CHEMICAL PROCESSES IN THE EARTH'S ATMOSPHERE DISTURBED BY VOLCANIC EJECTION

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The dynamics of formation of a stratospheric aerosol is traced on the basis of a one-dimensional photochemical model of a horizontally homogeneous atmosphere allowing for only vertical transfer of impurities. Calculations show that below 30 km sulfur is mainly in the form of CSO, whereas at higher altitudes it is in the form of sulfuric acid.

Volcanic eruptions cause disturbances in chemical, optical, and thermal structures of the surrounding atmosphere. An analysis shows that gaseous volcanic ejections consist mainly of water vapor and nitrogen dioxide, and also of CO, SO_2, H_2S, H_2, NH_3, CL, F, N_2, CS_2, CSO, and CH_2 [1]. Of special interest are sulfur compounds because a sulfuric acid stratospheric aerosol layer (SAL) consisting of crystals and droplets of sulfuric acid (an aqueous solution with an acid concentration of about 70-80%) is formed from them. Formation of sulfuric acid vapor in the stratosphere occurs mainly in the oxidation of sulfurous gas (SO_2). Our calculations and the estimates of [2] indicate that only about 4% of the SO_2 ejected into the atmophere enters the stratosphere, which amounts to about $3 \cdot 10^5$ tons per year. This is caused by the high photodissociation rate of SO_2 (Fig. 1).

Based on estimates of the rate constants of possible reactions of SO_2 oxidation (interaction with oxygen, ozone $\tau = 10^{10}$ sec, a hydroxyl group $\tau = 10^6$ sec, etc.) the leading role is assigned to the hydroxyl group

$$SO_2 + OH + M \rightarrow HSO_3 \quad k_{t11} = 5.0 \cdot 10^{-31} (T/300)^{-3.3} \text{ cm}^6/\text{sec},$$

$$H_2S + OH \rightarrow HS + H_2O \quad k_{b61} = 5.9 \cdot 10^{-12} \text{ cm}^3/\text{sec},$$

$$CS_2 + OH \rightarrow HS + CO_2,$$

$$CSO + OH \rightarrow SO + CO \quad k_{b62} = 1.1 \cdot 10^{-13} \exp(-1200/T) \text{ cm}^3/\text{sec},$$

$$HS + O_3 \rightarrow HSO + O_2 \quad k_{b63} = 9.7 \cdot 10^{-12} \exp(-280/T) \text{ cm}^3/\text{sec}.$$

The following chain of reactions is assumed to be a further path:

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \quad k_{b50} = 1.3 \cdot 10^{-12} \exp(-330/T) \text{ cm}^3/\text{sec},$$

$$SO_3 + H_2O \rightarrow H_2SO_4.$$

In the period of low volcanic activity sulfurous gas enters the atmosphere mainly due to photodissociation in the stratosphere of carbonyl sulfide (CSO) coming from the troposphere. It is virtually inert in the troposphere where its lifetime is about a year. Therefore, the mass fraction of CSO in the atmosphere changes slightly with altitude down to lower layers of the stratosphere where it is estimated at 1 mg/m^3. Active photodissociation of CSO under the effect of ultraviolet radiation begins in the stratosphere:

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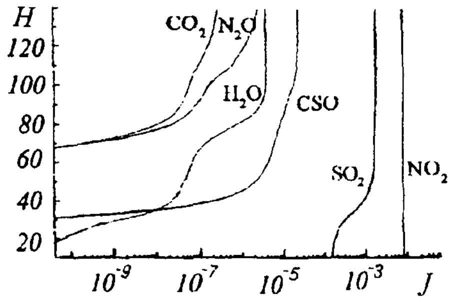


Fig. 1. Photodissociation rate for molecules of CO_2, H_2O, NO_2, N_2O, SO_2, and CSO. H, km; J, sec^{-1}.

$$CSO + h\nu \rightarrow S + CO\,,$$

$$CSO + O \rightarrow SO + CO \quad k_{b52} = 2.1 \cdot 10^{-11} \exp(-2200/T) \ cm^3/sec\,.$$

This results in a drop in the mass fraction of CSO with altitude and in the arrival of sulfurous gas

$$S + O_2 \rightarrow SO + O \quad k_{b53} = 2.3 \cdot 10^{-12} \ cm^3/sec\,,$$

$$SO + O_2 \rightarrow SO_2 + O \quad k_{b54} = 2.6 \cdot 10^{-13} \exp(-2400/T) \ cm^3/sec\,,$$

$$SO + O_3 \rightarrow SO_2 + O_2 \quad k_{b55} = 3.6 \cdot 10^{-12} \exp(-1100/T) \ cm^3/sec\,,$$

$$SO + NO_2 \rightarrow SO_2 + NO \quad k_{b56} = 1.4 \cdot 10^{-11} \ cm^3/sec\,,$$

$$SO_2 + h\nu \rightarrow SO + O\,.$$

To calculate the vertical distribution of small atmospheric components, we used a one-dimensional photochemical model in which photodissociation of molecular oxygen is the main source of odd oxygen

$$O_2 + h\nu\,(135 < \lambda < 175 \ nm) \rightarrow O(^1D) + O(^3P) \quad \Phi = 1\,,$$

$$O_2 + h\nu\,(175 < \lambda < 250 \ nm) \rightarrow O(^3P) + O(^3P) \quad \Phi = 1\,.$$

In the lower stratosphere where, as is seen from Figs. 2 and 3, the rate of photodissociation of molecular oxygen decreases sharply, the photodissociation of ozone, leading to the formation of oxygen either in the ground state

$$O_3 + h\nu\,(\lambda > 300 \ nm) \rightarrow O_2(^3\Sigma_g^-) + O(^3P) \quad \Phi = 1\,,$$

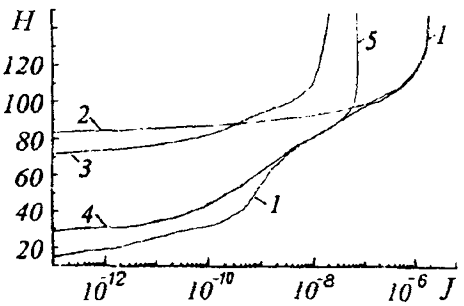
or in the first excited state $O(^1D)$

$$O_3 + h\nu\,(266 < \lambda < 320 \ nm) \rightarrow O_2(^1\Delta_g) + O(^1D) \quad \Phi = 0.9\,,$$

becomes the main source of oxygen atoms. The oxygen atoms in the ground state interact with molecular oxygen, forming ozone

$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad k_{12} = 6.0 \cdot 10^{-34}\,(T/300)^{-2.3} \ cm^6/sec\,.$$

They can also recombine directly in a three-body reaction



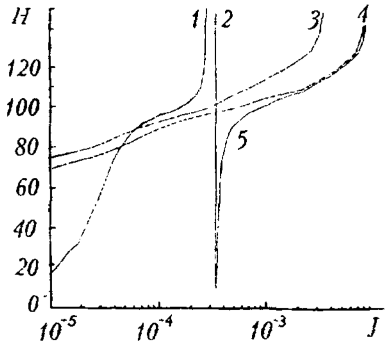


Fig. 2. Photodissociation rate of molecular oxygen: the total rate (1), in the Schumann–Runge continuum (2), in Lyman-alpha (3), in the Schumann–Runge bands (4), in the Herzberg continuum (5).

Fig. 3. Photodissociation rate of molecular ozone: in the Huggins band (1), in the Chappus bands (2) in the region of 200–266 nm (3), in the Hurtley band (4), the total rate (5).

$$O + O + M \rightarrow O_2 + M + 498 \text{ kJ} \quad k_{t1} = 3.6 \cdot 10^{-31} T^{-1} \exp(-170/T) \text{ cm}^6/\text{sec}$$

or with ozone

$$O + O_3 \rightarrow 2O_2 + 392 \text{ kJ} \quad k_{b1} = 1.1 \cdot 10^{-11} \exp(-2150/T) \text{ cm}^3/\text{sec.},$$

The excited oxygen atoms are usually deactivated in collision with the molecules of nitrogen, oxygen, and ozone

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2 \quad k_{q8} = 1.8 \cdot 10^{-11} \exp(150/T) \text{ cm}^3/\text{sec},$$

$$O(^1D) + O_2 \rightarrow O(^3P) + O_2 \quad k_{q9} = 3.2 \cdot 10^{-11} \exp(70/T) \text{ cm}^3/\text{sec},$$

$$O(^1D) + O_3 \rightarrow O_2 + 2O \quad k_{q10} = 2.5 \cdot 10^{-10} \text{ cm}^3/\text{sec},$$

$$O(^1D) + O_3 \rightarrow O_2(^1\Delta_g) + O_2 \quad k_{q11} = 2.5 \cdot 10^{-10} \text{ cm}^3/\text{sec}.$$

Excited molecular oxygen can be deactivated in collisions or relax radiatively

$$O_2(^1\Delta_g) + O_2(^3\Sigma_g^-) \rightarrow 2O_2(^3\Sigma_g^-) \quad k_{q3} = 2.4 \cdot 10^{-18} \text{ cm}^3/\text{sec},$$

$$O_2(^1\Delta_g) + N_2 \rightarrow O_2(^3\Sigma_g^-) + N_2 \quad k_{q4} = 1.4 \cdot 10^{-19} \text{ cm}^3/\text{sec},$$

$$O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g^-) + h\nu \quad (\lambda = 1.27 \text{ nm}) \quad k_{rr1} = 2.58 \cdot 10^{-4} \text{ sec}^{-1},$$

$$O(^1D) + O_3 \rightarrow O_2(^1\Delta_g) + O_2 \quad k_{q11} = 2.5 \cdot 10^{-10} \text{ cm}^3/\text{sec}.$$

Low-temperature oxidation of carbon oxide and methane ($T < 50^\circ$C) in the presence of catalysts – hydroxyl and nitrogen oxides – facilitates the formation of ozone

$$CO + OH \rightarrow H + CO_2 \quad k_{b23} = 5.1 \cdot 10^{-13} \exp(-300/T) \text{ cm}^3/\text{sec},$$

$$HO_2 + NO \rightarrow NO_2 + OH + 38 \text{ kJ} \quad k_{b22} = 3.7 \cdot 10^{-12} \exp(240/T) \text{ cm}^3/\text{sec}.$$

Methane is formed at the earth's level in the anaerobic decomposition of organic material at a rate of about $3 \cdot 10^{11}$ cm^{-2}/sec^{-1} [3]. This rate is sufficient to explain the main portion of CO to altitudes of 35–40 km. In the first stage methane interacts with hydroxyl, forming a highly active radical methyl

$$CH_4 + OH \rightarrow CH_3 + H_2O + 63 \text{ kJ} \quad k_{b10} = 5.5 \cdot 10^{-12} \exp(-1900/T) \text{ cm}^3/\text{sec}$$

or with excited oxygen $O(^1D)$

$$O(^1D) + CH_4 \rightarrow OH + CH_3 \quad k_{q18} \approx 3 \cdot 10^{-10} \text{ cm}^3/\text{sec},$$

$$O(^1D) + CH_4 \rightarrow CH_2O + H_2 \quad k_{q18} \approx 1.4 \cdot 10^{-11} \text{ cm}^3/\text{sec}.$$

Methyl reacts quickly with molecular oxygen, forming the methyl-peroxide radical

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \quad k_{t10} = 8.0 \cdot 10^{-31} (T/300)^{-3.3} \text{ cm}^6/\text{sec},$$

which is capable of oxidizing nitrogen oxide to dioxide

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \quad k_{b39} = 4.2 \cdot 10^{-12} \exp(180/T) \text{ cm}^3/\text{sec},$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \quad k_{b43} = 3.3 \cdot 10^{-13} \exp(800/T) \text{ cm}^3/\text{sec},$$

$$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O \quad k_{b44} = 1.5 \cdot 10^{-11} \text{ cm}^3/\text{sec}.$$

In interaction with molecular oxygen, methoxyl (CH_3O) forms formaldehyde and the perhydroxyl radical, which is reduced to hydroxyl

$$CH_3O + O_2 \rightarrow HO_2 + H_2CO \quad k_{b47} = 3.9 \cdot 10^{-14} \exp(-900/T) \text{ cm}^3/\text{sec},$$

$$HO_2 + NO \rightarrow NO_2 + OH + 38 \text{ kJ} \quad k_{b22} = 3.7 \cdot 10^{-12} \exp(240/T) \text{ cm}^3/\text{sec}.$$

Then formaldehyde oxidizes to CO_2 and H_2O or decomposes, as a result of photodissociation, forming hydrogen and carbon oxide

$$CO_2 + h\nu\ (\lambda < 160 \text{ nm}) \rightarrow CO + O(^1D),$$

$$H_2CO + OH \rightarrow HCO + H_2O \quad k_{b45} = 1.5 \cdot 10^{-11} \text{ cm}^3/\text{sec},$$

$$H_2CO + O \rightarrow OH + HCO \quad k_{b46} = 1.5 \cdot 10^{-13} \text{ cm}^3/\text{sec},$$

$$HCO + O_2 \rightarrow CO + HO_2 \quad k_{b48} = 3.5 \cdot 10^{-12} \exp(140/T) \text{ cm}^3/\text{sec},$$

$$HCO + OH \rightarrow H_2O + CO \quad k_{b49} > 1.5 \cdot 10^{-11} \text{ cm}^3/\text{sec},$$

$$H_2CO + h\nu \rightarrow H_2 + CO,$$

$$HCO + h\nu \rightarrow CO + H.$$

H_2O discharges by molecular photodissociation in the absorption of radiation in the Lyman-α line with $\lambda = 200$ nm

$$H_2O + h\nu\ (175 < \lambda < 190\ \text{nm}) \rightarrow OH(X^2\Pi) + H \quad \Phi = 1\,,$$

and as a result of interaction with atomic oxygen $O(^1D)$

$$O(^1D) + H_2O \rightarrow OH + OH^*_{(\nu \le 2)} + 120.5\ \text{kJ} \quad k_{q7} = 3.5 \cdot 10^{-10}\ \text{cm}^3/\text{sec}\,.$$

Above a level of 40 km, a very fast process of destruction of odd oxygen takes place; this process represents a catalytic cycle including free radicals of hydrogen

$$OH + O \rightarrow H + O_2 + 69.5\ \text{kJ} \quad k_{b3} = 2.2 \cdot 10^{-11} \exp(120/T)\ \text{cm}^3/\text{sec}\,,$$

$$H + O_2 + M \rightarrow HO_2 + M + 192.5\ \text{kJ} \quad k_{t3} = 6.7 \cdot 10^{-33} \exp(238/T)\ \text{cm}^6/\text{sec}\,,$$

$$HO_2 + O \rightarrow OH_{\nu<7} + O_2 + 230\ \text{kJ} \quad k_{b4} = 3.0 \cdot 10^{-11} \exp(200/T)\ \text{cm}^3/\text{sec}\,,$$

$$H + O_3 \rightarrow OH_{\nu<10} + O_2 + 322\ \text{kJ} \quad k_{b5} = 1.4 \cdot 10^{-10} \exp(-470/T)\ \text{cm}^3/\text{sec}\,,$$

$$H + O_3 \rightarrow O + HO_2 + 92\ \text{kJ} \quad k_{b6} = 1.4 \cdot 10^{-10} \exp(470/T)\ \text{cm}^3/\text{sec}\,,$$

$$O(^1D) + H_2 \rightarrow H + OH_{(\nu \le 4)} + 182\ \text{kJ} \quad k_{q12} = 2.5 \cdot 10^{-10}\ \text{cm}^3/\text{sec}\,.$$

In the middle part of the thermosphere, the temperature is rather high for an endothermal reaction

$$H_2 + O \rightarrow OH + H - 7.9\ \text{kJ} \quad k_{b27} = 7 \cdot 10^{-11} \exp(-5130/T)\ \text{cm}^3/\text{sec}$$

to be an important mechanism of H_2-to-H conversion. The primary reactions of photodissociation and oxidation are followed by a chain of reactions

$$OH + OH \rightarrow H_2O + O + 69.9\ \text{kJ} \quad k_{b19} = 4.2 \cdot 10^{-12} \exp(-240/T)\ \text{cm}^3/\text{sec}\,,$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 + 175.7\ \text{kJ}$$

$$k_{b21} = 1.7 \cdot 10^{-11} \exp(-500/T)\ \text{cm}^3/\text{sec}\,,$$

$$H_2O_2 + h\nu\ (190 < \lambda < 578\ \text{nm}) \rightarrow OH + OH \quad \Phi_\lambda = 1\,,$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \quad k_{b57} = 2.9 \cdot 10^{-12} \exp(160/T)\ \text{cm}^3/\text{sec}\,,$$

$$OH + HO_2 \rightarrow H_2O + O_2 + 301.7\ \text{kJ} \quad k_{b8} = 4.8 \cdot 10^{-11} \exp(250/T)\ \text{cm}^3/\text{sec}\,,$$

$$H_2 + OH \rightarrow H_2O + H \quad k_{b26} = 3.6 \cdot 10^{-11} \exp(-2590/T)\ \text{cm}^3/\text{sec}\,,$$

$$H + HO_2 \rightarrow 2OH \quad k_{b58} = 8.1 \cdot 10^{-11}\ \text{cm}^3/\text{sec}\,,$$

$$H + HO_2 \rightarrow H_2O + O \quad k_{b59} = 8.1 \cdot 10^{-11}\ \text{cm}^3/\text{sec}\,,$$

$$H + HO_2 \rightarrow H_2 + O_2 + 239.7 \text{ kJ} \quad k_{b25} = 4.2 \cdot 10^{-11} \exp(-350/T) \text{ cm}^3/\text{sec}.$$

In the tropopause range the reactions

$$OH + O_3 \rightarrow HO_2 + O_2 + 160 \text{ kJ} \quad k_{b7} = 1.3 \cdot 10^{-12} \exp(-956/T) \text{ cm}^3/\text{sec},$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \quad k_{b11} = 1.1 \cdot 10^{-14} \exp(-500/T) \text{ cm}^3/\text{sec}$$

are predominant.

Nitrogen components also act as catalysts in the decomposition of odd oxygen

$$NO_2 + h\nu \ (\lambda < 244 \text{ nm}) \rightarrow NO + O(^1D),$$

$$NO_2 + h\nu \ (\lambda < 397.5 \text{ nm}) \rightarrow NO + O,$$

$$NO + O_3 \rightarrow NO_2 + O_2 + 200 \text{ kJ} \quad k_{b13} = 1.7 \cdot 10^{-12} \exp(-1310/T) \text{ cm}^3/\text{sec},$$

$$NO_2 + O \rightarrow NO + O_2 + 192 \text{ kJ} \quad k_{b14} = 6.5 \cdot 10^{-12} \exp(120/T) \text{ cm}^3/\text{sec},$$

$$NO + O + M \rightarrow NO_2 + M + 306 \text{ kJ} \quad k_{t6} = 3.0 \cdot 10^{-33} \exp(940/T) \text{ cm}^6/\text{sec},$$

N_2O_5 is formed in the course of the reactions

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad k_{b30} = 9.8 \cdot 10^{-12} \exp(-3520/T) \text{ cm}^3/\text{sec},$$

$$NO_2 + O(^3P) + M \rightarrow NO_3 + M + 211 \text{ kJ}$$

$$k_{t7} = 9.0 \cdot 10^{-32} \exp(T/300)^{-2} \text{ cm}^6/\text{sec},$$

$$NO_3 + NO_2 \rightarrow N_2O_5 + 88 \text{ kJ} \quad k_{b33} \approx 5 \cdot 10^{-12} T^{1/2} \exp(-1000/T) \text{ cm}^3/\text{sec},$$

$$NO_3 + NO_2 \rightarrow NO + NO_2 + O_2 - 16.7 \text{ kJ}$$

$$k_{b34} \approx 3 \cdot 10^{-14} T^{1/2} \exp(-2000/T) \text{ cm}^3/\text{sec},$$

$$NO_3 + NO_3 \rightarrow 2NO_2 + O_2 + 75.3 \text{ kJ}$$

$$k_{b35} \approx 1.5 \cdot 10^{-13} T^{1/2} \exp(-3600/T) \text{ cm}^3/\text{sec}.$$

These reactions take place at night because in an illuminated atmosphere NO_3 is rapidly decomposed by photolysis. N_2O_5 decomposes in light during several hours or days depending on height and temperature

$$NO_3 + h\nu \ (\lambda < 580 \text{ nm}) \rightarrow NO_2 + O,$$

$$NO_3 + h\nu \ (\lambda = 500 - 700 \text{ nm}) \rightarrow NO + O_2 \quad \Phi = 0.18,$$

$$NO_3 + NO \rightarrow 2NO_2 + 92 \text{ kJ} \quad k_{b32} = 1.7 \cdot 10^{-11} \exp(150/T) \text{ cm}^3/\text{sec},$$

$$N_2O_5 + h\nu \ (\lambda > 300 \text{ nm}) \rightarrow NO_2 + NO_3,$$

$$N_2O_5 + h\nu\ (\lambda < 300\ \text{nm}) \rightarrow NO + O + NO_3$$

and, thus, plays an important role in diurnal fluctuations of the concentrations of NO and NO_2.

A flow of NO ($\sim 2 \cdot 10^8$ cm^2/sec [4]) directed downward from the thermosphere to the mesosphere is the main source of nitrogen-containing components in the mesosphere. In the stratosphere and the troposphere, the flow of NO is replenished due to photolysis and oxidation of N_2O by atomic oxygen $O(^1D)$:

$$N_2O + h\nu\ (185 < \lambda < 230\ \text{nm}) \rightarrow N_2(^1\Sigma^+) + O(^1D)\,,$$

$$N_2O + h\nu \rightarrow N_2O(^1\Sigma^+) \rightarrow N_2(^1\Sigma_g^+) + O(^1S)\,,$$

$$O(^1D) + N_2O \rightarrow 2NO \quad k_{q13} = 6.7 \cdot 10^{-11}\ \text{cm}^3/\text{sec}\,,$$

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \quad k_{q14} = 4.9 \cdot 10^{-11}\ \text{cm}^3/\text{sec}\,.$$

In the stratosphere, nitric acid is the main long-term reservoir for nitrogen oxides:

$$OH + NO_2 + M \rightarrow HNO_3 + M \quad k_{t5} = 4.8 \cdot 10^{-33}\ \text{cm}^6/\text{sec}\,,$$

$$HNO_3 + h\nu\ (\lambda < 598\ \text{nm}) \rightarrow OH + NO_2 \quad \Phi = 1\,,$$

$$HNO_3 + OH \rightarrow H_2O + NO_3 + 63\ \text{kJ} \quad k_{b24} = 1.3 \cdot 10^{-13}\ \text{cm}^3/\text{sec}\,,$$

$$NO + h\nu\ (173 < \lambda < 190\ \text{nm}) \rightarrow N(^4S) + O\,,$$

$$N(^4S) + O_2 \rightarrow NO + O \quad k_{b28} = 1.1 \cdot 10^{-14}\, T \exp(-3150/T)\ \text{cm}^3/\text{sec}\,.$$

Of a series of chlorine compounds present in the atmosphere, the only active ones are Cl and ClO. Chlorine atoms formed in the atmosphere react with ozone, producing chlorine oxide:

$$Cl + O_3 \rightarrow ClO + O_2 \quad k_{b15} = 2.8 \cdot 10^{-11} \exp(-257/T)\ \text{cm}^3/\text{sec}\,.$$

Chlorine oxide participates in two main reactions in the stratosphere

$$ClO + O \rightarrow Cl + O_2 \quad k_{b17} = 3.0 \cdot 10^{-11} \exp(70/T)\ \text{cm}^3/\text{sec}\,,$$

$$ClO + NO \rightarrow Cl + NO_2 \quad k_{b48} = 6.4 \cdot 10^{-12} \exp(290/T)\ \text{cm}^3/\text{sec}\,.$$

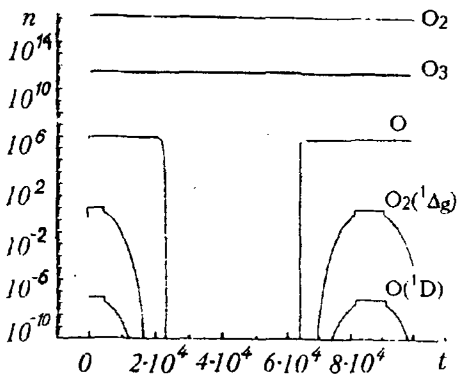
The intensity of one or another type of reactions occurring in the atmosphere is determined by solar radiation penetrating into the atmosphere at a certain angle which changes as a function of local time, season, or latitude. The expression for the cosine of a local zenith angle χ is written in the form [5]

$$\cos(\chi) = \cos\varphi \cos\delta \cos t + \sin\varphi \sin\delta\,.$$

The probability of molecular dissociation under the effect of solar radiation per second is determined by the formula

$$J = \int I_\lambda \Phi_\lambda q_\lambda\, d\lambda\ (\text{c}^{-1})\,.$$

The product $\Phi_\lambda q_\lambda$ is the photodissociation cross section for a wavelength λ. At smaller altitudes, where absorption is substantial, the rate of the incoming ultraviolet radiation is described by the relation



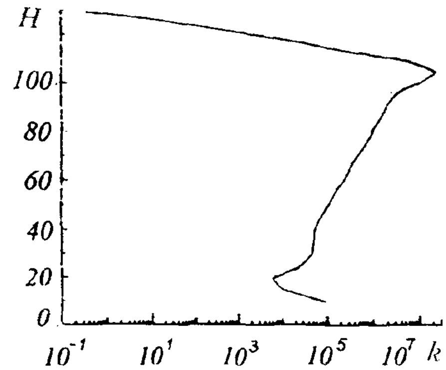


Fig. 4. Diurnal behavior of concentrations of oxygen components ($t = 0$ corresponds to midday). n, cm^{-1}; t, sec.

Fig. 5. Coefficient of turbulent diffusion k, cm^2/sec.

$$I(\lambda, z) = I_\infty(\lambda) \exp\left[-\mathrm{Ch}(\chi) \int_z^\infty \sum_k \sigma_k(\lambda)\, n_k(z)\, dz\right] + \int_{4\pi} I_k(\chi, z)\, d\Omega ,$$

where the integral describes the contribution of diffuse radiation [6]; $\mathrm{Ch}(\chi)$ is the Chapman function which for $\chi < 70^\circ$ becomes a simple relation $\mathrm{Ch}(\chi) = \sec(\chi)$. For $\chi > 70^\circ$

$$\mathrm{Ch}(x, \chi) = x \sin\chi \int_0^\chi \exp(x - x\sin\chi/\sin\lambda)\, \mathrm{cosec}^2 \lambda\, d\lambda ,$$

$x = (a + z)/H$. For $\chi = \pi/2$ (sunrise or sunset) $\mathrm{Ch}(x, \pi/2) = (\pi x/2)^{1/2}$. The diurnal behavior of the concentrations of small components is shown in Fig. 4 using oxygen components as an example.

In this model the entire transfer is presented as vertical diffusion. Equations of the form

$$\frac{\partial \rho c_i}{\partial t} + \frac{\partial F_i}{\partial z} = P_i - L_i$$

were solved, where c_i is the volumetric ratio of a mixture of the ith component (ratio of the number of component molecules to the number of air molecules per unit volume). Globally averaged vertical diffusion is described by the coefficient of turbulent diffusion (Fig. 5) which is determined by the behavior of long-lived components (N_2O and CH_4). These components are not formed in the atmosphere and the rate of their decomposition is comparable to the transfer time.

Boundary conditions for equations of vertical transfer were chosen in the following way: at the lower boundary we prescribed the values of all impurities formed in the atmosphere and vertical flows for CH_4, N_2O, CO_2, and NO. For O_3, we set its interaction with an underlying surface

$$\left(k\frac{\partial c_i}{\partial z} - \Theta c_i\right)\Bigg|_{z=z_0} = 0 ;$$

at the upper boundary (120 km), the condition of the equality of the flow to zero for all the impurities except for O_2, CO_2, $O(^3P)$, CO, and NO was used as a boundary condition. For O_2 and CO_2, the photodissociation rate is independent of altitude and it is assumed that these components are in diffusion equilibrium above 120 km:

$$F_{O(^3P)} = -2F_{O_2} ; \quad F_{CO} = -F_{CO_2} .$$

Ejection of a large amount of SO_2 into the stratosphere during volcanic eruptions can change the content of ozone due both to chemical reactions and the influence of aerosols. The presence of the latter changes the field of ultraviolet and infrared radiations, i.e., affects radiative balance of the atmosphere and the earth's temperature.

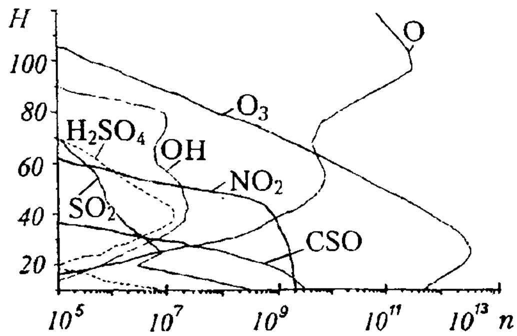


Fig. 6. Vertical distribution of ozone-active atmospheric components for zero zenith angle.

Thus, the processes of formation of SAL are tightly connected with a combination of chemical reactions in the stratosphere where many of the chemical transformations occur with the participation of solar radiation. As a whole, the structure and composition of the atmosphere are determined by a complex interaction between chemical, radiative, and dynamic processes. The observed concentrations of the majority of components in the atmosphere depend on the balance between the rates of photochemical formation and decomposition in the main reaction cycles and also on the rate of atmospheric transfer.

Figure 6 shows the calculated vertical profiles of ozone-active small atmospheric components corresponding to a zero zenith angle. The calculations show that below 30 km sulfur is mainly in the form of CSO, whereas at larger altitudes – in the form of sulfuric acid. Then, H_2SO_4 vapor is condensed on the available particles (heterogeneous nucleation) and also participates in generation of new particles (homogeneous nucleation).

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NOTATION

τ, lifetime of the ith component of the atmosphere; k_{t11}, rate of three-particle reaction; k_{b61}, rate of bimolecular reaction; k_{q8}, rate of reaction of quenching; k_{rr1}, velocity of radiative luminescence; T, atmospheric temperature; ν, frequency of radiation; h, Planck's constant; φ, latitude; δ, angle of the sun's depression, which changes with season; t, hour angle; J, probability of molecular dissociation; I_λ, intensity of radiation within the range of wavelengths $\lambda + d\lambda$; q_λ, absorption cross section within this range; Φ_λ, quantum efficiency of the process of photoionization; χ, zenith angle of the Sun; $\mathrm{Ch}(\chi)$, Chapman function; $I(\lambda, z)$, intensity of incoming ultraviolet radiation; $I_\infty(\lambda)$, intensity of incoming ultraviolet radiation at the upper boundary of the atmosphere; $\sigma_k(\lambda)$, cross section of absorption of ultraviolet radiation by the kth component of the atmosphere; $n_k(z)$, concentration of the kth component at the altitude z; a, Earth's radius; z, altitude; H, height of homogeneous atmosphere; c_I, volumetric ratio of a mixture of the ith component; F_i, vertical flow of the ith component; ρ, air density; P_i and L_i, intensities of formation and decomposition of the ith component; ^1D, ^3P, ^1S, atomic energy states; $^3\Sigma_g^-$, $^1\Delta_g$, $X^2\Pi$, molecular energy states. Index: v, oscillatory quantum number.

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