline{ClO + O \rightarrow Cl + O_2 \ ,} \\ &O + O_3 \rightarrow 2O_2 \ , \end{aligned}$$

The increase in the rate of destruction of the ozone layer associated with the growing manufacture of chlorofluorocarbons, predicted at the present time, can be arrested if an alternative to the Freons can be found[41]. The manufacture of fully halogenated Freons has been prohibited by the Montreal Protocol. It has been recommended that eight chlorofluorohydrocarbons, the simplest of which is Freon-22 (CF_2HCl), be used as an alternative[42]. It is believed that Freon-22 is much less dangerous to the ozone layer than Freons such as $CFCl_3$ and CF_2Cl_2, because it reacts comparatively rapidly with OH radicals, i.e.

$$CF_2HCl + OH \rightarrow CF_2Cl + H_2O,$$

the rate constant being $k = 1.2 \times 10^{-12} \exp -(1100 \pm 150)/T \text{ cm}^3 \text{ s}^{-1}$, and penetrates the stratosphere to a much lesser extent. Thus through the interaction of the OH radicals with the alternative Freons, a tropospheric-stratospheric coupling is established between the chlorine family of anthropogenic origin and the ozone layer. Freons exert the principal destructive influence at a height of ~40 km where the rate of their photodissociation becomes appreciable.

The influence of heterogeneous tropospheric factors on the stratospheric ozone was estimated by the present authors together with Zvenigorodskii and Smyshlyaev. In particular, the following scenario was examined.

Suppose that the release of all the Freons is modelled by the release of Freon CF_2HCl in an amount of one million tonnes per year. In this case, a steady state would be established after approximately eighty years in which the O_3 content at a height of 38 km would diminish by 8% relative to the Freon-free atmosphere. By varying the rate constants for elution and the scattering of radiation by the cloud cover within reasonable limits and by postulating the heterogeneous destruction of OH and HO_2 radicals on the tropospheric background aerosol, it is easy to obtain a two–three-fold diminution of the concentration of tropospheric hydroxyls. This would lead in its turn to an additional decrease in the ozone concentration at a height of about 40 km by 10%, so that the overall fall in the content of O_3 at these heights would be by 18%. The total degradation of the ozone column after 80 years would be 3% under these conditions. Thus heterogeneous processes controlling the content of $\dot{O}H$ radicals determine also the ozone content in the upper stratosphere. The aerosol contaminants of the troposphere, leading to a decrease in its $\dot{O}H$ content and to an impairment of the purity of the troposphere, promote under these conditions the entry of the alternative Freons into the ozonosphere and an increase in the risk of the decomposition of the ozone layer.

The principal products of the oxidation of the majority of alternative Freons are compounds of the phosgene series[42]; in particular, in the case of CF_2HCl the product is CF_2O. The higher the concentration of tropospheric hydroxyls, the smaller the amount of Freons penetrating the stratosphere. However, vigorous oxidation of Freon occurs closer to the Earth's surface the lower the content of aerosols. The intensification of the reactions of $\dot{O}H$ with Freon leads to the accumulation of toxic compounds (phosgenes) in the lower part of the atmosphere. Thus by ejecting alternative Freons into the atmosphere, we can be faced by the extremely sad prospect of the replacement of the ozone problem by the phosgene problem. Such trade-off between the ecological and toxicological problems is merely a hypothetical variant. It may be that the decomposition of phosgenes in water drops, i.e.

$$CF_2O + (H_2O)_{ж} \rightarrow CO_2 + 2HF$$

will eliminate the toxicological risk of the alternative Freons. All this requires more complete quantitative tests.

4. Heterogeneous reactions in polar stratospheric clouds and Antarctic spring ozone holes

The sensational phenomenon of the sharp decrease in the concentration of ozone in the Antarctic during the spring, observed comparatively recently[43], has been adequately discussed in the scientific literature and in the publications for general consumption (see, for example, Karol'[20]). A central place has been assigned to this problem in the annual international reviews of the state of the ozone layer, including the latest collection.[44] We shall concentrate attention on the heterogeneous processes which are believed to occur in the establishment of the precritical spring situation and possibly also during the development of the ozone "hole". Without going into the details of the dynamics of the development and of the scale of the Antarctic ozone holes, we shall only emphasise that, according to the observations at the Halley Bay station (76° S, 27° W), the spring decrease in the ozone content in the Antarctic during the period from 1957 to 1985 [43] did not begin until 1979. From 1979 until 1985, the overall ozone content in October fell from 300 to 200 Dobson units (1000 Dobson units correspond to a 1 cm thickness of the ozone layer at atmospheric pressure). Evidently the primary cause of this phenomenon is the anthropogenic release of Freons.[19]

It is believed at the present time that during the winter, when the stratosphere cools down and particles condense in polar stratospheric clouds (PSC), chemical processes leading to the removal of nitrogen oxides from the gas phase and the generation of molecules of the chlorine reservoir take place. These photochemically active chlorine components do not react during the winter with the PSC particles or with ozone in the gas phase or on the surface. During sunrise in the spring period, the reservoir chlorine molecules undergo photodissociation and are converted into a radical form which initiates the chain decomposition of ozone. This multistage concept is hardly complete in our view. We suggest that heterogeneous reactions can be also a direct and not merely an indirect cause of the decomposition of the Antarctic ozone. During the initial period of the polar night, after sunset there is a fairly rapid recombination of the active atmospheric components ($\dot{O}H$, ClO, and $\dot{H}O_2$) as well as the nitrogen oxides NO_x, which are converted into the reservoir gases H_2O, HCl, H_2O_5, HNO_3, H_2SO_4, and $ClONO_2$. The subsequent fate of the reservoir gases has been investigated in experiments under natural and laboratory conditions. In particular, it has been established that the coefficient of adhesion of the molecules of the acids HCl and HNO_3 to the surface of ice is close to unity[45,46] and that the composition of the PSC condensate is close to that of the nitric acid trihydrate[10] or contains 0.02–0.35 mol of HCl per mole of water[46] at temperatures below 195 K. Laboratory studies confirmed the conclusions reached from observations under

natural conditions that gas denitrification and dehydration reactions take place during winter (Scheme 1):

Scheme 1

(1) $N_2O_5 + (H_2O)_S \rightarrow 2(HNO_3)_S$,

(2) $N_2O_5 + (HCl/H_2O)_S \rightarrow (ClNO_2)_G + (HNO_3)_S$,

(3) $ClONO_2 + (H_2O)_S - (HOCl)_G + (HNO_3)_S$,

(4) $ClONO_2 + (HCl/H_2O)_S \rightarrow (Cl_2)_G + (HNO_3)_S$.

The subscripts G and S denote the gas and condensed phases respectively. In reactions (2)–(4) (Scheme 1), the chlorine component is converted into a new form, affording the readily photolysed reservoir gases Cl_2, HOCl, and $ClNO_2$ (or ClONO). They in fact ensure the development of the dramatic spring situation.

The values $\gamma_{O_3} \approx 10^{-6}$ attained under laboratory conditions in the study of the decomposition of ozone on ice and nitric acid particles[24] indicate the possibility, in principle, of the direct breakdown of O_3 during the long polar night.

Table 3. Heterophase reactions occuring under the conditions of the polar Antarctic night.

Reaction	Conditions	γ	Refs.
(1)	195 K	0.028±0.011	[47]
	185 K	$>10^{-3}$	[48]
(2)	$[HCl]/[H_2O] \leq 0.04$	~0.06	[47]
	—	$>3\cdot10^{-3}$	[48]
(3)	185–200 K	0.009	[49]
	—	0.02	[50]
	—	0.06	[45]
(4)	$[HCl]/[H_2O] = 0.015 \div 0.04$; 195 K	0.27	[45]
	$[HCl]/[H_2O] = 0.003 \div 0.01$; 200 K	0.05÷0.1	[50]

Measurements[24] are not inconsistent with estimates[47] according to which γ_{O_3}, γ_{NO}, and $\gamma_{NO_2} < 10^{-4}$ for ice. The results of studies on reactions (1)–(4) under conditions close to those during the Antarctic polar night (180–200 K) are presented in Table 3. It is seen that in all cases these low-temperature reactions proceed extremely effectively. Thus their characteristic time in polar stratospheric clouds does not exceed 24 h. The condensation of nitric acid has been reliably demonstrated in all four reactions. On the other hand, the gas-phase products and the possible routes to their further conversion have been less thoroughly investigated. In experiments[47,48] carried out using mass-spectrometric analysis, the products ClONO and $ClNO_2$ proved to be indistinguishable. Furthermore, one cannot rule out the possibility of their subsequent heterogeneous reactions.[45] It has been shown that HOCl is the gas-phase product of reaction (3). However, this is apparently merely an unstable intermediate, which reacts with ice, at least in the presence of $ClONO_2$, with formation of Cl_2O [50].

Although the measured rates of reaction (3) differ from one another by a factor of 6, they are nevertheless fairly high, so that this is not the reaction which limits the heterogeneous reaction of $ClONO_2$ in wintertime. The composition of products of reactions (2) and (3) (Scheme 1) and their behaviour in the presence of PSC require further refinement.

The heterogeneous reactions (1)–(4) in Scheme 1 lead to the capture of gas-phase nitrogen oxides and the formation of photochemically active gaseous Cl_2, HOCl, Cl_2O, and $ClNO_2$ molecules. It is at present difficult to say which of these makes the greatest contribution to the photolytic generation of Cl atoms at sunrise. However, the very fact of the high chlorine content in the radical form has been demonstrated by direct measurements of the concentration of ClO radicals[51,52,58], which at the beginning of the spring (September) at a height of about 20 km exceeds by a factor of 100 their concentration in the middle latitudes. Already in October, when the polar clouds break up and O_3 degradation processes cease, the Cl content in the Antarctic does not differ appreciably from its content in the middle latitudes. Apparently the main O_3 decomposition cycle is determined, as suggested by Molina and Milina[53] by the reactions

$$\begin{aligned} ClO + ClO + M &\rightarrow Cl_2O_2 + M \quad , \\ Cl_2O_2 + h\nu &\rightarrow Cl + ClO_2 \quad , \\ ClO_2 + M &\rightarrow Cl + O_2 + M \quad , \\ 2(Cl + O_3) &\rightarrow 2(ClO + O_2) \quad , \\ \hline 2O_3 + h\nu &\rightarrow 3O_2 \quad . \end{aligned}$$

The first, termolecular reaction which has been invetigated[54,55] limits the decomposition of O_3. Knowing the concentration ClO and the rate constant for this reaction, it is possible to calculate the rate of degradation of ozone, which proves to be close to the experimentally measured value. If the formation of Cl_2O_2 is indeed the rate-determining stage of the spring decomposition of O_3, then, by virtue of its non-linearity in relation to the chlorine content, its rate should change sharply with increase in the amount of Freons released into the atmosphere. This picture has in fact been observed since 1979 [43]. The recombination of ClO radicals can become dominant only in the presence of a low NO_2 content, but the rate of their reaction $ClO + NO_2 + M \rightarrow ClONO_2 + M$ is low. During the winter, the reservoir nitrogen oxide gases are converted into condensed nitric acid as a result of the occurrence of the heterogeneous reactions (1)–(4) (Scheme 1). Nitrogen oxides can therefore appear only after the evaporation of the PSC, which begins in October. The low NO_2 content in the winter and spring Antarctic atmospheres has been confirmed by many observations[55]. Apart from the purely chlorine-based zone decomposition cycle, a further two synergistic cycles with participation of BrO [56] or OH and HO_2 [57] radicals have been proposed. In the synergistic cycle

$$\begin{aligned} ClO + BrO &\rightarrow Cl + Br + O_2 \quad , \\ Cl + O_3 &\rightarrow ClO + O_2 \quad , \\ Br + O_3 &\rightarrow BrO + O_2 \quad , \\ \hline 2O_3 &\rightarrow 3O_2 \quad , \end{aligned}$$

note more than 10% of ozone relative to the purely chlorine-based cycle can decompose, since the BrO concentration is low compared

with that of ClO.[58] The hydrogen chloride cycle[57]

$$\begin{aligned} HOCl + h\nu &\rightarrow OH + Cl \quad , \\ Cl + O_3 &\rightarrow ClO + O_2 \quad , \\ OH + O_3 &\rightarrow HO_2 + O_2 \quad , \\ ClO + HO_2 &\rightarrow HOCl + O_2 \quad , \\ \hline 2O_3 &\xrightarrow{h\nu} 3O_2 \quad , \end{aligned}$$

is apparently relatively ineffective owing to the high probability of the destruction of OH radicals on the ice particles.[32] Thus the chlorine-based O_3 decomposition cycle with participation of the Cl_2O_2 dimer is apparently most effective.

After this review had been written, one of the authors received the manuscripts of papers[58,59] prepared for publication, which were sent by Prof. Brune. Brune and co-workers[59] carried out a detailed analysis of the contributions of various Antarctic ozone decomposition cycles on the basis of simultaneous measurements of the absolute concentrations of ClO, BrO, and O_3 carried out with an aeroplane in 1987 [58]. The latest data for the rate constants for the rate-limiting stages of the above homogeneous cycles (the ClO + ClO + M and ClO + BrO reactions[60]) and measurements under natural conditions[58] permitted the conclusion that the main contribution to the spring decomposition of ozone comes from the chlorine cycle and the chlorine-bromine cross cycle. In order to refine the contribution of the hydrogen chloride cycle, it is necessary to have direct measurements of the concentration of OH (or HO_2). According to estimates,[53] it is not more than 4%. The contribution of the first two cycles to the observed rate of the spring decomposition of O_3 can reach 40 and 20% respectively. In order to abolish the underestimate in the calculated rate, yet another catalytic cycle has been proposed:[59]

$$ClO + O_3 + M \rightarrow ClO.O_3 + M (k = 2 \times 10^{-35} \text{ cm}^6 \text{ s}^{-1} \text{ at } 200 \text{ K}),$$

$$\begin{aligned} ClO \cdot O_3 + h\nu &\rightarrow ClO_2 + O_2 \quad , \\ ClO_2 + M &\rightarrow Cl + O_2 + M \quad , \\ Cl + O_3 &\rightarrow ClO + O_2 \quad , \\ \hline 2O_3 + h\nu &\rightarrow 3O_2 \quad . \end{aligned}$$

Having included in the consideration also this sequence of reactions with the rate constant for the formation of complex $ClO.O_3$ indicated, it is possible to reconcile completely the experimentally observed kinetic relations for the spring decomposition of O_3 with the diurnal concentration of the ClO and BrO radicals. However, we believe that there is no need to introduce into consideration an exotic species such as the complex $ClO.O_3$. In order to account for the underestimate of the rate of the spring decomposition of ozone, one can examine the additional heterogeneous-homogeneous photolytic cycle

$$\begin{aligned} ClO + PSC &\rightarrow \tfrac{1}{2}(Cl_2 + O_2), \\ Cl_2 + h\nu &\rightarrow 2Cl \quad , \\ 2(Cl + O_3) &\rightarrow 2(ClO + O_2) \quad , \\ \hline 2O_3 + PSC + h\nu &\rightarrow 3O_2. \end{aligned}$$

The possibility of the existence of this hypothetical cycle has been confirmed by preliminary measurements of the probability of the destruction of ClO on the surface of ice ($\gamma_{ClO} \simeq 10^{-2}$).[47] A simple estimate showed that, when [ClO] = 2×10^9 cm^{-3}, the rate of decomposition of O_3 in the heterogeneous cycle can be close to the rate of its degradation in the homogeneous chlorine cycle. More detailed studies on the heterogeneous interaction of ClO radicals with the surface of ice are apparently necessary.

Yet another important heterogeneous reaction in the Antarctic spring may prove to be the process

$$ClO + (O_3)_{ads} \rightarrow OClO + O_2,$$

where $(O_3)_{ads}$ is the ozone molecule adsorbed on the PSC surface. This reaction can account for the variation of the ClO concentration over a period of 24 h. It is known that during the night ClO is almost fully converted into OClO. However, this does not lead to a change in [O_3] because ozone molecules are regenerated during the day by the reactions:

$$\begin{aligned} OClO + h\nu &\rightarrow O + ClO, \\ O + O_2 + M &\rightarrow O_3 + M. \end{aligned}$$

The heterogeneous catalytic reactions

$$ClO + (H_2O)_s \rightarrow \tfrac{1}{2}(Cl_2 + O_2) + (H_2O)_s,$$

and

$$ClO + (O_3).(H_2O)_s \rightarrow OClO + O_2 + (H_2O)_s,$$

proposed here can undoubtedly play a definite part in the chemical reactions occurring in the spring in the Antarctic. As regards the winter preparatory period, here too the heterogeneous reactions of the ClO precursor gases (HOCl, Cl_2O, $ClNO_2$, and ClONO) with solid PSC particles can be important. Apart from the study of these heterogeneous reactions, it is also essential to carry out measurements of the HOCl, Cl_2O, $ClNO_2$, and ClONO concentrations under natural conditions. We should like to point out also the possible influence of the direct decomposition of O_3 on PSC particles on the dynamics of the formation of the ozone hole in the Antarctic spring. A model of this process includes the change in the vertical air circulation in springtime, when the warm air of the troposphere, depleted in ozone, rises to the stratosphere, diminishing thereby the ozone concentration in the lower stratosphere. Measurements[24] indicate the possible decomposition of O_3 (within the limits of 10%) on PSC particles during the long polar night. This can afford additional support to the dynamic model, because during the winter the circulation of air is directed downwards and one cannot rule out the possibility that towards spring the troposphere is more depleted in ozone than in the absence of the direct decomposition of stratospheric ozone.

5. The influence of volcanic eruptions on the ozone content of the stratosphere

Powerful volcanic eruptions, which include a series of eruptions of the Mexcian El Chichon volcano (17° N latitute) at the beginning of April 1982 have exerted a large-scale influence on the stratosphere. Thus the aerosol cloud formed after the eruption of El Chichon extended from the equator to 50° N latitude, whilst the duration of its development and relaxation exceeded one year (Fig. 3). The scale of the eruption can be imagined from the amount of SO_2 ejected (3.3 million tonnes). The photochemistry of the stratosphere can be influenced greatly also by the ejection of HCl and water vapour. The components of the ejected material are apparently initially concentrated at a height of 25–35 km. However, after a time, as a result of photochemical oxidation mainly in the Junge layer, sulphuric acid aerosols containing 75% H_2SO_4 and 25% H_2O accumulate. Fig. 3 shows a distinct negative correlation between the content of the aerosol component and the amount of ozone, which has been the subject of controversy since the instant of its

observation during the winter of 1982–1983. Without being able to consider at length problems of the formation of volcanic clouds and the modelling of the effects of a volcanic eruption on the thermal and radiation conditions in the stratosphere, we shall merely point out that, according to estimates[21,61,62], the observed decrease in the concentration of ozone cannot be accounted solely by the change in temperature and in the solar radiation fluxes. The O_3 content begins to decrease not sooner than half a year after the eruption and is correlated with the formation of secondary sulphuric aerosols in the Junge layer.

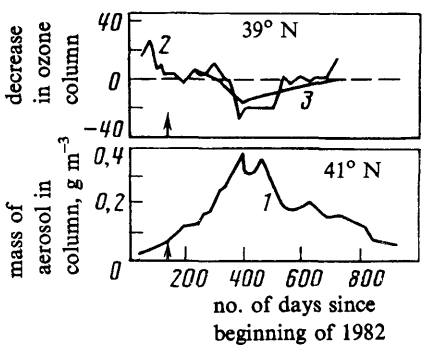


Figure 3. Variation of the contents of aerosols and ozone in the course of the evolution of the eruption cloud; *1*, aerosol; *2*, observed decrease in the amount of ozone of Dobson units (according to the data of Tolbert et al.[63]); *3*, calculated decrease in the amount of ozone for $\gamma_{OH} = 1$ (according to Anderson et al.[59]); the instant of the eruption of the El Chichon volcano is indicated by an arrow.

Two alternative models explaining the decrease in the amount of O_3 by the occurrence of heterogeneous reactions have been put forward recently. According to the first hypothesis[8,61,62], the decrease in the O_3 content in the cloud is caused by the heterogeneous destruction of OH radicals on the aerosol particles. The decrease in [ȮH] leads to an increase in [NO] and in the contribution of the nitrogen cycle (see above). The results of numerical modelling[59], based on the value $\gamma_{OH} = 1$, adopted on the basis of the measurements of γ_{OH} for ice and sulphuric acid[32] are presented in Fig. 3. Evidently the proposed hypothesis makes it possible to describe quantitatively the sharp diminution in the concentration of ozone in the volcanic cloud.

The second hypothesis is based on the measurements of the probabilities of the capture of HCl, $ClONO_2$ [63] and N_2O_5 [64] by the sulphuric acid solution and the temperature of the stratospheric volcanic clouds in wintertime (−65 °C). It follows from Table 4 that N_2O_5 is captured particularly effectively. On the hypothesis that nitric acid, evolved into the gas phase, is the product of the reaction of N_2O_5 with the H_2SO_4/H_2O surface and that the heterogeneous interaction of HCl and $ClONO_2$ leads to the generation of active chlorine, it has been possible to demonstrate[21] a decrease in the O_3 content in volcanic clouds after the eruption of the El Chichon volcano. Aerosols apparently exert an extremely varied influence. On the one hand, they convert N_2O_5 and nitrogen oxide into nitric acid, reducing the strength of the nitrogen-based O_3 decomposition cycle. On the other hand, their reactions with HCl and $ClONO_2$ generate chlorine, which initiates the operation of the chlorine-based ozone decomposition cycle:

$$\begin{array}{l} Cl + O_3 \rightarrow ClO + O_2 \quad , \\ \underline{O + ClO \rightarrow Cl + O_2 \quad ,} \\ O + O_3 \rightarrow 2O_2 \quad . \end{array}$$

Under the usual conditions, the effectiveness of this cycle in the lower stratosphere is low.

Table 4. Probabilities of the capture of HCl, N_2O_5, and $ClONO_2$ by the sulphuric acid surface at −65 °C.

γ	H_2SO_4, %			Refs.
	65	70	75	
γ_{HCl}	$1.5 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	$8 \cdot 10^{-5}$	[63]
γ_{ClONO_2}	—	$2.5 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	[63]
$\gamma_{N_2O_5}$	—	—	0.06	[64]

The second model of the heterogeneous decomposition of ozone in volcanic clouds is significantly more complex than the first, associated with the heterogeneous destruction of OH radicals. It contains more non-monitored parameters.

IV. Chemical processes in cloud drops

1. General characteristics of the aqueous component of the troposphere

In the set of objects and phenomena in the heterogeneous chemistry of the atmosphere, the chemistry of the processes in the liquid drop phase—in clouds, rain drops, mists, and smoke—is an important component which has been studied inadequately. Certain physical and physicochemical characteristics of these heterogeneous components of the troposphere are listed in Table 5.

On average, 54% of the Earth's firmanent is covered by clouds,[68] the thickness of the cloud layer amounting to tens and thousands of metres. Thus an appreciable proportion of the troposphere is constantly filled with clouds having a high moisture content. The air also moves constantly through the cloud layer at a velocity ranging from 0.1 to 10 m s^{-1} [69]. This flow of gases leads to a constant renewal of the gaseous environment of the cloud drops and hence to a virtual constancy of the gas composition outside and within the cloud layer. For these reasons, attention will be concentrated below on the cloud drops and the rain drops "associated" with them. The characteristic lifetime of the drops (from minutes for rain drops to a period of the order of 1 h for cloud drops) should be included among their main properties[70].

The dynamics of the formation and growth of cloud drops has been examined from different standpoints, with and without allowance for the dissolution in the drops of gaseous substances,

with variation of the size distribution for the condensation centres-nuclei, etc. These questions have been discussed fairly widely by Hill[71] and in the Proceedings of the Leningrad Conference on "Models of the Contamination of the Atmosphere and Their Employment" (1986). In the first seconds of drop formation, their size distribution ranging from 1 to 5 μm is characterised by a descending curve. In the 300th second of the life of the drops, a fairly narrow size distribution is attained with the most probable diameter $d \simeq 8$ μm. The average size of the cloud drops listed in Table 5 is a result of the averaging of the size distribution during the lifetime of the drop, which varies as a function of time.

Table 5. Physicochemical characteristics of the liquid drop constituents of atmospheric moisture.

Medium	Drop radius, μm	Moisture content, g m^{-3}	pH	Ionic strength	Refs.
Smoke	0.3—3	10^{-5}—10^{-4}	1—8	1	[65]
Mist	10	0.02—0.2	2—6	10^{-3}—10^{-2}	[66]
Cloud	10	0.1—3	3—6	10^{-3}—10^{-2}	[67]
Rain	200—2000	0.1—1	4—5	10^{-4}	[67]

An interesting effect of the growth of the drops with increase in their sulphuric acid content, first observed by Foster[72], has been thoroughly analysed[73]. On the whole, the physical picture of the formation and evolution of cloud drops has been studied in greater detail than the chemical processes in them.

Under natural conditions, chemical reactions take place in an open heterogeneous gas—liquid system; on the other hand, in the majority of laboratory studies, the reaction is investigated in solutions in the absence of transfer of substances from one phase to another.

The chemical process in cloud drops is accompanied by a change in the pH of the medium by 1—3 units and the corresponding change in the concentrations of the substances (including catalysts) in the ionised form; on the other hand, under laboratory conditions, one endeavours to discover the dependence of the rate of reactions on a particular parameter while keeping the remaining parameters constant.

The characteristic concentrations of stable substances in cloud drops (10^{-10}—10^{-5} M) are much lower than in the usual laboratory studies (10^{-4}—10^{-2} M). For such a large difference between the concentrations parameters, the extrapolation of the kinetic relations to the region of low concentrations is riddled with errors whose scale is difficult or impossible to estimate.

2. Kinetic analysis of processes leading to the formation of sulphate ions in cloud drops

The origin of the chemistry of clouds can be traced back to 1852 when Smith detected sulphate ions in the rain water of Manchester[74]. Subsequently ammonium ions and nitric acid were found in rain[75]. These are in fact the three main components of rain water whose concentration reaches 10^{-3} M for NH_4^+ and SO_4^{2-} and 10^{-4} M for NO_3^- in acid rain drops.

As industry developed and the analytical methods became more sensitive in the twentieth century, increasingly concentrations of the iron, manganese, lead, arsenic, mercury, etc. impurities began to be detected in rain deposits and in the snow cover. However, chemico-atmospheric studies during the last decade have shown that most of these substances are absent from cloud drops and are entrained by rain drops or are deposited on the snow cover from the layers of the troposphere near the earth. On the other hand, direct measurements have established the presence in cloud drops of iron (10^{-7}—10^{-4}) and manganese (10^{-8}—10^{-5} M) ions[76]. The anthropogenic origin of these ions is indicated by the approximately fivefold difference beween the contents of transition metal (predominantly iron) compounds in air over cities and over regions remote from cities. Hydrogen peroxide[77,78], formaldehyde, formic acid[79], methanesulphonic acid[80], and other substances have been detected in rain and cloud drops at variable concentrations, their amount being usually an order of magnitude smaller than that of sulphate, ammonium, and nitrate ions.

Analysis of the composition of rain drops does not require special aerological equipment. However, rain drop data are not particularly suitable as a quantitative characteristic of the composition of cloud drops. Despite the short time of their flight through the lower layers of the troposphere, they succeed in absorbing various gaseous substances and dust particles. Other processes also take place, as a result of which rain drops and cloud drops differ not only in composition but also in other fundamental properties (Table 5). The concentration of basic components in rain drops is usually lower than in cloud drops, although the opposite instances are also encountered. However, at a qualitative level, one can infer the "basic" chemical composition of cloud drops from the composition of the rain water.

Aerochemical studies have played and continue to play an important role in the understanding of the liquid-phase processes in the troposphere. Unfortunately, the present authors are unaware of any aerochemical study in which the dynamics of the increase in the NH_4^+, SO_4^{2-}, and H^+ concentrations in the drops of the cloud layer was traced and which was supplemented by measurements of the local gas-phase SO_2, H_2SO_4, HNO_3, NH_3, O_3, and H_2O_2 concentrations in this layer. Without these data, the question of the role of cloud drops—*concentrators* of the water-soluble oxidation products formed in the gas phase or *reactors* in which oxidation processes occur at a rate which is greater than, comparable to, or lower than in the gas phase—cannot be resolved with complete certainty. One should add that such measurements are by themselves not informative because the cloud is not an assembly of drops of "equal age"—drops are being constantly formed in the cloud. Formal kinetic analysis of the processes occurring in cloud drops is thus all the more important. The aim of such analysis is to establish the relations governing the formation of the oxidation products using the results of studies on oxidation processes in solutions. At the level of the mechanism of elementary reactions in the absence of adequate information about the rate constants, this problem reduces to determining the numerical rate constants for which oxidation products may be formed at the concentrations corresponding to the aerochemical data. An independent but important aspect of tropospheric calculations is comparison of the rates of the gas-phase and liquid-phase reactions involving the loss of free radicals, in the first place OH and HO_2. In particular, information about the Henry constants for substances A, i.e. $K_H = [A]/p_A$ mol litre^{-1} atm^{-1} (Table 6), is essential for the solution of such problems.

At pH $\leqslant$ 6 typical for cloud drops, the real solubility is characterised by the K_H of only the substances which do not enter into further reversible, chemical interactions with water. Among the substances listed in Table 6, this applies to only NO, CH_3OH, O_2, O_3, and H_2O_2. In order to calculate the equilibrium concentrations of other substances, it is necessary to take into account the proportions of the various forms in solution, so that the values of K_H characterise only the ratio $[A.H_2O]/p_A$. Thus the real solubility of CH_2O, which is in equilibrium with the free diol form $CH_2(OH)_2$, is reflected by the effective constant $K'_H = 6.3 \times 10^3$ mol litre atm^{-1}. Sulphur dioxide is present in solution in the forms $SO_2.H_2O$ (H_2SO_3), HSO_3^-, and SO_3^{2-} and the dissociation constants K_1, K_2, etc. have to be known in order to calculate the solubility. The characteristic time of attainment of acid-base equilibria of the substances in solutions is incomparably shorter than the rates of their possible chemical reactions.

Table 6. Henry constants (mol litre^{-1} atm^{-1}) for various substances present in the troposphere at 298 K.

Substance	K_H	Substance	K_H
SO_2	1.23	CH_3OH	220
NH_3	58	CH_2O	2
NO	$2\cdot10^{-3}$	HCOOH	83
NO_2	$7\cdot10^{-3}$	O_2	$1.6\cdot10^{-3}$
HNO_2	50	O_3	$1.1\cdot10^{-2}$
HNO_3	$2\cdot10^5$	H_2O_2	$1.6\cdot10^5$

The problem of the characteristic time of attainment of the gas–liquid equilibrium is more complex, since its solution requires that account be taken of the molecular diffusion of substances from the surface into the bulk of the drop, of the gas flux, of the drop diameter, etc. Analysis carried out in relation to SO_2 [81–83] showed that, at pH $\leqslant$ 6 and at the characteristic tropospheric SO_2 concentrations, the time of attainment of the gas–liquid equilibrium is negligible (< 1 s) compared with the lifetime of the drop. Thus, in the analysis of the reactions of substances in drops, one can use the equilibrium values of $[HSO_3^-]$ as well as $[O_2]$ and $[O_3]$, since the solubilities of the latter substances are low and the O_2 and O_3 fluxes are intense. Turning to substances with a high solubility (H_2SO_4, HNO_3, H_2O_2, NH_3), it is essential to estimate quantitatively their transfer to the drops at the specified concentrations of the substances in the gas and for the specified drop diameters. The equilibrium concentrations of the substances in the drops at different temperatures and at different concentrations of the substances in the gas phase are calculated from the equations[84]:

$$[SO_2]_0 = p_{SO_2}(1.23\exp\{3120\,t\})\{1 + (1.7\cdot10^{-2}\exp 2090t)/[H^+]\},$$

$$[NH_3]_0 = p_{NH_3}(58\exp\{4035\,t\})\{1 + 1.7\cdot10^{-5}\exp(-4325t)/[OH^-]\},$$

$$[O_3]_0 = p_{O_3}\times 1.1\times10^{-2}\exp\{2500t\},$$

$$[H_2O_2]_0 = p_{H_2O_2}\times 1.6\times10^5\exp\{6600t\},\ \text{etc.}$$

where $t = 1/T - 1/298$.

At heights of 1–5 km, the temperature differs from the terrestrial temperature by 6–30 K. At an average height of 1.5 km, which is close to the height of the maximum moisture content, the solubilities of the gases in the drops are assumed equal to the solubilities at 280 K. The concentrations of the test substances in the gas phase corresponding to this height[85] are listed in Table 7.

Table 7. Characteristic concentrations of SO_2 and of its potential oxidants in the background atmosphere at a height of 1.5 km at 280 K [85].

Substance X	$[X]_G$, cm^{-3}	p, atm	$[X]_{soln}$, M
SO_2	3.10^9 (Ref.86)	$1.1\cdot10^{-10}$	$7.8\cdot10^{-12}/[H^+]$
O_2	$4\cdot10^{18}$	0.15	$2.7\cdot10^{-4}$
O_3	$7\cdot10^{11}$	$2.6\cdot10^{-8}$	$5.2\cdot10^{-10}$
H_2O_2	$1.1\cdot10^{10}$	$4\cdot10^{-10}$	$3\cdot10^{-4}$

The quoted concentration of H_2O_2 in solution is a maximum, since all the concentrations of the substances belonging to the odd hydrogen family were calculated on the assumption of a high intensity of illumination and a high humidity[85]. Under the conditions of the real background atmosphere, the H_2O_2, HO_2, and OH concentrations can be several times smaller. Taking into account this correction, one can assume that the value of $[H_2O_2]_{soln}$ agrees with the experimental concentration of hydrogen peroxide in the rain drops[78,79].

The problem of the nature of the drops at pH→3, which fall in the form of acid rain and have negative ecological consequences for soil and water catchment areas, is important in the chemistry of the cloud layer. Clouds consisting of such drops are formed in the presence of an SO_2 content many times greater than its content in the background atmosphere.

We are unaware of attempts at a chemical interpretation of the mechanism of the formation of acid cloud drops. As regards the background atmosphere, the potential possibility of the occurrence in the latter of processes involving the oxidation of sulphite ions by oxygen, ozone, and hydrogen peroxide and of the catalytic acceleration of the oxidation of sulphide ions under the influence of iron and manganese ions has been considered.

During the lifetime of a cloud drop in the background atmosphere ($\sim10^3$ s), approximately 10^{-4} M sulphate ions accumulate together with a comparable amount of ammonium ions and the characteristic pH is 4.5–4.7.[87] At pH 3–6, the dominant form in which SO_2 is present in solution is HSO_3^-, since $K_1 = 1.7 \times 10^{-2}$ and $K_2 = 6 \times 10^{-8}$ M.

$$[SO_2]_0 = p_{SO_2}K_H\{1 + K_1/[H^+] + K_1K_2/[H^+]^2\}\ \text{M}.$$

The maximum HSO_3^- concentration at pH 6 is 8×10^{-6} M; as sulphate is formed and the acidity increases to pH 4.7, the maximum HSO_3^- concentration diminishes by a factor of approximately 20. The transition from HSO_3^- to SO_4^{2-} as $\overline{[HSO_3^-]} \simeq 2 \times 10^{-6}$ M takes place at an average rate $\overline{W} \simeq 10^{-4}/10^{-3} = 10^{-7}$ mol litre^{-1} s^{-1}.

We shall compare the above value of $\overline{W}$ with the available rates of oxidation of sulphite ions by oxygen, ozone, and hydrogen peroxide. Their oxidation by oxygen and ozone and an analysis of all the previous studies has been carried out in greatest detail by Larson et al.[87] In the pH range 4–12, the rate of oxidation is described by the expression

$$\frac{d[SO_4^{2-}]}{dt} = \{4.8\cdot10^{-3} + 8.9[H^+]^{0.5} + 3.9\cdot10^{-12}[H^+]^{-1}p_{O_2}\}\cdot\frac{6\cdot10^{-8}[HSO_3^-]}{[H^+]}$$

for O_2 and by

$$\frac{d[SO_4^{2-}]}{dt} = 4.4\times10^4[O_3][HSO_3^-][H^+]^{0.1} \text{ mol litre}^{-1}\text{ s}^{-1}.$$

for the oxidation by ozone.

At concentrations characteristic of cloud drops, these rates are of the order of 10^{-9} and 10^{-11} mol litre^{-1} s^{-1} respectively.

The catalytic oxidation of sulphite in the presence of iron ions at the real HSO_3^- and Fe^{3+} concentrations in the pH range 4–12 was investigated using radiochemical monitoring[88]. At pH 4.9, we have

$$-\frac{d[HSO_3^-]}{dt} = 10^2[Fe^{3+}]_0[HSO_3^-] \text{ mol litre}^{-1}\text{ s}^{-1}.$$

According to the data of Brimblecome and Spedding[88], the pH dependence of the rate constant has a maximum at pH 6. Using the maximum value ($\sim2.5\times10^2$) and the HSO_3^- concentration corresponding to pH 6, it is possible to estimate the minimum concentration of iron ions at which $\overline{W} = 10^{-7}$ mol litre^{-1} s^{-1} as 5×10^{-5} M. This value lies in the range of the limiting concentrations of Fe^{3+} in cloud drops[76], which, however, corresponds not to the background atmosphere but to a highly polluted atmosphere.

Unfortunately such accurate studies on the catalysis of oxidation by manganese ions at concentrations close to those obtained in nature have not been found in the literature. It has been noted that Mn^{2+} ions are more effective as a catalyst of the oxidation of sulphite ions than iron ions[89]. On the other hand, quantitative studies have been carried out in the ranges of $[Mn^{2+}]$ and $[HSO_3^-]$ which differ from the real concentration ranges. Thus the following expression has been put forward[90]:

$$-\frac{d[HSO_3^-]}{dt} = 16[Mn^{2+}]^2.$$

It was obtained for $[Mn^{2+}] = (0.2-5)\times10^{-3}$ M and $[HSO_3^-] = 10^{-3}$ M.

In a later study[91] the equation

$$W = 4.7[H^+][Mn^{2+}]^2,$$

was proposed for the ranges pH 0–3, $[Mn^{2+}] = 10^{-5}-10^{-3}$ M, and $[HSO_3^-] = 10^{-4}-10^{-3}$ M. The equation

$$W = 25[H^+][Mn^{2+}][HSO_3^-],$$

was put forward for the same pH range and $[Mn^{2+}]$ and $[HSO_3^-] \leqslant 10^{-6}$ M.

When this relation is extrapolated to pH 6, it is found that, in order to attain $W = 10^{-7}$, it is sufficient to have a concentration $[Mn^{2+}] \simeq 10^{-9}$ M.

However, in the presence of ferric ions the effective rate constant, which in the given instance is $25[H^+]^{-1}$, by no means varies linearly with $[H^+]^{-1}$ in the region with pH > 4 (this is apparently associated with the hydrolysis of metal ions). Whatever the true state of affairs, before catalysis by Mn^{2+} ions is subjected to a study similar to that carried out for ferric ions[88] the problem of the possible accumulation of sulphates in drops of the background atmosphere as a result of the catalytic oxidation of sulphite in the presence of manganese ions will remain open.

The interaction of sulphite ions with H_2O_2 constitutes the basis of the analytical method for the determination of SO_2, H_2SO_3, and HSO_3^-. The process is autocatalytic. The dependence of the rate of reaction on the reactant concentrations in the pH range 4–8 assumes the following form according to Hoffman and Edwards[92]:

$$-\frac{d[SO_2]_0}{dt} = [H_2O_2][SO_2]_0\{[H^+]/[H^+] + 6\cdot10^{-8}\}(5.8\cdot10^7[H^+] + 7.2\cdot10^2[HA])^{\ddagger}$$

At pH 6 and the corresponding H_2O_2 and HSO_3^- concentrations (see Table 7), the rate of reaction $W = 1.3\times10^{-7}$ mol litre^{-1} s^{-1}, which agrees with the value of $\overline{W}$.

The process considered differs from all those examined previously by the fact that its rate under the conditions of cloud drops does not diminish with decrease in the HSO_3^- concentration, since the fall in the equilibrium value of $[HSO_3^-]$ induces an increase in $[H^+]$ in strict agreement[92] with the stoichiometry of the reaction

$$2HSO_3^- + H_2O_2 \rightarrow + 2SO_4^{2-} + 2H^+.$$

The approximate kinetic analysis carried out leads to the conclusion that the most probable oxidation process in the cloud drops of the background atmosphere is the interaction of HSO_3^- with H_2O_2. In recent years, a similar view has been expressed frequently in a qualitative form, but attention has not been turned to the catalytic nature of this reaction. In mathematical models (see, for example, Hill et al.[93]), the rate of formation of sulphate ions was described by the equation

$$\frac{d[SO_4^{2-}]}{dt} = k_{H_2O_2}[H_2O_2][HSO_3^-] + k_{O_3}[O_3][HSO_3^-],$$

i.e. without taking into account the role of hydrogen ions as the catalyst. Nor can one rule out the possibility of the catalytic oxidation of HSO_3^- with participation of Mn^{2+} ions, although the characteristics of this process at the concentrations attained in cloud drops are not available.

3. Gas–liquid models of the formation of acid drops in the background and contaminated atmospheres

In a contaminated atmosphere, the average rate of oxidation of sulphite ions should be ten and more times higher than in the background atmosphere in order to ensure the formation of 10^{-3} M SO_4^{2-} after approximately 10^3 s. At first sight, the formation of sulphate can be explained by the autocatalytic oxidation of sulphite by hydrogen peroxide, by substituting in the corresponding equation the values of p_{SO_2} which exceed by a factor of 10 or more the values

‡ A misprint occurred in the communication of Hoffman and Edwards[92]: instead of 5.8×10^7, 5.8×10^1 is printed in the text. It is easy to demonstrate that the latter figure is erroneous by carrying out an approximate calculation of the characteristic reaction time at pH 4.5, which, was stated by the authors[92] becomes less than 2.5 ms and measurements by the stopped flow method become impossible.

of p_{SO_2} in the background atmosphere. However, in a contaminated atmosphere not only p_{SO_2} but also p_{CO} is higher than in the background atmosphere. On the other hand, the reaction of CO with OH constitutes one of the most important pathways leading to the loss of OH. An increase in p_{CO} entails a decrease in the stationary OH, HO_2, and H_2O_2 concentrations. On the other hand, when the H_2O_2 concentration diminishes by an order of magnitude, the possibility of such explanation evidently disappears. Attention should be drawn also to the fact that the bulk of sulphate ions (from 10^{-4} to 10^{-3} M) should be formed in the pH range from 4 to 3, i.e. for $[HSO_3^-]_0$ lower by a factor of 10 than in the background atmosphere. All these factors preclude the justification of a chemical mechanism of the formation of drops in acid clouds on the basis of the reactions considered. One cannot rule out in any way the possibility that in this case a physical mechanism of the absorption of H_2SO_4 by drops, and not a chemical mechanism, acquires decisive importance. The distribution of H_2SO_4 and HNO_3 between the gas and liquid phases is displaced towards the latter so much that at their typical concentrations in acid drops (10^{-3} and 10^{-4} M) and in the gas (10^{-11} and 10^{-10} atm [86]) the acid concentration can be regarded as equal to the product of the lifetime of the drops and the flux of the acid from the gas to the drops. For $[H_2SO_4]_G \simeq 2 \times 10^8$ cm^{-3} and for a drop diameter of 10 μm, the total H_2SO_4 flux is $\sim 10^5$ mol^{-1} s^{-1}.

Thus for an accommodation coefficient $\gamma \simeq 10^{-1}$, the accumulation of sulphate ions in drops can be explained by the absorption of H_2SO_4 from the gas phase.

Assuming that $\gamma \simeq 10^{-2}$ for H_2SO_4, as is usually done in the literature in the absence of measured values, we shall consider all the possibilities of the chemical route to the accumulation of sulphuric acid. The most important factor is that the flux of HO_2 and OH from the gas to the drops can significantly exceed the rate of formation of these radicals in the drops as a result of the photolysis of O_3 and H_2O_2 if the values of γ for the radicals are assumed to be 10^{-2} [94–96].

The first chemical-mathematical model of the oxidation processes in the drops of sea clouds taking into account the OH and HO_2 fluxes[97] included the following reactions (Scheme 2);

Scheme 2

(1) $\dot{O}H + HSO_3^- \rightarrow \ldots \rightarrow SO_4^{2-} + 2H^+$,
(2) $\dot{O}H + HSO_3^- \rightarrow H_2O + \dot{SO}_3^-$,
(3) $OH + CH_2(OH)_2 \rightarrow HCOOH + \dot{H}O_2$,
(4) $\dot{O}H + HCOOH \rightarrow CO_2 + H_2O + \dot{H}O_2$,
(5) $OH + H_2O_2 \rightarrow H_2O + HO_2$ and the equilibria $H\dot{O}_2 \rightleftarrows H^+ + O_2^-$ and $\dot{C}l + Cl^- \rightleftarrows Cl_2^-$,
(6) $\dot{H}O_2 + O_3 \rightarrow 2O_2 + \dot{O}H$,
(7) $\dot{SO}_4^- + Cl^- \rightarrow SO_4^{2-} + \dot{C}l$,
(8) $\dot{C}l + \dot{O}_2^- \rightarrow Cl^- + O_2$,
(9) $\dot{H}O_2 + \dot{O}_2^- \rightarrow HO_2^- + O_2$.

On the assumption that $\gamma \simeq 10^{-2}$, the $H\dot{O}_2$ and $\dot{O}H$ fluxes were assumed to be 9×10^{-9} and 1.4×10^{-9} mol litre^{-1} s^{-1} respectively, while $[H_2O_2] = 5 \times 10^{-5}$ M.

Within the framework of this model it proved possible to obtain the value $[SO_4^{2-}] = 8 \times 10^{-6}$ M, which is close to the value characteristic of sea clouds. The study quoted above[97] is particularly important also, because the rate constants for the elementary radical reactions were used in it for the first time in considering the oxidation processes in cloud drops. The reason why the ratio of the $H\dot{O}_2$ and $\dot{O}H$ fluxes in the above studies[97] is approximately 7 whereas in the tropospheric zone $[H\dot{O}_2]_G/[\dot{O}H]_G > 10^2$ and the molecular-kinetic characteristics of $H\dot{O}_2$ and $\dot{O}H$ do not differ all that much remains obscure.

In subsequent years it proved possible to determine experimentally the accommodation coefficients of all three tropospheric substances. These values are 0.11 for SO_2 [98], 0.18 for H_2O_2 [98], and 0.27 for $H\dot{O}_2$ [36] The last figure is particularly important, because it increases the calculated $H\dot{O}_2$ flux into the drops by a factor of approximately 30. In this connection, we attempted the mathematical modelling of the sulphite oxidation process in cloud drops via a radical mechanism. It is noteworthy that the true mechanism of this process—one of the first examples of radical chain reactions in solutions[99]—has not been ultimately elucidated to this day[100]. It is the general view that microadmixtures of variable-valence metal ions participate in the initiation stage. The radical-chain mechanism put forward by Backstrom[101] can be represented in the form (Scheme 3)

Scheme 3

$$i \rightarrow H\dot{S}O_3 (SO_3^{\cdot-})$$
(1) $SO_3^- + O_2 \rightarrow SO_5^{\cdot-}$
(2) $SO_5^{\cdot-} + SO_3^{2-} \rightarrow SO_5^{2-} + SO_3^{\cdot-}$ } ν
(3) $SO_5^{2-} + SO_3^{2-} \rightarrow 2SO_4^{2-}$
(0) $SO_5^- + SO_3^{\cdot-} \rightarrow O_2 + S_2O_6^{2-}$.

The reaction is sensitive to copper ion microimpurities present in solution at concentration of the order of 10^{-12} M (in an alkaline medium)[101]. When carefully purified reagents and deionised triply distilled water are used, initiation is effective by iron ions at concentrations of the order of 10^{-8} M [88]. The unsatisfactory reproducibility of the experiments and the high sensitivity of the rates reactions to small amounts of added alcohols and other inhibitors indicate a considerable chain length. As kinetic data accumulate, indicating that at pH < 6 the rate of reaction is independent of p_{O_2} [87], the chain termination reaction has come to be represented in the form

$$SO_5^- + SO_5^- \rightarrow S_2O_6^{2-} + 2O_2.$$

The ideas about the chain propagation put forward by Hayon et al.[102] are based on the study of the reactions of sulphur–oxygen radical-ions ranging from SO_2^- to SO_5^-. The authors[102] concluded that, after the formation of the sulphate ion and the SO_4^- radical-ion, the chain propagation in reaction (2) takes place as a result of the following process:

$$SO_4^{\cdot-} + HSO_3^- \rightarrow SO_4^{2-} + H^+ + SO_3^-.$$

The legitimacy of including in the process mechanism of reactions involving SO_4^- has been confirmed by measurements of the rate constants for the reactions of SO_5^- and SO_4^- with alcohol[102]. The interaction of alcohol with SO_4^-, and not with SO_5^-, is more effective.

Comparison of the values of pK for H_2O and $H\dot{O}$ and also for H_2O_2 and $H\dot{O}_2$ makes it possible to assume with a high degree of probability that in the range 3 < pH < 6 the dominant species are SO_3^- (and not $H\dot{S}O_3$) and $H\dot{S}O_5$ (and not SO_5^-) ($K_2 \simeq 10^{-10}$ mol litre^{-1} for H_2SO_5). Taking into account all the considerations

described, the mechanism of the oxidation of HSO_3^- can be represented by Scheme 4:

Scheme 4

$$i \rightarrow SO_3^{\cdot-}$$

(1) $SO_3^{\cdot-} + O_2 \xrightarrow{H} H\dot{S}O_5$,

(2) $H\dot{S}O_5 + HSO_3^- \rightarrow 2H^+ + SO_4^{2-} + SO_4^{\cdot-}$,

(3) $SO_4^{\cdot-} + HSO_3^- \rightarrow SO_4^{2-} + H^+ + SO_3^{\cdot-}$,

(0) $H\dot{S}O_5 + H\dot{S}O_5 \rightarrow 2O_2 + 2H^+ + S_2O_6^{2-}$.

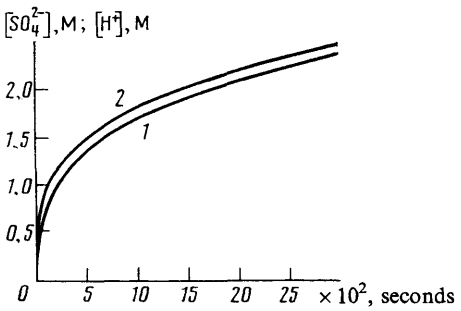


Figure 4. Kinetics of the accumulation of SO_4^{2-} (curve *1*) and H^+ (curve *2*) ions in water drops (calculated data).

We may note that the nature of the initiation reactions still remains obscure. This can be easily demonstrated by comparing the mechanism just presented or the one considered previously, without the participation of $SO_4^{\cdot-}$, with the experimental expression for the rate of reaction:

$$W = (k + k_2[H^+]^{0.5})[HSO_3^-],$$

which follows from studies analysed by Larson et al.[87] Taking into account the large chain length for the oxidation of sulphite, we obtain

$$W_i = k_0 W^2/k_2^2[HSO_3^-]^2 \quad \text{or} \quad W = [HSO_3^-]\, k_2^{0.5} \sqrt{W_i}/k_0^{0.5},$$

i.e. W_1 is independent of both $[O_2]$ and $[HSO_3^-]$. The question concerning the nature of initiation loses its importance in the presence of an external source of free radicals. In our model, as in the study of Chameides and Kiang,[97] the initiation reaction is that between HSO_3^- and the $\dot{O}H$ radicals entering the drops from the gas phase. Since the $H\dot{O}_2$ concentration and hence the flux of $H\dot{O}_2$ into the drop are approximately 10^2 higher than the flux of $\dot{O}H$, we included in the model the following chain termination reaction

$$H\dot{S}O_5 + H\dot{O}_2 \rightarrow HSO_5^- + H^+ + O_2,$$

as well as the reaction of HSO_3^- with H_2O_2 considered above. Apart from the $\dot{O}H$ and $H\dot{O}_2$ fluxes, account was also taken of the fluxes of H_2O_2 and NH_3 into the drop from the gas phase.

$\gamma \simeq 0.1$ was adopted for OH. The fluxes of H_2O_2 both into the drop and from the drop were taken into account. Analysis based on Smoluchowski's formula showed that an equilibrium distribution of H_2O_2 between the gas and liquid phases is established after 10 s (for drops with $d = 10$ μm). The NH_3 flux was regarded as a variable parameter normalised by the condition that in an acid drop $[NH_4^+]$ should be close to $[SO_4^{2-}]$. The values of $[H\dot{O}_2]_G$, $[\dot{O}H]_G$, and $[H_2O_2]_G$ were assumed to be 10 times smaller than in the background atmosphere. Thus the scheme includes the following fluxes of species from the gas into the drop:

$$\dot{O}H \rightarrow 10^{-8}\ HO_2 \rightarrow 5\times10^{-7}\ NH_3 \rightarrow 10^{-5}\ H_2O_2 \rightarrow 10^{-5}\ \text{mol litre}^{-1}\ \text{s}^{-1},$$

and the following elementary reactions (Scheme 5)

Scheme 5

(1) $\dot{O}H + HSO_3^- \rightarrow H_2O + SO_3^{\cdot-}$,	$k_1 = 9.5\cdot10^9$ litre mol^{-1} s^{-1}	(Ref.103)
(2) $SO_3^{\cdot-} + O_2 \xrightarrow{H^+} H\dot{S}O_5$,	$k_2 = 3\cdot10^9$	» (Ref.102)
(3) $H\dot{S}O_5 + HSO_3^- \rightarrow 2H^+ + SO_4^{2-} + SO_4^{\cdot-}$,	$k_3 = 5\cdot10^9$	» —
(4) $SO_4^{\cdot-} + HSO_3^- \rightarrow SO_4^{2-} + H^+ + SO_3^{\cdot-}$,	$k_4 = 1.5\cdot10^9$	» (Ref.102)
(5) $H\dot{S}O_5 + H\dot{S}O_5 \rightarrow 2H^+ + S_2O_6^{2-}$,	$k_5 = 1.0\cdot10^7$	» (Ref.102)
(6) $H\dot{S}O_5 + H\dot{O}_2 \rightarrow O_2 + H^+ + HSO_5^-$,	$k_6 = 10^8$	» —
(7) $\dot{O}H + H_2O_2 \rightarrow H_2O + H\dot{O}_2$,	$k_7 = 4.5\cdot10^7$	» (Ref.103)
(8) $\dot{O}H + H\dot{O}_2 \rightarrow H_2O + O_2$,	$k_8 = 7.0\cdot10^9$	» (Ref.103)
(9) $H\dot{O}_2 + H\dot{O}_2 \rightarrow H_2O_2 + O_2$,	$k_9 = 8.1\cdot10^5$	» (Ref.103)
(10) $H\dot{O}_2 + O_2^- \rightarrow HO_2^- + O_2$,	$k_{10} = 9.5\cdot10^7$	» (Ref.103)
(11) $H_2O_2 + H^+ + HSO_3^- \rightarrow H_2O + 2H^+ + SO_4^{2-}$,	$k_{11} = 5.8\cdot10^7$	» (Ref.92)

Apart from the values of k_i and $pK_{HO_2} = 4.88$ known from the literature[104], the approximate values of k_3 and k_6 were used in the calculation. In the estimation of k_3, it was assumed that the $H\dot{S}O_5$ radicals and not $SO_3^{\cdot-}$ participate in the chain termination reaction, i.e. that $[H\dot{S}O_5]\ [SO_3^{\cdot-}]$, while the rates of the chain termination reactions (2) and (3) (Scheme 5) are equal. The value of k_6 adopted may be too high, but the result of the calculation is relatively insensitive to changes in this rate constant by even one or several orders of magnitude. The principal chain termination reaction is stage (5) of Scheme 5. We did not take into account the possible interaction of HSO_5^- with HSO_3^-, which was regarded in Backstrom's mechanism[101] as the principal route to the formation of SO_4^{2-}. In the mechanism presented, the contribution of this reaction to the overall rate of formation of sulphate ions is much smaller than the contribution of reactions (3) and (4) of Scheme 5. We assume that $[SO_2]_G$ is 10 times greater while $[H\dot{O}_2]_G$, $[\dot{O}H]_G$, and $[H_2O_2]_G$ are 10 times smaller than in the background atmosphere. We note particularly that, if we neglected the NH_3 flux, then not only would we be unable to account for the presence of NH_4^+ in the drops but an appreciable decrease in the final value of $[SO_4^{2-}]$ would have resulted. The results of the calculation are illustrated in Fig. 4. Without over-estimating the importance of this calculation, we may note that it allows the possibility of a chemical explanation of the formation of acid drops at pH→3. The choice between the chemical and absorption mechanisms can be made after determining the accommodation coefficient of H_2SO_4.

It is noteworthy that, as shown by the calculation, a further increase in $[SO_2]_G$ does not lead to appreciable changes in $[SO_4^{2-}]$ and $[H^+]$, i.e. an increase in the amount of SO_2 waste ejected, which increases the volume of precipitated acid rain, should not entail an increase in its acidity. The results of the mathematical modelling of drop processes in contaminated and background atmospheres resorting to experimental data will be described in greater detail in a separate publication by Purmal' and Travin[105], whom the authors thank.

In conclusion, we may note that the rapid reactions of $\dot{O}H$ with HSO_3^- and of $H\dot{O}_2$ with O_2^- in drops necessitate taking into account the loss of OH_G and $H\dot{O}_{2G}$ to the drop when calculating their tropospheric concentrations in the cloud zone. Our estimates have shown that the losses cease to be negligible when the coefficient of the volume saturation of the gas phase by drops is 10^{-6} and less.

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