

# PHYSICS OF OUR DAYS

## Ecological problems of the earth's atmosphere

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The trends in the influence of man on the earth's atmosphere are discussed. The degree of pollution of the atmosphere and the energy consumption level at which the human influence on the earth's thermal budget and on the physical and chemical properties of the atmosphere will become significant are estimated. The formation and destruction of ozone in the stratosphere are described. The effects of human industrial activity on these processes are evaluated as they result from the production of mineral fertilizers and fluorocarbons, flights of supersonic aircraft, and detonations at high altitudes.

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### INTRODUCTION

The present composition of the atmosphere in which we live was created by living organisms. They have modified even the primordial climate of the earth. In the first stage of the earth's development, its atmosphere contained no free oxygen—the oxygen was bound into atmospheric carbon dioxide. This has been established from the chemical composition of iron compounds that were on the surface of the earth at that time<sup>[1]</sup>. Approximately 1.8 billion years ago (the earth has existed for 4.6 billion years), oxygen appeared in the atmosphere as a result of the activity of microorganisms. Its appearance resulted in the formation of an ozone belt that absorbs solar ultraviolet radiation in the upper atmosphere (at heights of 20 to 50 km). Living organisms, which had hitherto been able to develop only where the sun's rays could not reach them, now spread over the entire surface of the earth and, finding conditions favorable, were eventually able to exert a stronger influence on the composition of the atmosphere.

Thus, living organisms have modified the composition of the earth's atmosphere and made it different from the atmospheres of other planets.<sup>[1]</sup> At the present stage of human development, industrial production is beginning to influence the physico-chemical and optical properties of the atmosphere. The related changes in the composition of the atmosphere may have undesirable consequences, and special attention must therefore be given to any influence exerted by human industrial activity on the atmosphere. The actual effects of man on the earth's atmosphere may be manifested in various ways. On the one hand, they may affect the exchange of radiant energy between the atmosphere and the surface of the earth by changing the optical properties of the atmosphere. Thus does man affect the heat balance or climate of the earth. On the other hand, a change in the physical and chemical properties of the atmosphere may be reflected in the living conditions of man. This paper discusses certain

<sup>1)</sup>The atmospheres of other planets of the solar system consist basically [2,3] of carbon dioxide (Venus, Mars) or hydrogen, helium, and methane (Jupiter, Saturn, Uranus, Neptune).

aspects of the human influence on the earth's atmosphere that are now becoming topical. It concentrates attention on the physical picture of the phenomena that lead to the atmospheric changes under discussion.

### MODERN POWER SYSTEMS AND THE EARTH'S CLIMATE

The development of industrial production has been accompanied by an increase in energy consumption. During the past hundred years, the annual use of energy has increased by an order of magnitude, and the growth rate of power engineering has also increased. This situation poses a problem: how much power can be generated on the surface of the earth without disturbing its heat balance?

Let us estimate this power. Figure 1 represents the heat balance of the earth and atmosphere (see<sup>[4-8]</sup>). We shall assume that the ratio of the energy lost by the surface of the earth in the form of infrared radiation to the total energy loss does not change as the temperature rises. The flux of infrared radiation from the earth's surface is determined by the Stefan-Boltzmann law  $j = \sigma T^4$ , where  $\sigma = 5.87 \times 10^{-12} \text{ W/cm}^2 \text{ deg}^4$  is the Stefan-

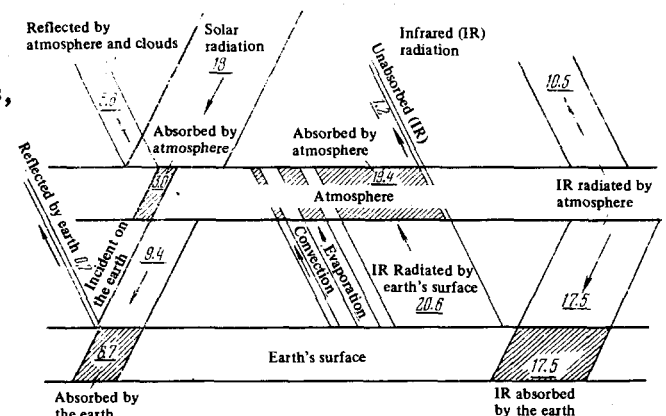


FIG. 1. The heat balance of the earth and atmosphere. The power converted by the earth's surface and atmosphere is expressed in units of  $10^{13} \text{ kW}$ .

Boltzmann constant and T is the temperature of the surface. A change in the temperature of the earth's surface by  $\Delta T$  will result in a change  $\Delta j = 4\sigma T^3 \Delta T = 4j_0 \Delta T/T$  in the radiant energy flux. From this we find that the release of an additional power  $\Delta J$  at the surface of the earth will produce in the earth's average surface temperature T a change  $\Delta T$  that is related as follows to  $\Delta J$  and the total power  $J \approx 3 \times 10^{14}$  kW dissipated by the surface of the earth:

$$\Delta J = 4J \frac{\Delta T}{T}. \quad (1)$$

It is believed that irreversible processes may begin on the earth after its temperature has been raised by an amount  $\Delta T$  of the order of one degree Centigrade. Hence we find that the order of magnitude of the maximum power that can be generated on the earth's surface should be  $4 \times 10^{12}$  kW.<sup>2)</sup>

This estimate is correct if the human power industry has no bearing on processes that occur upon absorption and radiation of energy by the earth and do not disturb these processes. If man created a power-generating system that could be incorporated in the cycle of the earth's energy processes, the maximum amount of power that could be produced might be considerably greater than the estimate given above. (One energy system of this type, based on efficient chemical methods of converting solar energy, was discussed by Semenov<sup>[9]</sup>.) The power industry that we have at the present time is not only not inscribed into the natural energy-process cycle, but interferes with these processes by affecting the physical properties of the atmosphere. Let us see how this happens.

We refer to Fig. 1, which represents the heat balance of the earth, and investigate the role played by the atmosphere in this balance. We see that the atmosphere transmits part of the solar radiation to the surface of the earth and returns much of the infrared radiation emitted by the earth's surface. This creates an additional energy flux to the surface of the earth, and the total amount of energy handled by the earth's surface is considerably larger than the amount incoming from the sun. This phenomenon is known as the greenhouse effect. As a result of the greenhouse effect, the temperature of the earth's surface is found to be considerably higher than the temperature that would be observed in the absence of the atmosphere. The infrared radiation flux onto the surface of the earth depends on the optical properties of the atmosphere, and it is necessary to understand what changes in the composition of the atmosphere may result in appreciable changes in its optical properties, i.e., changes in its emissive properties.

The earth's atmosphere consists basically of nitrogen, oxygen, and argon, a mixture of gases that are optically transparent to infrared radiation. Hence the emissivity of the earth's atmosphere is determined by gases that are present in the atmosphere in small quantities. Radiative transitions in the infrared are determined by molecular vibrational-rotational or rotational transitions. Accordingly, each gas absorbs or emits in a certain region of the spectrum. Consequently, the addition to the atmosphere of gas molecules whose absorption spectrum

lies in a part of the spectrum unoccupied by other molecules may affect the optical properties of the atmosphere even at low concentrations of the impurity. It is interesting to establish the impurity concentrations at which this effect will become appreciable.

To this end, we make the following estimate. We assume that the absorption spectrum of the molecules that we add to the atmosphere does not overlap the absorption spectra of the other atmospheric molecules. We assume further that the concentration of these molecules is low, so that a photon emitted by a molecule of the species in question will escape from the atmosphere without being absorbed along the way. We shall also assume for simplicity that all of the energy that reaches the earth's surface because of the impurity in question is radiated back by the earth's surface in the form of infrared radiation. Under the above conditions, we determine the impurity concentration that will bring about a  $1^\circ$  increase in the earth's surface temperature (i.e., an appreciable increase under our terms).

Let us carry the estimate through. To change the earth's surface temperature by  $\Delta T = 1^\circ$ , it is necessary to send an additional energy flux  $\Delta j = 4j_0 \Delta T/T$  to that surface' here  $j_0 = 0.04$  W/cm<sup>2</sup> is the infrared radiation flux emitted by the earth's surface and T is the effective temperature of the earth's surface. This additional flux is created by our impurity, whose effect is to send an infrared radiant energy of  $\hbar\omega \times N^*/2\tau$  to the surface of the earth from a unit volume of the atmosphere per unit time. Here  $N^*$  is the density of the radiating molecules,  $1/\tau$  is the emission frequency of the excited molecule, and  $\hbar\omega$  is the energy of the photon emitted. The factor  $1/2$  takes account of the fact that only half of the photons are emitted toward the earth. From this we find for the radiant energy flux due to the impurity

$$\Delta j = \frac{\hbar\omega}{2\tau} \int N^*(h) dh = \frac{\hbar\omega}{2\tau} N^*(0)L, \quad (2)$$

where h is the height of the layer above the earth's surface, L = 8.4 km is the effective thickness of the earth's atmosphere, and  $N^*(0)$  is the density of the excited impurity molecules at the surface. Using a Boltzmann excited-state distribution of the molecules, we obtain  $N^* = N_0 e^{-\hbar\omega/T}$ , where  $N_0$  is the density of the molecules in the ground state.

Thus we have the relation

$$4j_0 \frac{\Delta T}{T} = \frac{\hbar\omega}{2\tau} N_0 L e^{-\hbar\omega/T}. \quad (3)$$

It connects the density  $N_0$  of the impurity molecules with the surface-temperature change  $\Delta T$  caused by this impurity. Table I gives the values of the density  $N_0$  calculated from this formula for some of the most important

TABLE I

Molecule	Energy of transition considered, cm <sup>-1</sup>	Transition frequency sec <sup>-1</sup> , 10	Density $N_0$ , cm <sup>-3</sup>	Concentration*	Molecule	Energy of transition considered, cm <sup>-1</sup>	Transition frequency sec <sup>-1</sup> , 10	Density $N_0$ , cm <sup>-3</sup>	Concentration*
SO <sub>2</sub>	518	0.9	2·10 <sup>12</sup>	7·10 <sup>-8</sup>	SO <sub>2</sub>	1151	3.4	5·10 <sup>12</sup>	2·10 <sup>-7</sup>
SF <sub>6</sub>	613	2.9	8·10 <sup>11</sup>	3·10 <sup>-8</sup>	CH <sub>4</sub>	1306	7.3	4·10 <sup>12</sup>	2·10 <sup>-7</sup>
CO <sub>2</sub>	667	3	9·10 <sup>11</sup>	4·10 <sup>-8</sup>	SO <sub>2</sub>	1361	42	10 <sup>12</sup>	4·10 <sup>-8</sup>
SF <sub>6</sub>	932	110	7·10 <sup>10</sup>	3·10 <sup>-9</sup>	H <sub>2</sub> O	1595	16	7·10 <sup>12</sup>	3·10 <sup>-7</sup>
NH <sub>3</sub>	968	16	5·10 <sup>11</sup>	2·10 <sup>-8</sup>	NH <sub>3</sub>	1624	8	2·10 <sup>13</sup>	6·10 <sup>-7</sup>
O <sub>3</sub>	1042	10	10 <sup>12</sup>	4·10 <sup>-8</sup>	CO <sub>2</sub>	2349	400	8·10 <sup>12</sup>	3·10 <sup>-7</sup>

\*The ratio of the number of molecules of the impurity to the number of air molecules in a given volume.

<sup>2)</sup>Power is now being generated at a rate approaching  $10^{10}$  kW. If the worldwide growth rate of energy production observed during the last decade (5-7% per year) continues, this predicted output will be reached in the next century.

atmospheric impurities. If a given impurity is introduced into the composition of the atmosphere in such a way that its density is  $N_0$ , and in the absence of the impurity the atmosphere is transparent to the photons with energy  $\hbar\omega$ , introduction of this quantity of the impurity into the atmosphere will raise the earth's surface temperature by  $1^\circ$  solely as a result of the transition considered. As we see, the impurity exerts an influence at low concentration ( $10^{-9}$ – $10^{-7}$ ). Therefore the infrared radiation of the earth's atmosphere depends strongly on the nature of impurities that are present in the atmosphere in small amounts.

Formula (2) is valid for low densities of the component under consideration, at which the atmosphere has a small optical thickness in the particular region of the spectrum. At higher densities of the gas, it is necessary to consider the specific form of the absorption spectrum, which oscillates and whose maxima correspond to the centers of specific transitions. As an example, Fig. 2 shows the absorption-coefficient curve of carbon dioxide for the strongest vibrational-rotational transitions around  $15 \mu$ . A theory of infrared-radiation transfer with consideration of the actual form of the absorption coefficient has been developed quite completely and is presented in the monographs<sup>[11-14]</sup>.

The greenhouse effect has been analyzed widely in regard to the effect of atmospheric carbon dioxide on the earth's heat balance (see<sup>[15]</sup>). As a result of human industrial activity, the amount of carbon dioxide in the atmosphere is increasing by about 0.3% per year<sup>[16]</sup>, and its concentration by  $10^{-6}$  per year. Since the turn of the century, the amount of carbon dioxide in the atmosphere has increased by about 10%, and its concentration has risen from 0.029 to 0.032. Calculations indicate that doubling of the amount of carbon dioxide in a dry atmosphere would correspond to an increase of about  $2^\circ$  in the temperature of the atmosphere.

The greenhouse effect involving carbon dioxide was understood long ago. But what is the present significance of this phenomenon? We see from Table I that the greenhouse effect due to impurities becomes significant at low impurity concentrations. Such concentrations can be created by pollution from modern industrial activity. Thus, the burning of fossil fuels is accompanied at its present level by the discharge of about 7 billion tons of carbon into the atmosphere in the form of carbon dioxide. If it remained in the atmosphere, its concentration would

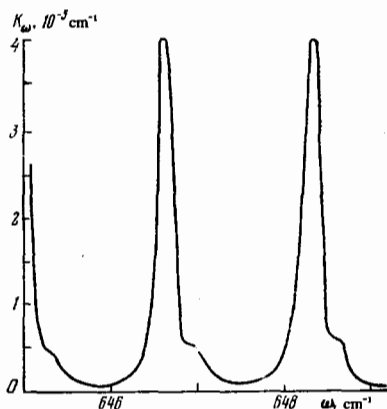


FIG. 2. Absorption coefficient of carbon dioxide at the earth's surface.

increase at an annual rate of  $3 \times 10^{-6}$ . Let us take another example. Coal and petroleum have average sulfur contents of 1 and 3%, respectively. Let us assume that all of the sulfur escapes into the atmosphere in the form of sulfur dioxide when coal and oil are burned, so that about 200 million tons of sulfur dioxide enter the atmosphere per year. If sulfur dioxide were not washed out by water, this annual discharge would produce a sulfur dioxide concentration on the order of  $2 \times 10^{-8}$ . These examples refer to the entire atmosphere as a whole. Air pollution may be stronger in small areas. The examples indicate that modern industry is capable of producing impurity densities in the atmosphere that may substantially affect its optical properties and influence the earth's climate.

The influence of air pollution on the earth's climate is not limited to the greenhouse effect alone. Photons leave the atmosphere from layers where the probability of their absorption along the way is smaller than unity. Therefore an increase in the concentration of a given component results in emission of the atmospheric radiation created by this component from higher layers of the atmosphere. And since these layers are at lower temperatures, they contain fewer excited atoms. Thus, as the concentration of a specific component increases, there is a decrease in the intensity of the infrared radiation that is emitted by molecules of this component and escapes from the atmosphere. Exact equality must prevail between the energies acquired and given up by the atmosphere. Therefore this pollution of the atmosphere is accompanied by additional hydrodynamic transfer of energy between the atmosphere and the earth, i.e., it is reflected in the climate of the earth.

While the introduction of absorbing molecules entering the earth's atmosphere raises the temperature of the earth, an increase in the dust content of the atmosphere has the opposite effect. Dust reflects solar radiation and thereby lowers the intensity of the solar radiation that reaches the earth's surface. Thus, according to Barret's calculations<sup>[31]</sup>, the introduction of  $2 \times 10^6$  tons of dust into the earth's atmosphere could lower the earth's temperature by  $0.4^\circ$ .

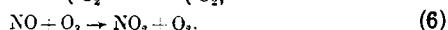
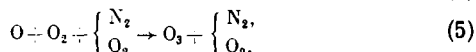
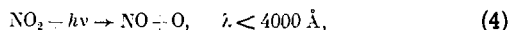
Thus, the properties of the earth as an energy machine depend strongly on the atmosphere. Human pollution of the atmosphere is capable at the present stage of its development of modifying the earth's heat balance.<sup>3)</sup> The change itself will depend on the nature of the pollution. The program suggested in<sup>[18, 19]</sup>, which involves study of the atmosphere and climate of large cities is of great interest in the context of studies of the influence of atmospheric pollution on the earth's climate. The urban climate now differs appreciably from the climate of the areas surrounding the cities. This is due both to the additional energy release and to the change in the composition of the air over the city. As industry develops further, these atmospheric changes will extend over larger areas. Investigation of the atmosphere and climate of large cities should therefore make it possible to establish trends in the global climatic succession under the influence of human activity and to prevent undesirable climate changes.

<sup>3)</sup>It is held in [17] that the worldwide cooling that is presently being observed and began in the 1940's is due to the increase in the amount of dust in the atmosphere.

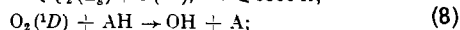
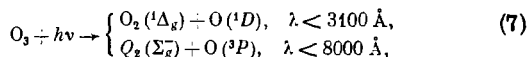
## PHOTOCHEMICAL SMOG

Photochemical smog is one example of the influence of the properties of polluted air on living conditions. The word "smog" derives from "smoke" and "fog." Smog was first observed in London at the end of the last century, taking the form of a suspension of soot, haze, and ash in fog. Photochemical smog, which was first observed in Los Angeles in the 1930's, is more dangerous. This smog appears on clear sunny days during the warm time of the year and is accompanied by the formation of toxic substances in the atmosphere that constitute a threat to human health. Below we give an account of the processes that determine the origins of photochemical smog.

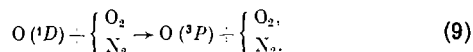
Nitrogen oxides formed in high-temperature systems, chiefly automobile engines, start the chain of events leading to photochemical smog. The principal transitions between nitrogen oxides are as follows:



Chemically most active among the above products are the O radical and the O<sub>3</sub> molecule. The OH radical may also be formed as a result of the reactions



here A is any of the radicals, in particular H, CH<sub>3</sub>, or OH. The photolytic decay of ozone (7) preserves the total spin of the ozone molecule, which equals zero. Therefore the decay products of ozone—the oxygen atom and the oxygen molecule—may be either in the ground state or both in an excited state. The reaction (8) is highly efficient (its rate constant at room temperature is approximately<sup>[20]</sup>  $3 \times 10^{-10}$  cm<sup>3</sup>/sec). The destruction of excited oxygen atoms corresponds to transfer of the electronic excitation to vibrational levels of the quenching molecules and is described by the equation



The rate constant for quenching of an excited atom on collision with a molecule is rather high for thermal energies, amounting<sup>[20, 21]</sup> to about  $5 \times 10^{-11}$  cm<sup>3</sup>/sec. Nevertheless the aggregate of the processes (7)–(9) is efficient formation of OH radicals.

The chemically active O<sub>3</sub>, O and OH particles formed with participation of nitrogen oxides give rise to complex chemical processes involving hydrocarbons (see the monograph<sup>[22]</sup>). Hydrocarbons are present in the atmosphere in appreciable quantities. Methane has natural origins and is released from the surface of the earth by bacterial activity. Its average concentration at the surface is  $1.5 \times 10^{-6}$ .<sup>[20, 22, 23]</sup> More complex hydrocarbons enter the atmosphere in automobile exhaust gases and as a result of the operation of petroleum refineries and other chemical plants. The air of industrial cities contains large total amounts of higher hydrocarbons. Thus, studies of the atmospheres of New York and Los Angeles<sup>[24]</sup> indicate a total content of higher hydrocarbons in excess of  $10^6$  carbon nuclei in these molecules per molecule of air.

The reactions of O<sub>3</sub>, O, and OH with hydrocarbon mo-

lecules result in the formation of such substances<sup>[22, 25-27]</sup> as propylene, transbutylene, isobutane, n-butane, formaldehyde, etc. Carcinogenic substances, which can affect the human organism more strongly than ozone in small quantities, appear as a result. Thus, photochemical smog is accompanied by a large number of specific chemical processes involving organic substances. The processes themselves and their products depend on the composition of the hydrocarbons in the atmosphere and on the conditions under which these processes advance. Depending on local conditions, therefore, photochemical smog may have different types of effects on humans and take a variety of apparent courses. Thus, American smogs are accompanied by yellowish-green<sup>[4]</sup> or dove-colored dry hazes, while white smogs are observed in Japan.

Let us estimate the amount of energy expended on formation of a photochemical smog. The total ozone and nitrogen-oxide concentration in smog is of the order of  $2 \times 10^{-7}$  [22]. Let us estimate the energy needed for formation of these molecules on the assumption that the entire chain of processes is triggered by nitrogen oxides formed on decomposition of air in high-temperature machines. Assuming that the "cost" of a molecule (the ratio of the invested energy to the number of molecules formed) is 20 eV<sup>[30]</sup>, we find that  $10 \text{ J/cm}^2 = 10^8 \text{ kJ/km}^2$  of energy must be expended. Let us assume that horizontal winds are absent in the area under consideration throughout a day (10<sup>5</sup> sec) (several days are involved in reality). We find in this case that the smogging concentration of chemically active particles can be reached at expended powers of  $10^3 \text{ kW/km}^2$ .

Assume that the smog is created by the operation of motor vehicles. Let us estimate the traffic density at which it is formed. We shall assume that the average power of an automobile engine is 5 kW (70 hp) and that the engine is running during 20% of the total time. We then find on the basis of the earlier estimate that 1000 automobiles per square kilometer are sufficient for the appearance of smog in calm sunny weather. The automobile densities in a busy city are higher.

Energy is now being consumed at a rate of  $10^{10}$  kW. If we distribute this uniformly over the entire land area of the globe, the average density of energy consumption is found to be somewhat higher, at  $10^2 \text{ kW/km}^2$ . This is only one order of magnitude below the estimate obtained for the energy density that results in the appearance of smog under appropriate weather conditions. Higher energy consumption densities are attained locally. For example, in Japan this density is  $1.9 \times 10^3 \text{ kW/km}^2$ , and for the industrialized Ruhr of West Germany it is  $2 \times 10^4 \text{ kW/km}^2$ . Thus, the capacity of the present-day power industry is such that it can produce on small areas of the earth amounts of chemically active substances that may create intolerable living conditions for humans.

## THE PROBLEM OF ATMOSPHERIC OZONE

It is difficult to overestimate the importance of atmospheric ozone for processes that take place in the upper atmosphere and biosphere. Atmospheric ozone

<sup>4)</sup>This results from the processes  $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$  and  $\text{NO}_2 \xrightarrow{h\nu} \text{NO} + \text{O}$ , the photon having a wavelength  $\lambda$  [28, 26] from 5200 to 8100 Å. This emitted-photon wavelength explains the greenish or yellowish color of the haze.

TABLE II. Parameters of standard atmosphere

Height, km	15	20	25	30
Temperature, °K	217	217	217	235
Density, cm <sup>-3</sup>				
[N <sub>2</sub> ]	3.1 · 10 <sup>18</sup>	1.5 · 10 <sup>18</sup>	6.6 · 10 <sup>17</sup>	2.9 · 10 <sup>17</sup>
[O <sub>2</sub> ]	8.5 · 10 <sup>17</sup>	4.0 · 10 <sup>17</sup>	1.8 · 10 <sup>17</sup>	7.8 · 10 <sup>16</sup>
[N <sub>2</sub> ] + [O <sub>2</sub> ]	4.0 · 10 <sup>18</sup>	1.9 · 10 <sup>18</sup>	8.4 · 10 <sup>17</sup>	3.7 · 10 <sup>17</sup>
[O <sub>3</sub> ]	10 <sup>15</sup>	2.5 · 10 <sup>15</sup>	4 · 10 <sup>15</sup>	3.5 · 10 <sup>15</sup>
[O]	10 <sup>8</sup>	5 · 10 <sup>8</sup>	3 · 10 <sup>8</sup>	2 · 10 <sup>7</sup>
Height, km	35	40	45	50
Temperature, °K	251	265	274	274
Density, cm <sup>-3</sup>				
[N <sub>2</sub> ]	1.4 · 10 <sup>17</sup>	6.5 · 10 <sup>16</sup>	3.4 · 10 <sup>16</sup>	1.8 · 10 <sup>16</sup>
[O <sub>2</sub> ]	3.6 · 10 <sup>16</sup>	1.8 · 10 <sup>16</sup>	9.1 · 10 <sup>15</sup>	5.0 · 10 <sup>15</sup>
[N <sub>2</sub> ] + [O <sub>2</sub> ]	1.7 · 10 <sup>17</sup>	8.3 · 10 <sup>16</sup>	4.3 · 10 <sup>16</sup>	2.3 · 10 <sup>16</sup>
[O <sub>3</sub> ]	2 · 10 <sup>15</sup>	5 · 10 <sup>14</sup>	2 · 10 <sup>14</sup>	5 · 10 <sup>14</sup>
[O]	10 <sup>8</sup>	5 · 10 <sup>8</sup>	2 · 10 <sup>9</sup>	6 · 10 <sup>9</sup>

absorbs hard ultraviolet radiation with wavelengths  $\lambda < 3000 \text{ \AA}$ , which have deadly effects on living organisms. Atmospheric ozone also absorbs part of the solar radiation in the ultraviolet ( $\lambda = 3100\text{--}3500 \text{ \AA}$ ) and some in the optical region of the spectrum ( $\lambda = 4700\text{--}7400 \text{ \AA}$ , the Chappuis bands), thereby raising the temperatures of the stratosphere and mesosphere (at heights of 20–50 km).

Below we shall consider the channels in which atmospheric ozone is formed and destroyed and ascertain how these processes may be influenced by human practical activity. The rates of the processes depend on the geographical location of the atmospheric region under study, the time of day, the season, and various other factors. Accordingly, the ozone density at a given height depends on these factors, as does the relative contribution of each of the channels to the ozone destruction rate. Since we are interested in a general qualitative picture of the processes, we shall henceforth average over these factors by assuming a standard model of the atmosphere<sup>[11, 32, 33]</sup> with constant parameters at a given height. Moreover, we shall neglect vertical particle transport. The related information is included in the vertical distribution function, which is taken from observations.

Table II presents averaged parameters of the atmosphere at the heights at which most of the ozone is concentrated. The vertical temperature and density distributions of the principal components were taken for the standard atmosphere of<sup>[11, 32, 33]</sup> and the ozone density distribution was based on<sup>[20, 34–39]</sup>. We shall henceforth use these values as a basis for study of the atmosphere's ozone balance. Atmospheric ozone is formed from atomic oxygen as a result of the ternary process (5)



where M is a nitrogen or oxygen molecule. The room-temperature rate constant of this process, averaged over a number of literature sources<sup>[43–48]</sup>, is  $6 \times 10^{-34} \text{ cm}^6/\text{sec}$ . It increases with decreasing temperature, amounting to  $1.2 \times 10^{-33} \text{ cm}^6/\text{sec}$  at  $T = 218^\circ\text{K}$  when  $M = \text{N}_2$ . Atomic oxygen is formed in the atmosphere as a result of photodissociation of molecular oxygen under the action of sunlight:



This process leads to the formation of oxygen radicals, which then spend most of the time in the form of ozone. The flux of solar photons that are absorbed with photodissociation of molecular oxygen is about  $2 \times 10^{13} \text{ cm}^2 \text{ sec}^{-1}$ . Distributing this value uniformly over the surface

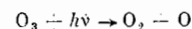
of the earth (i.e., dividing by four) and assuming that each photon generates two radicals, we find that the number of oxygen radicals formed per unit time per unit area is approximately  $10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$ . Below we consider in sequence the principal channels through which oxygen (atomic oxygen and ozone) radicals are lost in the atmosphere.

### The Oxygen Cycle (Chapman Cycle) [49]

Ozone and atomic oxygen are destroyed in this channel as a result of the reaction



The rate constant of this process, which has been measured in<sup>[48, 50–54]</sup>, varies from  $2 \times 10^{-15} \text{ cm}^3/\text{sec}$  at  $217^\circ\text{K}$  ( $h = 15 \text{ km}$ ) to  $10^{-14} \text{ cm}^3/\text{sec}$  at  $274^\circ\text{K}$  ( $h = 50 \text{ km}$ ). The atomic oxygen in process (11) is formed on absorption of sunlight by ozone:



(hard ultraviolet radiation is absorbed by ozone in higher layers of the atmosphere, where a small fraction of the ozone is concentrated). Assuming that atmospheric ozone absorbs 3% of the solar radiation<sup>[6]</sup> (for the most part at  $3000\text{--}3300 \text{ \AA}$  and  $5500\text{--}6500 \text{ \AA}$ <sup>[11]</sup>), we find that ozone absorbs a photon flux of  $3 \times 10^{15} \text{ cm}^{-2} \text{ sec}^{-1}$ . This gives  $\tau_7 = 2 \times 10^5 \text{ sec}$  for the average lifetime of a single ozone molecule.

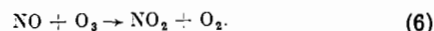
Thus, the oxygen cycle of ozone destruction consists in the following. The photodecay of the ozone molecule (7) and the ternary capture of the oxygen atom by the molecule (5) result in the formation of atomic oxygen, whose equilibrium density equals

$$[O] = \frac{[O_3]}{\tau_7 K_5 [M] [O_2]}, \quad (12)$$

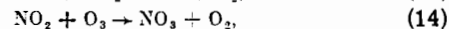
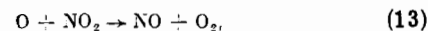
where [M] is the density of the air molecules. The atomic oxygen and ozone then enter into reaction (11), which results in destruction of the radicals. Table II lists atomic-oxygen densities (12) and Table III gives oxygen-radical loss rates in the oxygen cycle as obtained from the preceding data from Table II and the reaction rate constants given earlier.

### The Nitrogen Cycle

The nitrogen cycle of atmospheric-ozone destruction includes reactions in which nitrogen oxides participate. The most important one is



This process is accompanied by the following reactions with participation of nitrogen oxides, ozone, and atomic oxygen:



The rate constant of process (6) was measured in<sup>[48, 53, 55–61]</sup> and varies approximately from  $3 \times 10^{-15} \text{ cm}^3/\text{sec}$  at  $217^\circ\text{K}$  ( $h = 15 \text{ km}$ ) to  $10^{-14} \text{ cm}^3/\text{sec}$  at  $274^\circ\text{K}$  ( $h = 50 \text{ km}$ ). According to the measurements of<sup>[48, 53, 62–67]</sup>, the rate constant of process (13) depends weakly on temperature range considered and is about  $10^{-11} \text{ cm}^3/\text{sec}$ . According to<sup>[43, 48, 61]</sup>, the rate constant of process (14) varies at stratospheric temperatures from  $4 \times 10^{-18} \text{ cm}^3/\text{sec}$  at  $217^\circ\text{K}$  to  $1.2 \times 10^{-15} \text{ cm}^3/\text{sec}$  at  $274^\circ\text{K}$ . The

TABLE III

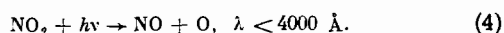
	Height h, km								Total ozone loss in cycle, $\text{cm}^3 \text{sec}^{-1}$
	15	20	25	30	35	40	45	50	
Destruction of radicals per unit volume per unit time, $\text{cm}^{-3} \text{sec}^{-1}$ :									
Oxygen cycle	70	$9 \cdot 10^2$	$8 \cdot 10^3$	$7 \cdot 10^4$	$4 \cdot 10^5$	$10^6$	$2 \cdot 10^6$	$1.5 \cdot 10^6$	$3 \cdot 10^{12}$
Nitrogen cycle $2K_{13} [O][NO_2]$	$2.6 \cdot 10^2$	$10^4$	$1.6 \cdot 10^5$	$1.9 \cdot 10^6$	$4 \cdot 10^6$	$2.7 \cdot 10^6$	$1.3 \cdot 10^6$	$2.8 \cdot 10^5$	$5 \cdot 10^{12}$
Hydrogen cycle	$8 \cdot 10^3$	$4 \cdot 10^4$	$10^5$	$4 \cdot 10^5$	$5 \cdot 10^5$	$3 \cdot 10^5$	$10^5$	$3 \cdot 10^4$	$7 \cdot 10^{11}$
Chlorine cycle	$5 \cdot 10^6$	$6 \cdot 10^6$	$4 \cdot 10^6$	$2 \cdot 10^6$	$2 \cdot 10^6$	$10^6$	$10^6$	$2 \cdot 10^6$	$1 \cdot 10^{13}$

TABLE IV. Nitrogen oxide densities in the stratosphere,  $10^8 \text{cm}^{-3}$ 

Height h, km	15	20	25	30	35	40	45	50
[NO]	2	5	7	8	6	5	4	3
[NO <sub>2</sub> ]	1.3	10	26	47	20	2.7	0.32	0.023
[NO <sub>3</sub> ]	0.3	2.5	7.3	16	9.4	0.4	0.024	0.036

rate constant of the process (15) is approximately  $8 \times 10^{-12} \text{cm}^3/\text{sec}$  according to<sup>[32, 43, 46]</sup> in the temperature range of the stratosphere.

In addition to reactions (6), (13), and (14), which result in destruction of oxygen radicals, there is a process in which atomic oxygen is formed on photodecay of the nitrogen dioxide molecule:



Let us evaluate the importance of this process. The NO<sub>2</sub> molecule is decomposed by photons with wavelengths of 3300–4000 Å, which are not absorbed by the upper ozone layer. The average photodecay cross section of the NO<sub>2</sub> molecule in this wavelength range is  $\sigma = 5 \times 10^{-19} \text{cm}^2$ <sup>[22, 66]</sup> with a quantum yield (i.e., a ratio of the photodissociation probability to the probability of total photoabsorption) of about unity. The flux of photons incident on the earth's atmosphere in this frequency range is approximately  $j_0 = 2 \times 10^{16} \text{cm}^{-2} \text{sec}^{-1}$ <sup>[22, 66]</sup>. Hence the lifetime of a molecule on the sunlit side of the earth is somewhat greater than  $10^2 \text{sec}$ , while the average lifetime of the nitrogen dioxide molecule to photodestruction is somewhat longer than  $2 \times 10^2 \text{sec}$ .

Let us determine the role of nitrogen oxides in the atmosphere's ozone balance. The mutual reactions between nitrogen oxides (4), (6), (13), (14), and (15) take place rapidly compared to the times for transfer of nitrogen oxides between layers of the atmosphere. A photochemical equilibrium is therefore established between the various nitrogen oxides in each layer of the stratosphere, and the density ratios of these oxides can be found for each layer of the stratosphere from the rate constants of the corresponding reactions. Table IV gives the densities obtained for the oxides NO<sub>2</sub> and NO<sub>3</sub> from the photochemical-equilibrium condition. The density values for the NO molecule are based on the data of<sup>[40-42]</sup>. The values given in Table IV for the density of nitrogen dioxide in the lower stratosphere agree roughly with measurements of this quantity<sup>[40-42, 70]</sup>.

The net result of the processes (4), (6), and (13)–(15)

is destruction of ozone. The total number of ozone molecules destroyed per unit time over a unit area, with consideration of the above processes, is

$$\int dh \frac{d}{dt} ([O] - [O_3]) = 2 \int k_{13} [O] [NO_2] dh = 5 \cdot 10^{12} \text{cm}^{-2} \text{sec}^{-1}.$$

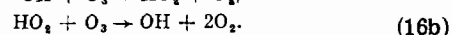
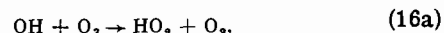
Here all processes except (13) result in transfers of atomic oxygen between nitrogen oxides, while process (13) is accompanied by destruction of atomic oxygen and formation of molecular oxygen.

We note that the formation of atomic oxygen (and then ozone) as a result of the photodecay of nitrogen dioxide (4) takes place at the rate of  $3 \times 10^{13} \text{cm}^2 \text{sec}^{-1}$ . This process is offset by the destruction of atomic oxygen and ozone at about the same rate. Therefore the destruction of atomic oxygen and ozone in the nitrogen cycle proceeds against a background of fast processes, and the slow processes must be taken into account correctly to obtain an accurate result. Processes involving NO<sub>3</sub> may have been left out of account in the nitrogen-cycle scheme considered here. The NO<sub>3</sub> molecule decomposes readily under natural conditions and the processes in which it takes part have not been studied nearly as thoroughly as the others.

Thus, it can be concluded from this calculation, which is presented for orientation only, that the nitrogen cycle is important in the atmospheric ozone balance. Here the actual contribution of the nitrogen cycle to the ozone balance may depend on slow processes with participation of nitrogen oxides, including reactions of the oxides with impurities, with participation of oxygen. Here the rate of formation of the oxygen radical in the process (6). These processes are the strongest ones and maintain the equilibrium between the amounts of ozone and nitrogen dioxide. The slower processes shift this equilibrium, and it is they that will determine the atmospheric ozone balance. The direction in which the nitrogen cycle affects atmospheric ozone, i.e., whether it results in the formation or destruction of ozone, will also depend on the slow processes involving nitric oxide and nitrogen dioxide. It is evident that a change in the composition of the impurities in the atmosphere may also affect the direction in which the nitrogen cycle influences the atmospheric ozone balance.

### The Hydrogen Cycle

The participation of hydrogen oxides in the destruction of ozone reduces to the reactions



The rate constant of reaction (16a) at room temperature is  $5 \times 10^{14} \text{cm}^3/\text{sec}$ <sup>[71-76]</sup>, while that of (16b) is  $1.2 \times 10^{15} \text{cm}^3/\text{sec}$ <sup>[76, 77]</sup>. The activation energy is 2.2 kcal/mole for the first reaction<sup>[75]</sup> and approximately the same for the second.

We do not have reliable data for the OH and HO<sub>2</sub> density profiles. Measurements made in the stratopause<sup>[78]</sup> (44 and 62 km) indicate that the total OH and HO<sub>2</sub> density in this region is of the order of  $7 \times 10^7 \text{cm}^{-3}$ , and measurements of the total amount of OH at heights from 45 to 70 km indicate  $(2-9) \times 10^6 \text{cm}^{-2}$ <sup>[79]</sup>. Calculations of the density profiles of these components made with the rate constants of the reactions in which the components participate yield similar density distributions. On the

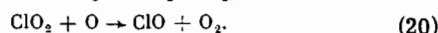
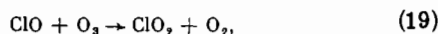
basis of the OH and HO<sub>2</sub> density profiles calculated in [37, 80], we find that the total ozone loss is  $6 \times 10^{11} \text{ cm}^{-2} \text{ sec}^{-1}$  on the basis of reaction (15) and  $10^{11} \text{ cm}^{-2} \text{ sec}^{-1}$  due to reaction (16).<sup>5</sup> These values are more than an order of magnitude below the rate of ozone formation due to photodecay of molecular oxygen. We may conclude from this that the hydrogen cycle does not play a material role in the atmospheric ozone balance.

### The Chlorine Cycle

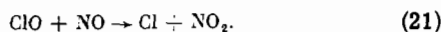
The chlorine cycle of ozone destruction includes the reactions



The room-temperature rate constant of reaction (17) is  $1.8 \times 10^{-11} \text{ cm}^3/\text{sec}$  [66], and that of reaction (18) is  $5.3 \times 10^{-11} \text{ cm}^3/\text{sec}$  [81, 82]. As in the previously discussed cycles, the initial radical is restored after decomposition of two oxygen radicals. There are the following two parallel reactions:

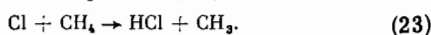
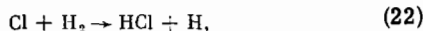


At room temperature, the rate constant of (19) is smaller than  $5 \times 10^{-15} \text{ cm}^3 \text{ sec}^{-1}$  [52], while the room-temperature rate constant of reaction (20) is  $5 \times 10^{-13} \text{ cm}^3/\text{sec}$  [83]. Reaction (18) may be replaced by

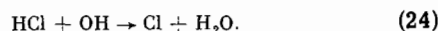


Atomic chlorine is reduced more efficiently as a result of this reaction at low heights. The room-temperature rate constant is  $1.7 \times 10^{-11} \text{ cm}^3/\text{sec}$  [66].

Like atoms of other halogens, atomic chlorine reacts with molecular hydrogen and hydrocarbons:



Chlorine has an interesting property in that its atoms can be reduced:



At the temperatures corresponding to heights of 15–20 km in the atmosphere, the rate constant of reaction (22) varies in the range  $(1-7) \times 10^{-15} \text{ cm}^3/\text{sec}$  [84–86], that of reaction (18) in the range  $(1-7) \times 10^{-14} \text{ cm}^3/\text{sec}$  [87, 88], and that of (19) from  $(2-5) \times 10^{-13} \text{ cm}^3/\text{sec}$  [89, 90].

The ratio in which the densities of the various chlorine-containing compounds stand is highly important. If most of the chlorine were in the form of HCl, as is the case near the earth's surface, the chlorine cycle would be ineffective because of the absence of Cl and ClO radicals. Let us assume that equilibrium is maintained between the various chlorine compounds by the reactions displayed above. Then the equilibrium ratios between the densities of the chlorine compounds take the form

$$\frac{[\text{Cl}]}{[\text{ClO}]} = \frac{k_{18}[\text{O}] + k_{25}[\text{NO}]}{k_{17}[\text{O}_3]},$$

$$\frac{[\text{Cl}]}{[\text{HCl}]} = \frac{k_{19}[\text{OH}]}{k_{22}[\text{H}_2] + k_{23}[\text{CH}_4]}.$$

<sup>5</sup>According to the calculations in [80], the average rate of ozone destruction in the hydrogen cycle is  $2 \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$ , while those of [37] give  $7 \times 10^{11} \text{ cm}^{-2} \text{ sec}^{-1}$ .

Here  $k_1$  is the rate constant of the particular process and the processes (19) and (20) have been disregarded because they are inefficient compared to (17) and (18). We shall use the above relations with a molecular-hydrogen concentration of  $5 \times 10^7$  [20, 91] and a methane concentration of  $(2-10) \times 10^{-7}$  [20, 37, 91]. We then find on considering the range of variation of the OH density [37, 77–80] that an appreciable part of the chlorine is in the form of the compound ClO at the heights considered.

Under our conditions, the loss of oxygen radicals in the chlorine cycle is governed by the reactions (17) and (18), and since  $[\text{Cl}] \ll [\text{ClO}]$ , the number of oxygen radicals destroyed per unit volume per unit time is

$$2k_{18}[\text{ClO}][\text{O}] + k_{18}[\text{ClO}][\text{NO}]$$

Table III includes the vertical distribution of the radical loss in the chlorine cycle as determined from this formula. In accordance with [37], an activation energy of 1 kcal/mole was used for reactions (17), (18), and (21). It was further assumed that the chlorine concentration is the same in the stratosphere as in the lower atmosphere, where it is  $10^{-9}$  [80, 92]. In addition, the calculated results of [37] were used for the relative concentration of the ClO ( $[\text{ClO}]/([\text{ClO}] + [\text{HCl}])$ ), which is of the order of unity.

According to this calculation, which is of the nature of an estimate, the total loss of oxygen radicals in the chlorine cycle is  $10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$ .<sup>6</sup> This is comparable with the rate of formation of oxygen radicals ( $10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$ ). This estimate is high. Chlorine of natural origin is present in compounds of the HCl type. It is therefore easily washed out by water and its concentration is lower in the stratosphere than at the surface. Nevertheless, it may be concluded on the basis of the above estimate that the chlorine cycle is important in the atmosphere's ozone balance.

Summarizing the data in Table III, we can form the following picture of the destruction of atmospheric ozone. The chlorine, nitrogen, and oxygen cycles are basic to the process. The destruction of atmospheric ozone is uniform through the thickness of the stratosphere in the chlorine cycle, occurs in the middle layers of the stratosphere in the nitrogen cycle, and for the most part in the upper atmosphere in the oxygen cycle. The actual values of the decay rates given in Table III are of tentative nature. This is due in part to the simplified calculating scheme, in which, at the very outset, we averaged the principal characteristics over geographic area and over time and did not take account of the effects of the various ozone-destruction cycles on one another.

The basic error of the calculation results from our inaccurate knowledge of the component concentrations used in the calculation and our neglect of certain processes. For example, if the chlorine cycle lacked the process (21), which is of no fundamental importance for it, the loss of ozone in this cycle would have been reduced by two-thirds. We note that the stratosphere contains large numbers of electronically excited oxygen molecules, O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>), whose concentration is comparable with that of the nitrogen oxides. In addition, more than a few of the molecules in the stratosphere are in a vi-

<sup>6</sup>According to calculations by Stolarki and Cicerone [37] for the chlorine concentration considered here ( $10^{-9}$ ), the rate of ozone destruction in the chlorine cycle is  $7 \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$ , while the calculations of Wofsy and McElroy [80] give  $2 \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$ .

brationally excited state. Molecules and radicals with which it is difficult to work in the laboratory are also present in the stratosphere. All of these things may result in processes that are specific for the atmosphere and difficult to observe under laboratory conditions, but nevertheless influence the atmospheric ozone balance.

According to Table III, the total ozone loss amounts to  $2 \times 10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$ , or double the rate of formation of atmospheric ozone. The disagreement between these figures characterizes the error of the results given in Table III, which must be regarded as estimates. Nevertheless, they convey the general picture of stratospheric ozone destruction correctly.

### Ecological Problems of Atmospheric Ozone

Thus, we find that the oxygen, nitrogen, and chlorine cycles are basic in the atmospheric ozone budget. Therefore any appreciable change in the amount of nitrogen oxides or chlorine in the atmosphere will disturb the existing amount and distribution of ozone in the atmosphere. Unfortunately, human practical activity is beginning to contribute precisely to the principal cycles in which atmospheric ozone is destroyed—the nitrogen and chlorine cycles. This state of affairs is naturally disquieting and requires attentive analysis.

As for the nitrogen cycle, the effect of human activity is to increase the amount of nitrogen oxides in the atmosphere. Nitrogen oxides are not formed effectively in the atmosphere. This requires breaking the bond of the nitrogen molecule, which has an energy of 9.8 eV. The same applies to the destruction of the oxides. Thus, the reactions examined above involve transitions between different types of oxides, but not with their destruction to form nitrogen molecules. Therefore the input of nitrogen oxides into the atmosphere is small.

Approximately  $10^{34}$  molecules of nitrogen oxides enter the stratosphere by natural means each year<sup>[93]</sup>. One American supersonic airplane produces  $5 \times 10^{31}$  molecules of nitrogen oxides annually<sup>[94]</sup>. Although the amount of nitrogen oxides entering the stratosphere as a result of supersonic flights depends strongly on the type of aircraft and the altitude at which they are flying, this estimate indicates that supersonic aviation is capable of changing the nitrogen-oxide content of the atmosphere at the present level of its development<sup>[80, 93-96]</sup>.

If we assume that the "cost" of one nitrogen oxide [molecule] is 20 eV<sup>[30]</sup>, we can establish that a power on the order of  $10^6$  kW is necessary to produce the nitrogen oxides that enter the atmosphere. This is much lower than the natural powers. (For example, a power of  $8 \times 10^{10}$  kW is expended on the photolytic destruction of nitrogen dioxide, and the power industry also produces  $10^{10}$  kW at the present level of its development.) Therefore the formation of nitrogen oxides in quantities that exceed the natural values may become a side effect of human industrial activity.

Large amounts of nitrogen oxides may be formed in the production of fertilizers. Approximately<sup>[97]</sup> 60 million tons<sup>7)</sup> of bound nitrogen are now being produced each year (nature produces about as much), and this

<sup>7)</sup>If it is assumed that the bound nitrogen is formed in the reaction  $2\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{NH}_3 + 3\text{O}_2 - 263 \text{ kcal/mole}$ , the "cost" of forming a molecule of bound nitrogen is the same as that for an NO molecule—2.8 eV. From this we find that  $4 \times 10^7$  kW of power are expended in the production of this amount of bound nitrogen.

figure shows a tendency to double every 7 years. Bound nitrogen is nitrogen that has been separated from molecular nitrogen and has entered into the composition of other chemical compounds. These chemical compounds are oxidized in the atmosphere and the nitrogen goes over into the oxide form. Nitrogen-containing chemical fertilizers evaporate, so that the bound nitrogen enters the atmosphere. The input of bound nitrogen into the atmosphere in the form of ammonia over fertilized areas in summer is about  $10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$ <sup>[98]</sup>. If this input were maintained over all of the earth's land areas throughout the year, this would result in an annual escape of more than  $10^{37}$  nitrogen atoms into the atmosphere in molecules of chemical compounds. However, these compounds are readily washed out by water and returned to the earth before they reach the stratosphere. Nevertheless, an increase of soil-bound nitrogen will result in an increased quantity of nitrogen oxides entering the stratosphere.

The injection of nitrogen oxides into the atmosphere increases as a result of high-altitude explosions. Research<sup>[94, 99-102]</sup> that has been done in this area indicates that high-altitude nuclear explosions influence the stratospheric nitrogen-oxide content. For example, according to the calculations of<sup>[94, 98]</sup>, about  $10^{34}$  nitrogen oxide molecules were formed in the atmosphere as a result of nuclear explosions in 1961–1962. This number is comparable to the natural yearly injection of nitrogen oxides into the atmosphere. We note that the effects of a nuclear explosion are also felt after the explosion as radioactive substances decay in the atmosphere.

The influence of human industrial activity on the chlorine cycle of atmospheric-ozone destruction is manifested in the accumulation of freons (the compounds  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$ ) in the atmosphere. World freon production is now approaching 1 million tons per year and doubling approximately every four years.<sup>8)</sup> Large amounts of these inert gases eventually enter the atmosphere. The concentration of freons at the earth's surface is now above  $10^{-10}$ <sup>[103, 107]</sup>, an amount that has been produced by human activity alone and is increasing steadily. Freons are carried by atmospheric convection currents into the stratosphere, where they decompose under the action of solar radiation, forming chlorine atoms and radicals.

Let us estimate the role of the chlorine in ozone-destruction processes after it is formed by the photodecay of freons in the stratosphere. Let us assume in accordance with<sup>[105]</sup> that the  $\text{CF}_2\text{Cl}_2$  concentration is  $10^{-10}$  and the  $\text{CFCl}_3$  concentration  $6 \times 10^{-11}$ , so that the total concentration of chlorine atoms in the atmosphere due to freons is  $4 \times 10^{-10}$ . Using the estimate obtained in analysis of the chlorine cycle, we find that this amount of chlorine in the atmosphere will cause the loss of  $4 \times 10^{12}$  ozone molecules per second per square centimeter of the earth's area. Although this estimate is on the high side, it indicates that the introduction of freons into the atmosphere is capable of influencing the atmospheric ozone budget even at the present level of their production.

### The Ion Cycle

The ion cycle of ozone destruction is determined by the content of ozone molecules with negative ions, and proceeds according to the scheme

<sup>8)</sup>If all of the freon produced were released into the atmosphere and remained in it, the atmosphere would have a freon concentration of  $2 \times 10^{-10}$ .





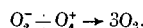
Positive ions do not participate in this process because the ionization potential of the oxygen molecule is lower than that of the ozone molecule and charge transfer from  $\text{O}_2^+$  to  $\text{O}_3$  is not energywise favored. According to the measurements of [108, 109], the rate constant for the process (25) at room temperature is  $k_{25} = 4 \times 10^{-10}$  cm<sup>3</sup>/sec. The rate constant  $k_{26}$  for the next process is about the same.

To arrive at understanding of the possible role of the ion cycle in the destruction of ozone, we make the following estimate. Assuming the ion density to be vertically constant, we establish the ion density at which the rate of ozone destruction under the action of the ion is equal to the rate of its formation by photodissociation of molecular oxygen. This estimate takes the form

$$\int [\text{O}_3] (k_{25} [\text{O}_2^+] + k_{26} [\text{O}_3^-]) dh = 10^{13} \text{ cm}^{-2}/\text{sec}^{-1}$$

and gives  $N_i = [\text{O}_2^+] + [\text{O}_3^-] \approx 2 \times 10^3$  cm<sup>-3</sup> for the unknown ion density.

Let us estimate the amount of energy that must be expended to maintain this ion density. The stratosphere loses complex ions as a result of pair recombination, a process of the type<sup>9)</sup>



At stratospheric temperatures, this process has a recombination coefficient  $\alpha = 4 \times 10^7$  cm<sup>3</sup>/sec,<sup>[110]</sup> so that the recombination rate per unit time per unit volume needed to maintain the above ion density  $N_i$  is  $\alpha N_i^2 \approx 2$  cm<sup>-3</sup> sec<sup>-1</sup>. Assuming that an energy of 30 eV is expended in forming a pair of ions, we find from this that the power required to maintain this ion density over a unit area is  $4 \times 10^{-11}$  W/cm<sup>2</sup> or, for the entire area of the earth,  $2 \times 10^4$  kW. This is many orders smaller than the power consumed by industry at the present time.

Let us analyze the results. Ions are formed in the atmosphere under the action of cosmic rays and streams of high-energy particles of cosmic origin, and also by the decay of radioactive nuclei. These conditions of charged-particle formation can vary sharply, and the charged-particle density itself also varies with them. The average ion density in the stratosphere is considerably below the estimate obtained, so that the ion cycle of ozone destruction does not contribute to the atmospheric-ozone budget. Nevertheless, this cycle requires special attention. It follows from the above estimates that this cycle is capable of clearing ozone artificially from limited areas, e.g., as a result of sowing of radioactive nuclei above them. The number required for this purpose is easily attainable in practice according to energy estimates. And in such a situation the contrary is also possible — ions may be formed as a byproduct of some industrial process and subsequently influence atmospheric ozone. Therefore the ion cycle of ozone destruction must be included among the ecological problems of the atmosphere.

## CONCLUSION

We have examined certain concrete problems arising from the effects of human industrial activity on the

<sup>9)</sup>Under stratospheric conditions, electrons are captured by the molecule in the process  $e + \text{O}_2 + (\text{N}_2, \text{O}_2) \rightarrow \text{O}_2^- + (\text{N}_2, \text{O}_2)$ . Therefore negative charge is transferred only by negative ions.

TABLE V

Energy fluxes in nature and as a result of human activity, kW/km <sup>2</sup> :	
Solar radiation to the earth	4 · 10 <sup>5</sup>
Evaporation, convection	10 <sup>5</sup>
Energy consumption in the Ruhr (West Germany)	1 · 10 <sup>4</sup>
Photodecay of ozone in the stratosphere	10 <sup>4</sup>
Energy consumption in Japan	2 · 10 <sup>3</sup>
Smog threshold	10 <sup>3</sup>
Photodecay of nitrogen dioxide in the stratosphere	200
Photosynthesis	200
Photodissociation of oxygen in the upper atmosphere	80
Geothermal heat flux	60
Average energy consumption	20
Natural release of methane from the earth's surface	4
Production of bound nitrogen in nature	0.07
Production of bound nitrogen by man	0.07
Formation of NO in the stratosphere	0.002
Maintenance of stratospheric degree of ionization at which the rate of ozone destruction is doubled	0.035

properties of the earth's atmosphere. Owing to a lack of information and the complexity of the phenomena in the atmosphere, we shall not always be able to determine not only the orders of magnitude characterizing the variation of the atmosphere's parameters, but even the direction that this influence takes. Nevertheless, it can be said for any of the cases considered that these types of human effects on the atmosphere are becoming significant at the contemporary level of industrial development and require careful investigation. In particular air pollution is capable at the present level of energy production of influencing the optical properties of the atmosphere and hence climate, not only in certain areas of the earth, but over the entire globe. Further, the present-day level of energy consumption makes possible the development of photochemical smog, other conditions favorable, not only over cities, but also over large industrial areas and even over specific highly developed countries. The production of mineral fertilizers and freons and the flights of supersonic aircraft in the stratosphere are beginning to influence the atmospheric ozone balance in the stratosphere. All of these problems require careful study. The level on which human industrial activity influences the atmosphere is established primarily from the amounts of energy expended. The concluding Table V therefore lists the data used above for the energy flows generated in nature and by man.

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