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EARLY STAGES IN THE EVOLUTION OF THE ATMOSPHERE AND CLIMATE ON THE EARTH-GROUP PLANETS

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Translation of "O rannikh etapakh evolyutsii atmosfery i klimata na planetakh zemnoy gruppy," Academy of Sciences USSR, Institute of Space Research, Moscow, Report PR-337, 1977, pp. 1-50.

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16. Abstract The early evolution of the atmospheres and climate of the Earth, Mars and Venus is discussed, based on a concept of common initial conditions and main processes (besides known differences in chemical composition and outgassing rate). It is concluded that: 1) liquid water appeared on the surface of the earth in the first few hundred million years; the average surface temperature was near the melting point for about the first two eons; CO_2 was the main component of the atmosphere in the first 100-500 million years; 2) much more temperate outgassing and low solar heating led to the much later appearance of liquid water on the Martian surface, only one to two billion years ago; the Martian era of rivers, relatively dense atmosphere and warm climate ended as a result of irreversible chemical bonding of CO_2 by Urey equilibrium processes; 3) a great lack of water in the primordial material of Venus is proposed; liquid water never was present on the surface of the planet, and there was practically no chemical bonding of CO_2; the surface temperature was over 600°K four billion years ago.

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ANNOTATION

The early evolution of the atmospheres and climates of the Earth, Mars and Venus is discussed, based on a concept of common initial conditions and main processes (besides some known differences in chemical composition and rate of outgassing). Primary conclusions are: (1) Liquid water appeared on the terrestrial surface in the first few hundred million years. The average surface temperature was near the melting point for approximately the first two eons. Some quasiperiodical variations of temperature, albedo and atmospheric CO_2 were possible. More CO_2 was in the atmosphere during all this period than recently. CO_2 was the main component of the terrestrial atmosphere in the first 100-500 million years. (2) Much more temperate outgassing and low solar heating led to the much later appearance of liquid water on the Martian surface. This event took place only one or two billion years ago. At this time, a Martian era of "paradise" began (rivers, relatively dense atmosphere, warm climate), which ended as a result of irreversible chemical bonding of CO_2 by Urey equilibrium processes. (3) Contemporary physical conditions on Venus are most simply explained if a great lack of water in the primordial material from which Venus was born is proposed. Liquid water was never present on the surface of the planet, and there was practically no chemical bonding of CO_2. The temperature of the venusian surface was already more than 600 °K four billions years ago.

EARLY STAGES IN THE EVOLUTION OF THE ATMOSPHERE AND CLIMATE ON THE EARTH-GROUP PLANETS

V.I. Moroz and L.M. Mukhin

1. Introduction: Composition of the Primitive Atmosphere

The atmospheres of the Earth-group planets differ greatly in chemical composition from the average cosmic abundance of the elements. Moreover, the content of nonradiogenic inert gas isotopes is close together in the atmosphere of the Earth and in normal chondrites [34]. The proposal arises from this that the atmosphere of the Earth and other planets of the Earth-group separated out by outgassing of their solid bodies. It is significant that the average composition of the planetary lithospheres is close to that of chondrites. The latter is explained naturally, if it is assumed that the planets were formed in the process of accretion of meteorite particles. These concepts are generally accepted. However, the early stages of evolution of the planetary atmospheres have been very poorly studied. One possible hypothetical alternate version of the evolution of the atmosphere and climate of the Earth, Mars and Venus is considered in the present work. /5

The comparative characteristics of the present atmospheres of the Earth-group planets are given in Table 1. For the Earth and Mars, besides the composition of the atmosphere, the total volatile compound content is given, including the hydrosphere, cryosphere and sedimentary rocks. The data in this table show that the main products of outgassing of the Earth and Mars are H_2O and CO_2, in a 5:1 ratio or 10:1 by mass. This ratio is many orders of magnitude less for Venus (10^{-3}:1).

The CO_2:N_2 ratio is 100 for the Earth and Mars and probably close to that for Venus. There are large amounts of free oxygen only in the atmosphere of the Earth, owing to biochemical processes. In analysis of the gas content of chondrites, precisely H_2O and CO_2 are the main components. This naturally is in agreement with the concept of the formation of the atmospheres reported above. The mass of CO_2 released during outgassing of the Earth and Venus is approximately the same. The Martian lithosphere released one and a half or two orders of magnitude less CO_2 and H_2O (per unit area of the surface) than that of the Earth. /7

The question as to how the outgassing process was distributed over time is unclear. The hypotheses of catastrophic and uniform outgassing can be pointed out, as alternative points of view. The former proposes rapid evolution of the main mass of the atmosphere in some initial epoch [7] and the latter, gradual separation of the

TABLE 1. COMPOSITION OF THE ATMOSPHERE OF THE EARTH, VENUS AND MARS (BASIC COMPONENTS)

[a] Газ	[b] Земля		[c] Венера	[d] Марс	
	Современная [e] атмосфера г.см$^{-2}$	Атмосфера + гидросфера + осадочные пор-оды, г.см$^{-2}$ [f]	г.см$^{-2}$	Современная [e] атмосфера г.см$^{-2}$	Полная масса продуктов дегазации /оценки по ^{36}Ar и ^{15}N/^{14}N /, г.см
H_2O	$\simeq 1.0$	$3.3 \cdot I0^{5}$	IC^{3} **	10^{-3}	$I.5 \cdot I0^{3}$ $(I,5 \cdot I0^{4})$***
CO_2	$4.6 \cdot I0^{-4}$	$5 \cdot I0^{4}$ *	$I,I \cdot I0^{5}$	I6	$2 \cdot I0^{2}$ $(2 \cdot I0^{3})$***
N_2	$8 \cdot I0^{2}$	$8 \cdot I0^{2}$	$\leq 5 \cdot I0^{3}$	$2.5 \cdot I0^{-I}$	4 (40)***
O_2	$2 \cdot I0^{2}$	$2 \cdot I0^{2}$	$\leq I0^{2}$	$2 \cdot I0^{-I}$	$2 \cdot I0^{-I}$

* According to Poldevaart [27]; an estimate of $2 \cdot 10^{4}$ g·cm^{-2} for CO_2 is given by Rubey [29].

** From Venera-9 and -10 measurements [23]; the remaining estimates for Venus have been taken from the review of Moroz [22].

*** First figure, most likely estimate; second (in parenthesis), maximum. The estimates of Owen and Bieman [26], Bieman et al [4] and McElroy et al [21], obtained from Viking data, were used.

Key:
- a. Gas
- b. Earth
- c. Venus, g·cm^{-2}
- d. Mars
- e. Present atmosphere, g·cm^{-2}
- f. Atmosphere + hydrosphere + sedimentary rocks, g·cm^{-2}
- g. Total mass of outgassing products (estimates from ^{36}Ar and ^{15}N/^{14}N), g·cm^{-2}

volatiles during the entire geological history of the planet [17]. It is possible that outgassing initially took place rapidly and, then, became more or less uniform. Orogenic cycles [36] should have produced a definite irregularity. We subsequently will adhere to the uniform outgassing hypothesis, and we would like to emphasize that this is only one of the conceivable alternate versions. We will subsequently consider the outgassing rate to be constant. However, it is significant that deviations from uniformity (if they are not too rapid) can result in a change in the time scale, but they evidently do not qualitatively affect the nature of the processes under consideration.

Substantial difficulties arise in the problem of the evolution of the atmosphere and hydrosphere of the earth, in comparing geological data on the history of development of the earth with astrophysical models of evolution of the sun. The fact is that calculations of models of the internal structure of the sun indicate a gradual increase in its luminosity in the period of its stay on the main sequence (see, for example, the book of Schwarzschield [35]). During the lifetime of the solar system ($4.6 \cdot 10^{-9}$ years) its luminosity has increased approximately 40%. /8 This should have caused low average temperatures on the surface of the primitive Earth, below the freezing point of water. At the same time, paleological data indicate the presence of life and open water basins on the Earth $3.5 \cdot 10^{-9}$ years ago [30]. This discrepancy apparently was first noted by Sagan and Mullen [33]. They proposed a possible explanation of this contradiction, that small (10^{-4}-10^{-5}) additions of NH_3 to the atmosphere could have provided the necessary greenhouse effect, to maintain the temperature of the surface of the earth above 273°K.

The hypothesis is frequently expressed, that the primitive atmosphere of the earth was reducing, and that it contained considerable amounts of NH_3, CH_4 and H_2. It should be noted that there are no irrefutable geological proofs of the presence of these gases in the primitive atmosphere. The primary argument is considered to be that the reducing atmosphere supposedly was necessary for the synthesis of prebiological organic matter. However, one author [24] has recently shown that prebiological synthesis takes place fairly actively in volcanoes and that, consequently, this major argument in favor of the reducing primitive atmosphere is not convincing. The question of possible relationships of reducing and oxidizing components in the early atmosphere of the earth will be examined in detail in a separate work.

To speak specifically of ammonia, the possibility of its presence in the primitive atmosphere is highly debatable. It dissolves extremely rapidly in water, and it also is destroyed by the ultraviolet radiation of the sun [1] and by chemical reactions with oxygen. Estimates of the oxygen abundance in the early atmosphere of the earth, generated by means of the dissociation of H_2O and CO_2, are from 0.2 $g \cdot cm^{-2}$ [3] to approximately 20 $g \cdot cm^{-2}$ [6]. The lower limit evidently excludes the presence of appreciable steady state concentrations of ammonia. /9

Since the existence of the hydrosphere by the end of the first eon can be considered indisputable, other components must be considered, which are capable of providing the melting temperature by means of the greenhouse effect, despite the low luminosity of the sun. It seens natural that they could have been CO_2 and H_2O. Carbon dioxide is the main component of the atmosphere of Mars and Venus; the carbon dioxide content of the present atmosphere of the earth is low, 0.03%. Nevertheless, precisely by virtue of the low luminosity of the sun in the early stages of its development, the earth could have had a fairly dense carbon dioxide atmosphere, which leads to a number of interesting consequences, which will be considered below.

2. Climate of the Primitive Earth and CO_2 Accumulation

A. Outgassing and climate

We propose that, in the initial stage of development of the earth, four and a half billion years ago, the gas pressure on its surface was not over 10^{-3}-10^{-2} atm. Under such conditions, the effect of the atmosphere on the thermal regime can be disregarded, and the average surface temperature was close to the average effective temperature of the planet.

$$\sigma \bar{T}_e^4 = \frac{E}{4}(1 - A) + q \qquad (1)$$

where E is the solar constant, A is the spherical albedo, σ is the Stefan-Boltzmann constant and q is the internal heat flux. The average temperature of the surface of the planet, devoid of atmosphere, is

$$\bar{T}_S = \bar{T}_e \ \varepsilon^{-1/4} \qquad (2)$$

where ε is the coefficient of radiation of the surface. $\bar{T}_S$ differs from $\bar{T}_e$ by a total of a few degrees, if $\varepsilon \simeq 0.9$, a typical value for rocks. Term q, under present earth conditions, is negligibly small; however, in the first hundreds of millions of years, the situation could have been different. We will disregard this term in thermal regime calculations for this epoch. /10

We will propose subsequently that, in the initial stage of outgassing, the albedo of the earth was rather small ($\gtrsim$ 0.05), by analogy with the moon and Mercury. After the appearance of an atmosphere, it increased, due to the condensation of water (on the surface and in clouds) and weathering. Besides, we propose that the value of the solar constant in this effort was 40% less than at present ($1.37 \cdot 10^6$ $\text{erg} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$).

The average temperature of the planets vs. albedo is shown in Fig. 1, for two values of the solar constant, the present and 40% below the present. We see that, at $A=0.05$, the initial average temperature of the surface of the earth was about 248°K and was considerably below the condensation temperature of H_2O. The initial average temperature of Mars was above 200°K and that of Venus about 288°K.

Formula (1) was derived on the assumption that a planet, on which a flux $\pi R^2 E$ is incident, reradiates the absorbed fraction of it (1-A) uniformly on all sides, with an area πR^2, at temperature $\bar{T}_e$. The actual surface temperature is close to $\bar{T}_s = \bar{T}_e$, only in the event there is some mechanism which equalizes it. In the case of a planet devoid of an atmosphere, rotation and the change of seasons (the latter to a very much smaller extent and with a fairly large inclination of the equator to the ecliptic) are such mechanisms. When the mass of the atmosphere becomes sufficiently large, advection (the transport of heat from the equatorial regions to the middle and polar latitudes) and condensation, which releases the latent heat in colder regions, led to equalization of the temperature.

If the atmosphere contains a gas which absorbs the infrared radiation of the surface and, at the same time, is fairly transparent to solar radiation, it produces a greenhouse effect, and the value of $\bar{T}_s$ then can considerably exceed $\bar{T}_e$. H_2O and CO_2, the main products of outgassing, are very effective in this sense, and their accumulation in the gas phase should have resulted in a greenhouse effect. In consideration of H_2O and CO_2 accumulation, the possibility of their change to the condensed phase (especially H_2O) and chemical bonding in sedimentary rocks must, however, be taken into account. /11

The main mechanism of the flow of carbon dioxide entering the atmosphere is reactions with silicates, as a result of which, the latter are converted into carbonates [37]. At temperatures of ∿ 300°°K and below, this process occurs practically, only in the presence of liquid water (the water dissolves CO_2 and the solution reacts with the silicates). However, because of the low temperature in the initial epoch, there was no liquid phase of H_2O, the flow mechanism did not operate, and carbon dioxide should have accumulated in the atmosphere and become its main component for a long time. The increase in CO_2 concentration gradually raised the temperature of the surface. This resulted in an increase in the amount of water vapor in the atmosphere which, in turn, increased the greenhouse effect. CO_2 accumulation continued, until the greenhouse effect ensured an increase in temperature to the melting point of ice. The appearance of liquid water resulted in turning on the CO_2 flow mechanism. As a result, the carbon dioxide content should have automatically been maintained at that level, which provided the melting point, right up until the time when the solar constant reached a sufficiently high value (approximately 0.8 of the present value).

B. Greenhouse effect

The greenhouse effect in planetary atmospheres has been considered repeatedly, especially in connection with the thermal regime of the present atmosphere of Venus. A survey of the literature and a rather detailed report of the problem can be found in the work of Sagan [31]. /12

In the case when there is only radiant heat transport, the coefficient of absorption does not depend on wavelength ("gray" atmosphere and optical thickness $\tau_0 >> 1$), and the brightness temperature of the surface T_{Bs} is connected with the effective temperature by the formula

$$(T_{Bs}/T_e)^4 = 1 + 3/4 \cdot \tau_0 \qquad (3)$$

This expression can be used for an atmosphere with a coefficient of absorption which changes with wavelength, by using the Rosseland average as τ_0. If the coefficient of absorption reverts to zero in some wavelength intervals, the Rosseland average also reverts to zero and, in this case, τ_0 must be averaged by other methods (the Planck average, transparency window approach). A procedure for calculation of the average optical thickness τ_0, which permits the correct value of $\bar{T}_s$ to be obtained by means of equation (3), both in the case of the transparency window and with great optical thickness at all wavelengths, is described in the Appendix. It evidently gives probable estimates of $\bar{T}_s$ in the intermediate case.

Optical thickness τ_0 is a function of composition, pressure and temperature. The transmission of an atmosphere consisting only of CO_2 vs. the amount of it u_{CO_2}, for the Earth, Venus and Mars, is presented in Fig. 2. For the earth and Venus, it is practically coincident, and it differs somewhat for Mars, because of the lower value of the acceleration of gravity (this results in lower pressures at the same u_{CO_2}). The transmission spectrum of a pure carbon dioxide atmosphere is characterized by wide transparency windows, which "close," only with very large abundances of it ($\geq$ 10 $kg \cdot cm^{-2}$). /13

The addition of H_2O, in amounts of 1-10 $g \cdot cm^{-2}$, produces noticeable opacity in these windows (Fig. 3), and it sharply increases τ_0 . If the amount of H_2O released by outgassing of the interior is much greater than necessary for saturation (at the temperature of the lower layers of the atmosphere), the H_2O partial pressure will be close to the saturation pressure. In this case, the H_2O content of the atmosphere and, together with it, τ_0 depend strongly on temperature.

It may turn out that, during H_2O release, the temperature due to the greenhouse effect increases so rapidly, that the T (P_{H_2O}) curve goes above the saturation curve. The data presented in Fig. 4 show that, for Venus and even for the earth, in principle, such a possibility could have occurred. Then, all the incoming water remains in the atmosphere in the form of vapor, the accumulation of which rapidly increases the opacity, and a runaway greenhouse develops. It is assumed that the process occurred in just this manner on Venus [28].

The absence of the liquid phase explains why so much carbon dioxide remained in the atmosphere of Venus, and only where the water went then is unclear. The partial pressure of H_2O vapor reached several hundred atmospheres, if it is assumed that water was released in the same amount as on Earth.

In a formal approach, the curves presented in Fig. 4 can be interpreted as an effective argument in favor of a reduced value of the solar constant in the distant past. In fact, with its value equal to the present value, we obtain the absence of the liquid phase and a runaway greenhouse on the primitive Earth, just as on Venus. Actually, the conclusion as to the runaway greenhouse, obtained in this manner, is wrong, since this approach /14 assumes that the temperature is the same at all points on the planet. Moreover, in just the initial stage of outgassing, when the mass of the atmosphere was small, advection does not equalize the latitudinal temperature variation, and effective cold traps develop in the polar regions, which collect H_2O. We present quantitative estimates of the polar region temperature, which determine their effectiveness as cold traps, in Section 2C for the Earth and Section 4 for Venus.

Below, we consider two alternate versions of an equalibrium greenhouse effect, dry (no H_2O in the atmosphere) and wet (H_2O abundance close to saturation). Dry models are utilized with a small mass of the atmosphere and wet, with large; we also have approximately determined the boundary separating the regions of applicability of these two alternate versions in Section 2C.

In the wet models, it is assumed that the H_2O pressure is half the saturation pressure (corresponding to T_s) and that the altitude scale is one fourth of the average. With $T_s \lesssim 273°$ K, the latter is practically determined by carbon dioxide. The water vapor distribution in the present atmosphere of the earth has similar characteristics. The assumed H_2O content in the vertical column, consequently, equals

$$u_{H_2O} = \frac{1}{8} m_{H_2O} \frac{p_{sat}\bar{H}}{kT} \approx \frac{1}{8} \frac{m_{H_2O}}{m_{CO_2}} \frac{p_{sat}}{g}. \qquad (4)$$

Here, m_i is the molecular weight. We note that wet models for Mars are characterized by larger values of u_{H_2O} and τ_0 than for the earth, with the same g. Since p_{sat} depends strongly on temperature in wet models, τ_0 depends very much more strongly on T_s than in the dry models.

Equilibrium values of T_s can be found by graphical solution of equation (3), with function τ_0 (T) taken into account. An example of such a solution is given in Fig. 5 (Earth and Venus). /15
The equilibrium values are determined by the intersection of the T_s (τ_0, T_e) and τ_0 (T_s) curves. Curves of τ_0 are given for the dry and wet versions. Equilibrium value T_s vs. CO_2 content in the vertical column is presented in Fig. 6, in both versions with different T_e.

If the T_s (τ_0, T_e) and τ_0 (T) curves do not intersect, it means that thermal equilibrium cannot be achieved with radiant heat exchange alone. In this case, convection is included, which removes the excess heat flux. Convection can occur in the presence of intersecting T_s (τ_0, T_e) and τ_0 (T) curves, if the temperature gradient in the atmosphere reaches a certain critical value (adiabatic gradient).

The left deflected upper part of the T_s (u_{CO_2}) curves, corresponding to the wet models (Fig. 6), undoubtedly do not materialize, because of convective instability. The kind of change expected in this picture, due to convection, is shown by a dashed line in Fig. 6. It was conditionally assumed that, in the case of convective transport, 100 $g \cdot cm^{-2}$ CO_2 remains above the tropopause level, that the temperature at this level does not equal T_e, and that there is a dry adiabatic gradient below. Such a scheme satisfactorily describes the structure of the present atmosphere of Venus.

The amounts of CO_2 necessary to provide a temperature of 273° K on the earth and Mars through the greenhouse effect are presented in Table 2. On Venus, the melting point was reached in the very beginning.

TABLE 2. AMOUNT OF CO_2 IN THE VERTICAL COLUMN REQUIRED TO REACH H_2O MELTING POINT ON THE EARTH AND MARS, WITH LOW INITIAL SOLAR ILLUMINOSITY (SOLAR CONSTANT = 0.6 OF THE PRESENT VALUE)

Планета	Возраст эоны	A = 0.05			A = 0.2		
		T_e °K	CO_2, г.см$^{-2}$		T_e °K	CO_2, г.см$^{-2}$	
			сух.мод.	вл.мод.		сух.мод.	вл.мод.
Земля	0	242	700	12	232	2500	40
Марс	0	197	20000	200	188	50000	300
Марс	3*	215	8000	110	207	15000	160

*An approximately uniform increase in the solar constant is assumed; at t = eon 3, E = 0.9 E_0 is adopted for Mars, where E_0 is the present value of the solar constant.

Key:
- a. Planet
- b. Age, eons
- c. CO_2, $g \cdot cm^{-2}$
- d. Dry model
- e. Wet model
- f. Earth
- g. Mars

It follows from the data presented in the first line of Table 2 that, for the earth, the amount of CO_2 required to reach the melting point is

$$700 < u^* < 2500 \ g \cdot cm^{-2} \qquad (5)$$

in the dry model and

$$12 < u^* < 40 \ g \cdot cm^{-2} \qquad (6)$$

in the wet. Estimate (5) corresponds to approximately 0.02-0.1 /16
of the total amount of CO_2 given off during outgassing (see Table 1). Based on the assumption of a uniform outgassing rate, we reached the conclusion that not over $5 \cdot 10^8$ years was required for its release. In the wet model, this amount can be reduced by at least a factor of 10. In the next section, we consider the problem of a choice between the dry and wet models.

We have not considered the effect of cloud cover on the thermal regime at all. In principle, with increase in the H_2O content of the atmosphere, the cloud cover should increase on the average, resulting in an increase of A and a decrease of $\bar{T}_e$. Thus, clouds should result in slowing down the increase of $\bar{T}_s$ with increase in u_{CO_2} and increase in $u_{CO_2}^*$. However, this increase would scarcely be significant. It is known that, in the approximate theory of the climate of the present Earth, the effect of change in cloud cover area can be disregarded [5]. Actually, the increase in albedo connected with the development of clouds is /17 compensated by a reduction in the outgoing radiation flux (that part which goes out through the transparency windows decreases). We can obtain an estimate of the maximum u^*, without taking account of this compensating effect. We assume that, because of clouds, $A=0.5$ (one and a half times more than for the present Earth). Then, $T_e=208°$ K, $u^* \simeq 10$ kg$\cdot$cm^{-2} in the dry model and about 300 g$\cdot$cm^{-2} in the wet. In fact, with an average earth temperature of about 0° C, the cloud cover should be less developed, of course, than in the modern epoch, and the value $A=0.2$ adopted above appears to be completely reasonable.

C. <u>Effect of uneven temperature distribution</u>

Up to the present time, we have not considered the circumstance that the surface temperature undergoes considerable changes (daily, seasonal, latitudinal). The latitudinal variations of the average annual temperature are the most significant. It should be appreciably colder at the pole than at the equator, especially with a thin atmosphere. Condensation of H_2O will primarily take place precisely here. Moreover, in an early epoch on the earth, at least seasonal condensation of CO_2 as well, as occurs on the present Mars, is not excluded. How the uneven temperature distribution can affect our estimates of u^* must be examined.

The average daily temperature at the equator, in the absence of an atmosphere,

$$T_{se} = \bar{T}_s \, (4/5)^{1/4}, \tag{7}$$

if the inclination of the equator to the ecliptic $i=0$. With other inclinations, this value depends on the time of year; however, at $i \leq 30°$, the variations are small, and the very difference of T_{se} from $\bar{T}_s$ is within 10°. With albedo $A=0.05$, for the primitive Earth, we have $\bar{T}_{se}=288°$K, higher than the melting point of water.

The maximum local temperature on the planet (if the thermal /18 conductivity of the soil is disregarded) is

$$T_{max} = \sqrt{2}\cdot\bar{T}_s \tag{8}$$

or 342° K, with albedo $A=0.05$. This value decreases by approximately 20°, with thermal conductivity taken into account, even if the latter is very small (just as on the present Mars). However, nevertheless, the excess above the melting point proves to be highly significant. When the total pressure became greater than 6.1 mbar (the triple point of water), the appearance of liquid water in the daytime proved to be possible, in the equatorial and middle latitudes. Theoretically, this circumstance could have cancelled the entire proposed concept or, in any case, strongly slowed down the accumulation of CO_2. However, actually, there evidently was no water in the equatorial and moderate regions in this epoch. Water released from the interior should have been transferred to the cold polar "traps." In the middle latitudes, part of it accumulated in the permafrost layer. There is now a very similar pattern on Mars.

We consider the question of the polar temperatures quantitatively. In the absence of an atmosphere, the average annual temperature at the pole is determined by the equality

$$\sigma \bar{T}_{sp}^{4} = \frac{\sin i}{\pi} (1 - A_p), \qquad (9)$$

where A_p is the albedo at the pole. With $A_p = A$,

$$\bar{T}_{sp} = \bar{T}_s \left(\frac{4 \sin i}{\pi}\right)^{1/4} = 0.844\, \bar{T}_s. \qquad (10)$$

H_2O condensation in the polar caps undoubtedly gives $A_p > A$. The average annual temperatures of the pole of the primitive Earth vs. albedo, calculated by formula (10), are presented in Table 3. The present inclination of 23.5° is assumed. Ward [39] showed that its secular changes, in the case of the earth, is within the ± 5° range; these calculations could hardly be extrapolated so far into /19
the past, but there is no other choice. The CO_2 and H_2O pressures corresponding to equilibrium with the solid phase at the calculated temperatures (P'_{CO_2} and P'_{H_2O}) also are given in Table 3.

We attempt to recreate the pattern of accumulation of volatiles on the primitive Earth, with the low temperatures at the poles taken into account. Even with a very low albedo of 0.05 (which could have occurred at the very beginning of the outgassing process), practically all the water reaching the surface went to the polar regions. Glaciers with an average thickness of 100 m covered the area beyond the northern and southern polar circles (equal to approximately 0.1 of the surface of the planet), during a total time of only 10^7 years, if uniform outgassing is assumed. In the present polar regions of the earth, the albedo of the surface + atmosphere system $A_p \simeq 0.6$ [5]. If this value is adopted for the primitive Earth, we obtain $T_p = 169°$ K and $P'_{CO_2} = 50$ mbar.

When the CO_2 pressure reached the P'_{CO_2} level during outgassing, the accumulation of CO_2 condensate could have started in the polar regions. However, the question as to whether it really began requires more thorough discussion, with advection taken into account. Advection increases T_p, and it can prevent the formation of permanent CO_2 caps. Under the conditions adopted, of reduced luminosity of the sun on the earth, seasonal polar CO_2 caps had to form without fail (alternately, in one hemisphere and the other). However, the capacity of the present reservoir is small (5-10 $g\cdot cm^2$, calculated over the entire surface of the planet), and it can be disregarded in our analysis. /20

TABLE 3. POLAR TEMPERATURE OF PRIMITIVE EARTH

A_p	T_p, °K	P'_{H_2O}, мб [a]	u_{H_2O}, г.см$^{-2}$ [b]	P'_{CO_2}, мб [a]
0,05	2I0	$8\cdot I0^{-3}$	$3\cdot I0^{-8}$	I 860
0,2	20I	$3\cdot I0^{-3}$	$I\cdot I0^{-3}$	950
0,4	I87	$3\cdot I0^{-4}$	$I\cdot I0^{-4}$	250
0,6	I69	$6\cdot I0^{-6}$	$2\cdot I0^{-6}$	50
0,8	I42	$2\cdot I0^{-9}$	$8\cdot I0^{-I0}$	I,5

100% humidity and the same altitude scale of H_2O as for CO_2 are assumed here (since the temperature drops relatively slowly with altitude in the polar regions).

Key: a. mbar
b. $g\cdot cm^{-2}$

The upper limit of the thickness of permanent CO_2 caps is bounded by the triple point of carbon dioxide. When the pressure and temperature at the base of the layer reaches a sufficiently high value, liquid carbon dioxide forms, which flows out around the edges. Sagan [32] discussed such a limiting mechanism for Mars. However, it is now clear that the permanent caps on this planet consist of H_2O ice (in distinction from the seasonal caps of CO_2). At the triple point of CO_2, T=216° K, and pressure P=5 atm. Due to the geothermal gradient, the required temperature can be reached, with a layer of dry ice about 1 km thick. If it is considered that the area of the permanent caps is limited to regions beyond the polar circle, outgassing of about 10 $kg\cdot cm^{-2}$ of CO_2 (averaged over the entire planet), i.e., about 10% of the present level was required to reach such a thickness. Actually, besides CO_2 and H_2O, noncondensing gases, primarily nitrogen, also entered the atmosphere. The accumulation of nitrogen, in the amount of 30-50 $g\cdot cm^{-2}$, was sufficient to destroy the CO_2 caps on the earth, because of advection. Since the question is about the first hundred million years of existence of the earth, the internal heat (term q in equation (1)) could have played a supplementary part in preventing the formation of the polar caps. Most likely, there were not permanent polar CO_2 caps on the primitive Earth.

Even on the present Mars, which receives 2.3 times less heat than the earth, the polar cap residues which disappear in /21 the summer consist of H_2O, and CO_2 evidently does not accumulate in them. The polar caps of the primitive Earth also probably consisted mainly of ordinary ice and snow, but it was cold enough to effectively remove water from the atmosphere and, thereby, to weaken the greenhouse effect. Of the two previously considered models of it, dry and wet, the dry operated at first. The gradual increase in mass of the atmosphere entailed an increase in advection, which resulted in an increase in T_p, a decrease in the polar ice cover and effectiveness of the poles as cold traps. The present difference in the average annual temperatures at the pole and the equator is about 50°, approximately half that on the primitive Earth.

An approximate theory of the general circulation of planetary atmospheres [14] gives the following expression for the temperature difference between the pole and the equator:

$$\delta T = \left(\frac{\varepsilon}{2}\right)^{1/2} \left(\frac{\lambda_1}{k}\right)^{1/4} \frac{(q_A/4)^{9/16}}{\sigma^{1/16}\; c_p{}^{3/4}} \left(\frac{R}{M}\right)^{1/2}, \qquad (11)$$

where M is the mass of the column of the atmosphere ($g \cdot cm^{-2}$), c_p is the heat capacity ($0.85 \cdot 10$ $cm^2 \cdot sec^{-2} \cdot$ degree^{-1} for CO_2), $\lambda_1 = \pi FR\ell/2c$, $\ell = 2\omega \sin \tau$ is the Coriolis parameter (ω is the angular velocity and ϕ is the latitude), c is the speed of sound (250 $m \cdot sec^{-1}$ for CO_2 at T=250° K). Table 4 contains δT vs. M, calculated by formula (11), for the present value of ω and four times as much (it is possible that the earth rotated faster when it was young).

It is clear from Table 4 that, at pressures of 100-300 mbar, advection appreciably levels the temperature difference between the pole and the equator. Basically, this occurs due to an increase in polar temperatures; the equatorial temperatures change considerably less. For the present earth, formula (11) gives understated values; however, it is clear that a pressure of ~ 1 atm is sufficient for a change to the wet model of the greenhouse /22 effect. In this manner, the uneven temperature distribution increases the amount of CO_2 required for the transition through the melting point several times over that of the wet model, calculated for an average temperature (although this amount is less than the dry model gives).

D. Flow rate and possibility of development of cyclic processes

With increased CO_2 partial pressures and, correspondingly, lower pH, the predominant form of carbonate sediments should have been dolomite. The solubilities of pure dolomite, calcite and magnesite are close together at low CO_2 partial pressures, while dolomite is the least soluble of these carbonates, at CO_2 partial pressures of ∿ 1 atm. Moreover, calcium sulfate, scarcely affecting dolomite at high (∿ 1 atm) P_{CO_2} and forming a stable paragenesis with it, dedolomitizes the system at lower P_{CO_2}, by extracting Mg from it and leaving calcite as the stable phase. The concentrations of such minerals as siderite ($FeCO_3$) and nahcolite ($CaHCO_3$), which are stable at high CO_2 partial pressures, /23 also evidently should have been increased in the Precambrian sediments. We note in addition, that acid hydrolysis of silicates at high CO_2 partial pressures could cause the formation of iron quartzites. We also note that the solubility of carbonates under these conditions is more than a factor of ten higher, than for the present pH and carbon dioxide partial pressure. It is possible that precisely this explains the smaller amount of carbonate residues in the Precambrian than in later geological epochs. Here, we are considering purely inorganic processes, which supposedly occurred in the atmosphere and hyrosphere of the primitive Earth. Of course, it must be kept in mind that the first living organisms appeared on the earth $3.5 \cdot 10^9$ years ago. They introduced significant corrections into these processes. Thus, for example, all the regularities of formation of carbonate deposits could have changed, with the development of life. Photosynthesis also powerfully affected the evolution of the atmosphere. However, we have consciously isolated only the "inorganic" part of evolution of the atmosphere and hydrosphere, since complete accounting for all the facts appears to be difficult.

TABLE 4. POLE-EQUATOR TEMPERATURE DIFFERENCE VS. MASS OF ATMOSPHERE (EFFECT OF ADVECTION)

	Масса атмосферы М, г.см$^{-2}$ / ≃ Р, мб для Земли/[a]			
	30	I00	300	I000
Земля, период[b] вращения 24^h	II3	60	36	27
Земля, период[c] вращения 6^h	I60	85	5I	38
Марс, период[d] вращения 24,5^h	70	38	22	I2

Key: a. Mass of atmosphere M, $g \cdot cm^{-2}$ (≃ P, mbar for earth)
b. Earth, rotation period 24 hours
c. Earth, rotation period 6 hours
d. Mars, rotation period 24.5 hours

The characteristic time of the flow process can be evaluated only very approximately, although it is obvious that it is small on the geological time scale. Since the limiting stages of the CO_2 flow from the atmosphere (in time) is carbonate formation processes, this time can be considered known to be less than $\sim 10^6$ years. Based on the most general considerations, it can be thought that, with the higher CO_2 partial pressure under primitive Earth conditions, the flow rate was at least not less than at present, although, of course, weathering processes could have been not so active. Since the characteristic flow time is definitely less than than the accumulation time, the climatic situation on the earth probably underwent cyclic changes. /24

We pointed out a possible specific mechanism in an earlier report [25]. We briefly recall its principle of action: with the passage of the average temperature through the melting point, the albedo decreases, T_e and T_s increase, and the flow mechanism begins to operate. During a period on the order of 10^6 years, the CO_2 content decreases, until the water on the planet does not freeze again. The albedo increases by jumps, and T_e and T_s decrease. Then, the accumulation process is again repeated and, as a result, something like a hysteresis loop forms in the T_s (u_{CO_2}) curve. The present Earth can be in two stable states, "white" and "black" planet (with a higher albedo, complete covering with ice and with a low albedo (see the book of Budyko [5]). Exactly such a situation apparently occurred on the primitive Earth, only, in addition to this, the triggering mechanism of the generation of cyclic variations described above also operated. We note that it is specific to just the early epochs, since it is connected with a low initial solar constant and a great abundance of CO_2 in the atmosphere.

How the atmosphere and climate of the earth changed, according to the concept reported above, is shown schematically in Fig. 7a. The change in composition of the atmosphere, albedo of the planet and surface temperature are shown. It must be remembered that we have not considered all factors. Variations in the solar constant, evidently superimposed on its continual increase, orogenic cycles resulting in variations of the outgassing rate, and changes in the basic astronomical characteristics of the earth as a planet (inclination and eccentricity of the orbit) have not been taken into account.

3. Mars

The mechanism of outgassing of the earth is volcanic eruptions /25 and the emissions of hydrothermal systems. The presences of volcanic formations on Mars permits it to be thought that the same mechanism operates there, although its output obviously is very much less. The present abundance of CO_2 in the atmosphere of Mars is a total of only 80 matm (16 $g \cdot cm^{-2}$) and, besides, approximately half of this amount is in the condensed phase in the seasonal polar caps. Besides the seasonal polar caps, there are small permanent caps consisting of H_2O ice on Mars, which do not melt away in the summer. It was supposed that there may be a certain amount of CO_2 in the northern permanent cap. Measurements of its temperature and the atmospheric H_2O content above it, carried out by the Viking-2 orbiter [19,9], refuted this hypothesis.

Numerous traces of water erosion activity, recorded on photographs of the planet obtained from aboard Mariner-9, Mars-5 and Vikings-1 and -2, show that Mars, at some period of its geological history ($\sim 10^9$ years ago) had liquid water on the surface and, consequently, a denser atmosphere. Evidently, in this period, part of the carbon dioxide was irreversibly bound in carbonates. Another part may be physically adsorbed by the regolith layer [8]. The water released during outgassing has now been redistributed between the permanent caps, permafrost and the regolith; part of it is chemically bound (limonite).

The most reliable estimates of the outgassing rate of volatiles on Mars are based on the abundance of nonradiogenic isotropes of the inert gases, measured by Vikings-1 and -2 [26]. Estimates based on ^{36}Ar show that the total mass of carbon dioxide released during outgassing is from 10^2 to $2.5 \cdot 10^2$ $g \cdot cm^{-2}$ and, of water, $4 \cdot 10^2$-10^3 $g \cdot cm^{-2}$. This amount of water could be completely put into the permanent polar caps. /26

Another estimate is based on the difference in the $^{15}N/^{14}N$ isotrope ratios on Mars and the Earth -- still another important result of the atmospheric composition measurements by the Vikings [21]. If it is assumed that the heavy isotrope enrichment on Mars was caused by the dissipation of nitrogen atoms (receiving superthermal velocities, as a result of some chemical reactions in the upper atmosphere), according to the estimate of McElroy et al [21], the mass of nitrogen released during outgassing is from 5 to 75 $g \cdot cm^{-2}$. If the CO_2/N_2 and H_2O/N_2 ratios are assumed to be the same as on the earth, this gives from $3 \cdot 10^2$ to $7.5 \cdot 10^3$ $g \cdot cm^{-2}$ CO_2 and from $2 \cdot 10^3$ to $3 \cdot 10^4$ $g \cdot cm^{-2}$ H_2O. The lower limit assumes that the nitrogen is not bound by the surface rocks, and the upper was obtained on the assumption that there is a chemical flow of N_2 (formation of HNO_2 and HNO_3 in the atmosphere, which react with minerals).

The upper ^{36}Ar limit is in agreement with the lower nitrogen limit, and this gives a basis for adopting 200-300 $g \cdot cm^{-2}$ CO_2 and 1500-2000 $g \cdot cm^{-2}$ H_2O as the initial figures, for the total mass of outgassing products, approximately 200 times less than on the earth.

The above-named estimate of the CO_2 mass released during outgassing in the entire geological history of Mars is close to the critical value u*, at which, on the earth, upon the passage of ∿ 10^8 years after completion of accretion, liquid water appeared. Here, it becomes possible for us to explain a puzzle in the history of the Martian climate. What occurred very rapidly on the earth, apparently occurred comparatively recently on Mars, one or two billion years ago.

The Tables 2 and 3 data confirm the quantitative correctness of this conjecture. On the one hand, 200-300 $g \cdot cm^{-2}$ of CO_2 ensures the appearance of liquid water in the wet greenhouse effect scheme and, on the other hand, it sufficiently strongly smooths the pole-equator temperature difference, to ensure conditions for operation of the wet version. As a consequence of the smaller size of the planet, advection on Mars more effectively evens out the temperature difference than on the Earth. We note that advective smoothing δT, as a function of M, was calculated for Mars in the work of Gierash and Toon [12] more strictly than the Table 3 data; the results are in satisfactory agreement. /27

Based on the facts and ideas reported above, the following approximate scheme of evolution of the atmosphere and climate on Mars can be proposed (see also Fig. 7b):

1. After completion of accretion, slow outgassing of the interior takes place. The initial pressure was low. The average initial temperature of the planet was about 200° K. Water definitely condensed at the poles, gradually forming ice shields. The accumulation of carbon dioxide in the polar caps probably occurred in this period.

2. The solar constant and the mass of volatiles also gradually increased. In the period when $u_{CO_2} \approx 10^2$ $g \cdot cm^{-2}$ was reached, advective instability destroyed the accumulation of solid carbon dioxide in the polar caps, and it transferred to the atmosphere, the greenhouse effect developed according to the moist scheme, and the temperature reached the melting point. This event could have occurred 1-2 billion years ago. An occasional increase in the solar constant could possibly made a definite contribution [16]. Open water reservoirs appeared and numerous river flows developed on Mars in this period. The Martian hydrosphere undoubtedly was considerably more modest than that of the earth; however, it could have included relatively large basins. It might be suspected that one such sea was in the northern polar region, but it probably remained covered with ice, even in the warming period. /28

3. The development of an open water surface resulted in binding. The sharply increasing erosion increased the effective reaction cross section of the atmosphere with the surface. The mass of the atmosphere began to decrease, and δT increased. The

albedo of the planet also increased (as a consequence of the formation of limonite). The water on the surface of Mars froze, and it was concentrated in the polar caps and permafrost; the planet reached its present state.

If the occasional changes in the solar constant are removed, it has to be assumed that the warming period was unique in the history of the planet and is not repeated in a period on the order of an eon. However, occasional changes can make the picture very much more complicated and lead to the development of several sequential warmings and glaciation periods alternating with them.

It is now impossible to answer the question, as to whether there was even one sufficiently long warming on Mars to give birth to a biosphere. The search for living organisms conducted by Viking has not given definite results, and only further research can resolve this problem.

4. Venus

As we have mentioned (section 2B), the beautiful theory of the greenhouse instability, explaining the absence of liquid water and CO_2 flow processes on Venus, turns out to be in great doubt, if the obligatory existence of cold-polar "traps" in the "initial /29
accumulation" period is taken into account. It must be remembered that the axis of Venus is almost perpendicular to the plane of the ecliptic. The rotational elements adopted by the International Astronomical Union give a total inclination of about 2°; in any case, it is less than 6° [20]. As a result, the temperatures of the polar regions should be extremely low, with a thin atmosphere. If $i=6°$, $A=0.6$ and a solar constant 40% less than at present are assumed, formula (10) gives

$$T_p = 141°K \qquad (12)$$

Thus, the accumulation of CO_2 in the polar regions on Venus was more likely than on the earth, and the accumulation of H_2O took place beyond any doubt. If the accumulation of CO_2 condensate did not occur, destruction of the polar caps occurred rapidly, after release of 100-300 $g \cdot cm^{-2}$ of carbon dioxide from the interior; if the carbon dioxide froze, 5-10 $kg \cdot cm^{-2}$ could have accumulated in the solid state. In any case, in the transition period from the dry greenhouse to the wet on Venus, liquid water should have developed and a CO_2 flow process started.

This conclusion does not depend on the correctness of our initial assumption of a low initial solar constant. If the present value is used, we obtain $T_p=160°$ K and, all the same, the cold trap is very effective for H_2O although the accumulation of condensed CO_2 is in doubt.

We now see two possible independent explanations of the large amount of CO_2 in the atmosphere of Venus:

1. Very little water was released during outgassing;

2. Much carbon dioxide accumulated in the polar caps of the primitive Venus in the solid phase, the release of which occurred catastropically, in a time $t \lesssim 10^6$ years; liquid water appeared on the planet for a short time, it failed to absorb the increasing CO_2, due to destruction of the caps, and it evaporated. /30

If hypothesis (1) is correct, it must be explained why the interior of Venus proved to be deficient in water. It is possible that closeness to the sun prevented the formation of ice particles in the corresponding protoplanetary cloud [17]. If, as we propose, the initial solar constant was low, this explanation does not seem obvious. Moreover, in the accretion period, hydrated silicates could have contained a substantial amount of H_2O [13].

If hypothesis (2) is true, it must be explained, what happened to the water. Rasool and de Bergh [28] consider that almost the entire mass of H_2O was dissociated and that hydrogen was ejected into interplanetary space. The reality of this mechanism causes doubt, since high temperatures in the upper atmosphere of the planet are required, which substantially exceed the present temperatures.

Purely intuitively, hypothesis (1) seems to be less strained, but it is now impossible to make a valid choice between them. If exploration of the Venusian surface detected traces of water erosion, this would unambiguously confirm the second hypothesis. The absence of such traces, however, would not be a refutation of it, since they could have been completely obliterated by erosion of a different nature.

The conclusion as to the possibility of formation of CO_2 polar caps on Venus in the first hundreds of millions of years does not appear to be very realistic at first glance, since it refers to the early period of evolution, when traces of the initial heating could have shown up. Nevertheless, this possibility cannot be rejected, if the necessity for very substantial fluxes of internal heat for the prevention of CO_2 condensation at the pole, with $i \simeq 0$, is taken into account. In order to establish a temperature of 160° K (it corresponds to $P'_{CO_2}=50$ mbar), due to internal heat, a flux of $3.8 \cdot 10^4$ erg$\cdot$sec^{-2} is necessary, 50 times greater than on earth at present. /31

A scheme of evolution of the atmosphere of Venus, in accordance with hypothesis (1), is given in Fig. 8. If carbon dioxide polar caps developed in the initial epoch, they existed for no more than 10^8 years, and the surface temperature exceeded 600° K more than four billion years ago. In calculation of T_S, we used the previously mentioned simple convective model: the tropopause is at a level, where the temperature is T_e; there is 100 g·cm^{-2} CO_2 above the tropopause; there is an adiabatic gradient below the tropopause.

Conclusion

We have considered the early evolution of the atmospheres and climates of the Earth, Mars and Venus, based on the following premises:

1. The solar constant gradually increased during the entire history of the planets ($4.6 \cdot 10^9$ years); the initial level was 60% of that at present.

2. Outgassing occurred uniformly. The ratios of the outgassing rates of CO_2, H_2O and N_2 were the same on the earth and Mars, and the absolute rates on Mars were two orders of magnitude less. The CO_2:N_2 ratios and absolute outgassing rates on the earth and Venus were approximately equal; the H_2O:CO_2 ratio on Venus was approximately 4 orders of magnitude less.

3. The initial pressure was low ($\sim 10^{-2}$ atm).

The following conclusions were obtained:

1. The first open water reservoirs appeared on the earth in the first hundred or few hundred millions of years; however, over a long period (about 2 billion years), the average temperature fluctuated close to the melting point. During this entire period, there was more carbon dioxide in the atmosphere than now and, in the first 200-300 million years, this gas was the main component. /32

2. Because of the slower outgassing rate and the smaller amount of heat obtained from the sun, open water reservoirs developed much later on Mars, in the third or even the fourth billion years. The period of warm climate, liquid water and dense atmosphere ended, because of irreversible chemical binding of CO_2.

3. The present physical conditions on Venus are explained most simply, if it formed with a great H_2O deficit. Water never was present in the liquid phase on the surface of Venus, and chemical binding of CO_2 did not occur. As a result, all the carbon dioxide remained in the atmosphere. The surface temperature exceeded 600° K four billion years ago.

APPENDIX

Method of Calculation of Greenhouse Effect

Calculation of the greenhouse effect is carried out comparatively simply, in two cases: 1. An atmosphere with wide transparency windows, separated by practically opaque sections ("transparency window" approximation); 2. an atmosphere, the transparency of which does not depend on wavelength ("gray atmosphere" approximation). It is assumed that only radiant heat transport occurs in the atmosphere; in the case of convection, the problem becomes significantly more complicated. We will disregard convection. We also assume that attenuation of solar radiation due to actual absorption does not occur in the atmosphere. Attenuation due to pure scattering is permitted. Its effect is automatically taken into account if, in calculation of $\bar{T}_e$ by formula (1), we use the albedo of the surface + atmosphere system as A. The measured spherical albedo of the planet is just such a quantity. /33

We initially examine approximation (1). It requires the introduction of still another simplifying assumption (specifically for this approximation), which is that surface absorption of infrared radiation occurs in sharply limited ranges $\Delta_i\lambda$, outside which the atmosphere is completely transparent. In this case, the average surface temperature T_s, as it is easy to see, is determined by the equality

$$\varepsilon T_s^4 (1-\beta) + T_a^4 \beta = T_e^4 \qquad \text{(A1)}$$

where T_a is the temperature of the stratosphere.

$$\beta = \frac{\sum_{\lambda_i} \int^{\lambda_{i+1}} \varepsilon_\lambda \, B(T_s, \lambda)\, d\lambda}{\sigma \cdot \varepsilon \cdot T_s^4}, \qquad \text{(A2)}$$

$B(T_s,\lambda)$ is the Planck function; λ_i and λ_{i+1} are the limits of the i-th range of $\Delta_i\lambda$; ε_λ and ε are the spectral and mean coefficients of radiation of the surface (we will assume that $\varepsilon_\lambda \equiv \varepsilon$ and, then, β is independent of ε); β is the fraction of the thermal radiation of the surface absorbed by the atmosphere; $1-\beta$ is the fraction of the thermal radiation going directly out into space. The left side of equation (A1) is, to within coefficient , the flux of outgoing thermal radiation (per unit area of the planet) and the right side is the flux of solar radiation absorbed by the planet. The effective temperature T_e is determined by formula (1). /34

If the stratosphere is in radiant equilibrium with the lower layers of the atmosphere and space, its temperature is determined from the condition $2\sigma T_a^4 \beta \tau_c = \sigma T_e^4 \beta \tau_a$, where $\tau_c << 1$ is the optical thickness of the stratosphere. The flux going upward and downward from the stratosphere is on the left side, and the flux absorbed by it on the right. This condition gives a simple connection between T_a and T_e:

$$T_a = 2^{-1/4} \cdot T_e. \qquad (A3)$$

We note that the temperature is higher in the present terrestrial atmosphere than is given by formula (A3), due to true absorption of the ultraviolet radiation of the sun by ozone. To estimate the temperature of the stratospheres of primitive planets, formula (A3) has to function satisfactorily; in any case, it results in correct estimates of the temperatures of the present stratospheres of Mars and Venus, which are practically devoid of ozone. By means of formula (A3), equation (A1) can be reduced to the form

$$\varepsilon T_s^4 = T_e^4 \frac{2 - \beta}{2(1-\beta)}. \qquad (A4)$$

In case (2) (gray atmosphere approximation), the connection between T_s and T_e is described by another type of expression: /35

$$\varepsilon T_s^4 = T_e^4 \left(1 + \frac{3}{4}\tau_0\right), \qquad (A5)$$

where τ_c is the total optical thickness of the atmosphere. By definition,

$$\tau_0 = \int_0^\infty k\,dz, \qquad (A6)$$

where k is the bulk coefficient of absorption and z is the altitude. Equation (A5) is derived for the case, when $\tau_0 >> 1$ and is independent of wavelength. Expressions (A4) and (A5) are identical, if, as the definition of the average optical thickness by wavelength $\bar{\tau}_0$ for an atmosphere with transparency windows, the following is formally adopted:

$$\tau_0 = \tau_W = \frac{2}{3}\,\frac{\beta}{1-\beta} \qquad (A7)$$

In the general case, if the coefficient of absorption and optical thickness depend on wavelength, it is customary to use other methods of averaging. Two of them are known: The Planck average and the Rosseland average. The Planck average τ_p can be determined by various methods, for example,

$$e^{(-3/2)\tau_p} = \frac{\int_0^\infty B(T_s, \lambda)\, e^{(-3/2)\lambda}\, d\lambda}{\sigma T_s^4}, \qquad (A8)$$

where the coefficient 3/2 is the inverse value of the average cosine in the Eddington approximation. For an atmosphere with transparency windows (A8) gives

$$\tau_p = \frac{2}{3}\beta, \tag{A9}$$

which coincides with (A7) at small β.

The Rosseland average equals

$$\tau_r = [{}_0\int^\infty \frac{1}{\tau_\nu} G(\alpha)d\alpha]^{-1} \tag{A10}$$

where ν is the frequency,

$$G(\alpha) = \frac{15}{45} \cdot \frac{e^\alpha \alpha^4}{(e^\alpha - 1)^4}. \tag{A11}$$

If even a small portion of the spectrum $\tau_\nu=0$, this method of estimation of the average obviously is not suitable, since it automatically gives $\tau_R=0$. The region of application of the Rosseland method of the average, consequently, is limited to cases, when there is appreciable absorption at all frequencies. /36

In actual planetary atmospheres, the situation frequently is intermediate between cases 1 and 2. The transparency windows are actually only partially transparent, and none of the methods listed for calculation of τ_0 is suitable. Moreover, it is clear that (a) the development of absorption in the windows can only increase τ_0 over τ_W and (b) a further increase in absorption has to result in $\tau_0 \to \tau_R$. If these conditions are satisfied, the average optical thickness can be determined as the sum

$$\tau_0 = \tau_W f(\frac{\tau_R}{\tau_W}) + \tau_R \tag{A12}$$

where f(x) is a certain function close to 1 at small x and to 0 at large x; we have used function $f(x)=e^{-x^2}$. This definition gives $\tau_0=\tau_W + \tau_R \simeq \tau_W$ with small t_R and $\bar{\tau}_0=\tau_R$ with large τ_R. A working formula for calculation of T_S/Te is (A5), but $\bar{\tau}_0$ is determined in such a manner that, under the conditions of the corresponding approximation 1, it is identical to formula (A1).

It is useful to consider a numerical example. Let $T_S=290°K$, the atmosphere be opaque in the $\lambda<8$ μm and $\lambda>13$ μm regions, and τ_λ =const and changes from 0 to 10, within the interval $8<\lambda<13$ μm. With $\tau_\lambda \approx 0.05-0.10$, this pattern occurs in the atmosphere of the present earth. Values of τ_W, τ_p, τ_R and $\bar{\tau}$, as well as of T_S/Te as a function of τ_λ are given in Table 3.

TABLE 3. τ_0 AND T_S/T_e VS. τ_λ IN AN ATMOSPHERE WITH A "WINDOW" IN THE 8-13 μm REGION (τ_λ IS THE OPTICAL THICKNESS INSIDE THE WINDOW), WITH T_S=290°K

τ_λ	τ_W	τ_P	τ_R	τ_0	T_S/T_e
0	I,4I	0,75	0,00	I,4I	I,20
0,I	I,4I	0,85	0,22	0,68	I,22
I,0	I,4I	I,75	2,2	2,49	I,30
I0	I,4I	I0,75	22	22	2,04

The effective temperature of the present Earth is about 250°K, and T_S/T_e=1.16, i.e., it is quite close to the results of calculations for small τ_λ in the 8-13 μm range. The discrepancy is explained by the increased temperature of the stratosphere /37 (it is clear from formula (A1) that $T_S \to T_e$, as $T_a \to T_e$).

For an atmosphere consisting of CO_2 and a small amount of H_2O (which is considered in the main part of this work), with $u_{CO_2} \leq 200$ g·cm^{-2}, $\tau_0 \simeq \tau_W$ and, $u_{CO_2} \geq 20$ kg·cm^{-2}, it is known that $\tau_0 \simeq \tau_R$. The exponential coefficient in formula (A12) operates only in the vicinity of $u_{CO_2} \simeq 2$ kg·cm^{-2}.

We have used data on the CO_2 and H_2O coefficients of absorption, taken from the following works: Vorob'yev, Gal'tsev, et al [38] for the 15 μm CO_2 band: Gal'tsev and Odshiariya [10], on the CO_2 bands in the 7-11 μm regions and the 15 μm band: Gal'tsev, Osipov and Shari [11], for the entire CO_2 absorption spectrum in the region from 3 to 100 μm; Goody [15], for the H_2O rotational band; Zuyev [40], for the 6.3 μm H_2O band; Andreyev and Gal'tsev [2], for the H_2O absorption in the 8-13 μm window.

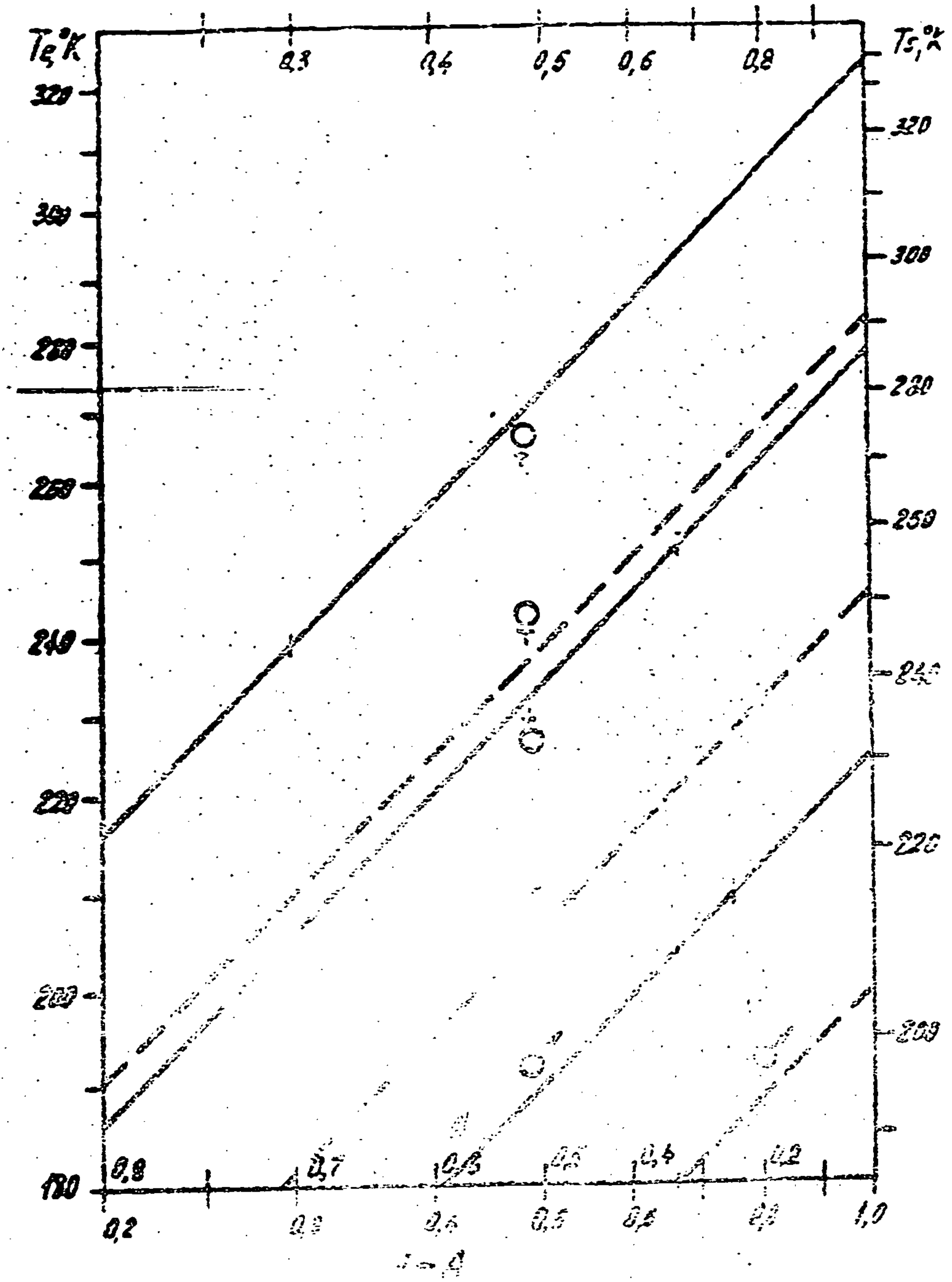

Fig. 1. Effective temperature of the Earth, Venus and Mars vs. albedo A: quantity 1-A plotted on abscissa in logarithmic scale ; temperature also given in logarithmic scale; on the ordinate, T_e on the left and T_s on the right (given for the case, when the atmosphere is optically thin to thermal radiation of the surface and does not affect its temperature); solid lines correspond to present values of solar constant E_0, dashed lines, 0.6 E_0; present values of A and T_e are noted by vertical dashes.

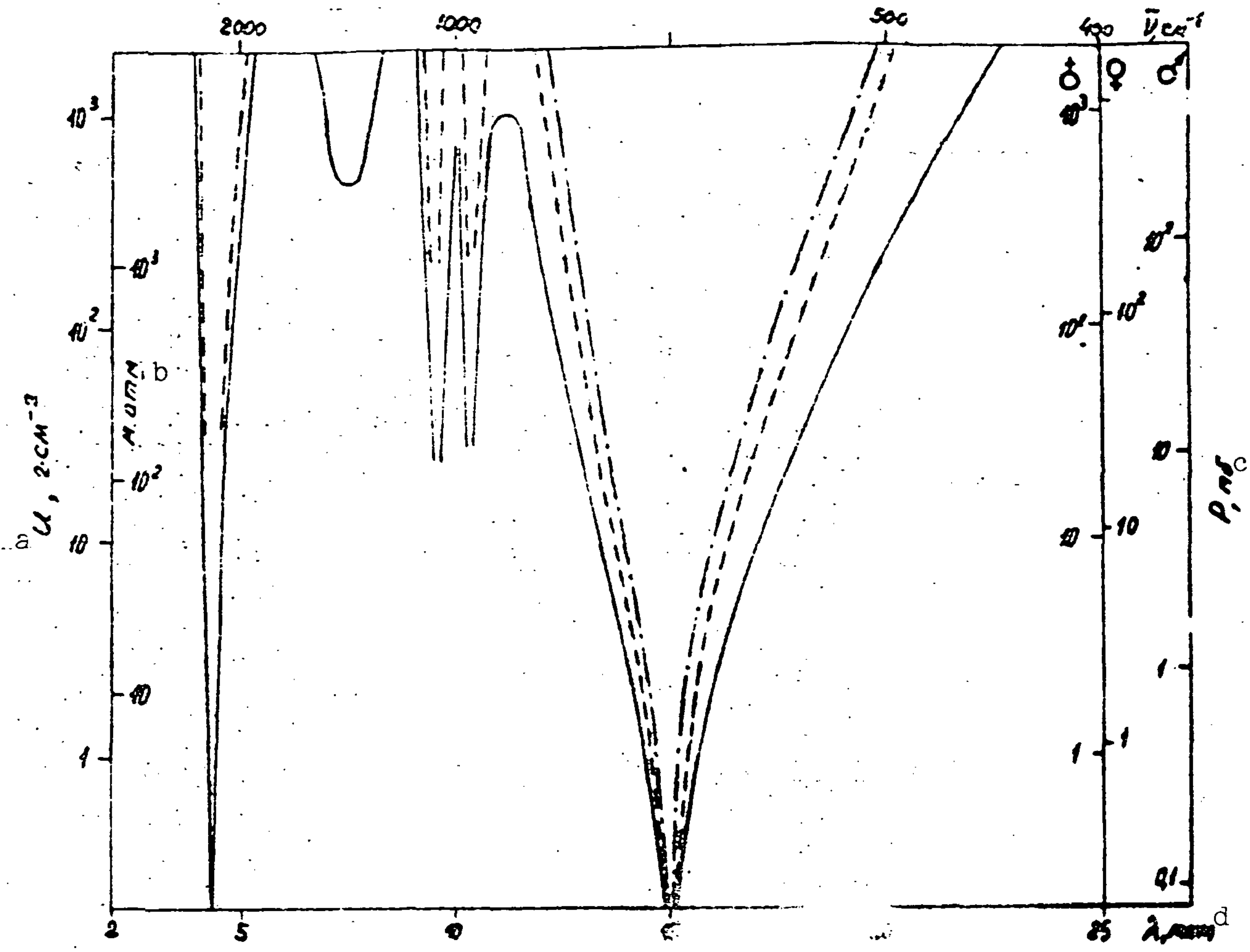

Fig. 2. Absorption of infrared radiation by carbon dioxide: wavelength λ and wave numbers $\tilde{\nu}$ on abscissa; CO_2 content of 1 cm^2 cross section atmospheric column and corresponding pressures in the atmospheres of the Earth, Venus and Mars on the ordinate (it is assumed that CO_2 is the main component); the curves presented are the geometric locations of points corresponding to twofold attenuation of radiation; regions with attenuation exceeding that indicated are above curves; sections of these regions with u=const straight lines give equivalent absorption bandwidths; solid line corresponds to T=300°K and pressures at a given u in the atmosphere of the Earth (for Venus, the same curve functions with an accuracy on the order of a few percent); dashed line, T=200°K for the Earth; dot-dash line, T=200°K for Mars (only in the 15 μm band band); two bands around 10 μm are "hot"; their intensity depends most strongly on T; absorption around 10 μm is induced, and it sharply increases with increase in pressure; in the calculation, it was assumed in all cases that the effective pressure equals half the pressure at the surface.

Key: a. u, $g \cdot cm^{-3}$ c. P, mbar
b. matm d. λ, μm

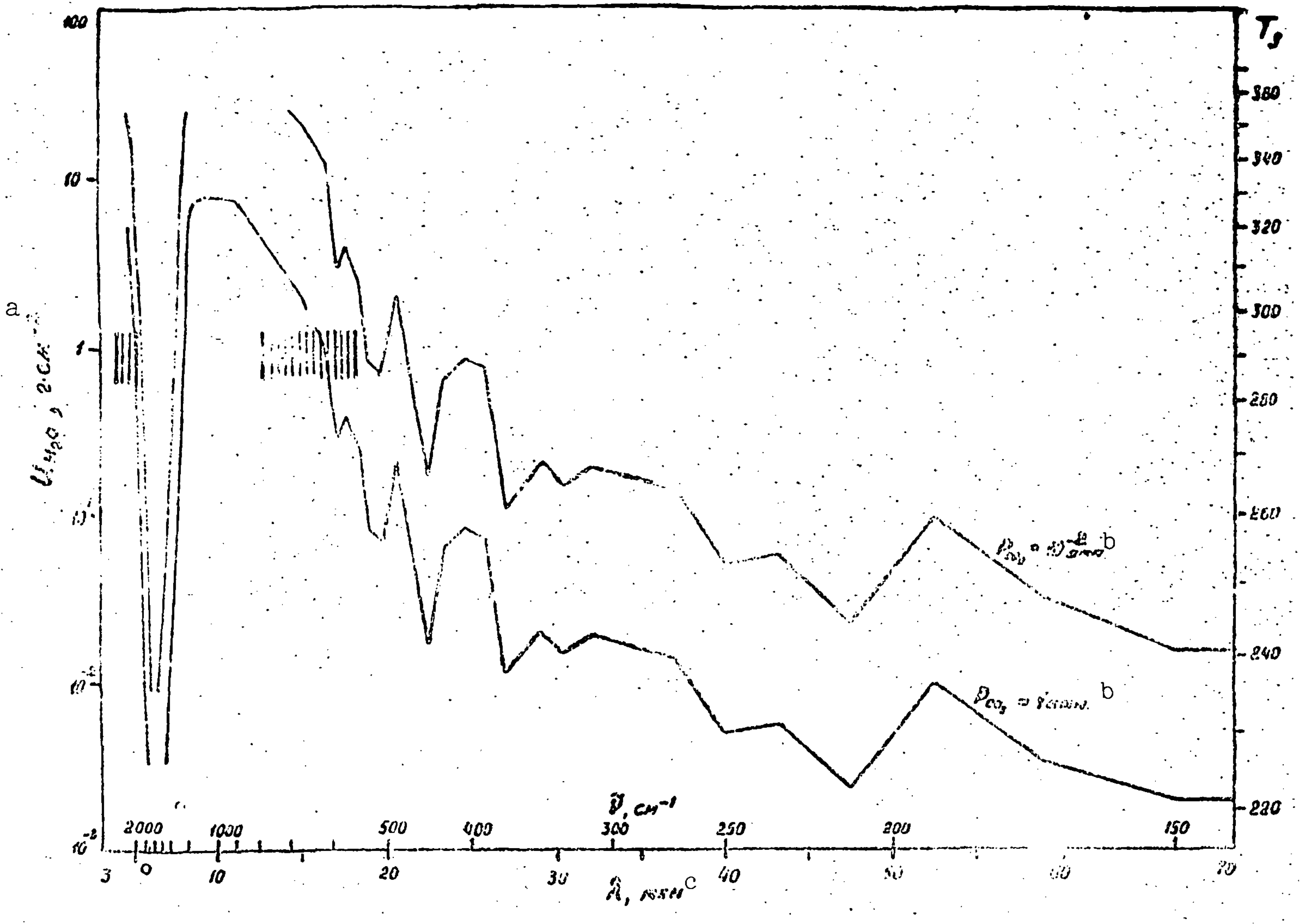

Fig. 3. Absorption of infrared radiation by water vapor: wavelength λ and wave numbers $\tilde{\nu}$ on abscissa; amount of absorbing matter and surface temperature T_s corresponding to this amount on ordinate (calculated by formula (4)); geometric location of points corresponding to twofold attenuation (for the Earth and Venus), given: locations of λ 15 μm and 4.3 μm CO_2 bands shown provisionally by vertical dashes.

Key: a. u_{H_2O}, $g \cdot cm^{-2}$
b. atm
c. λ, μm

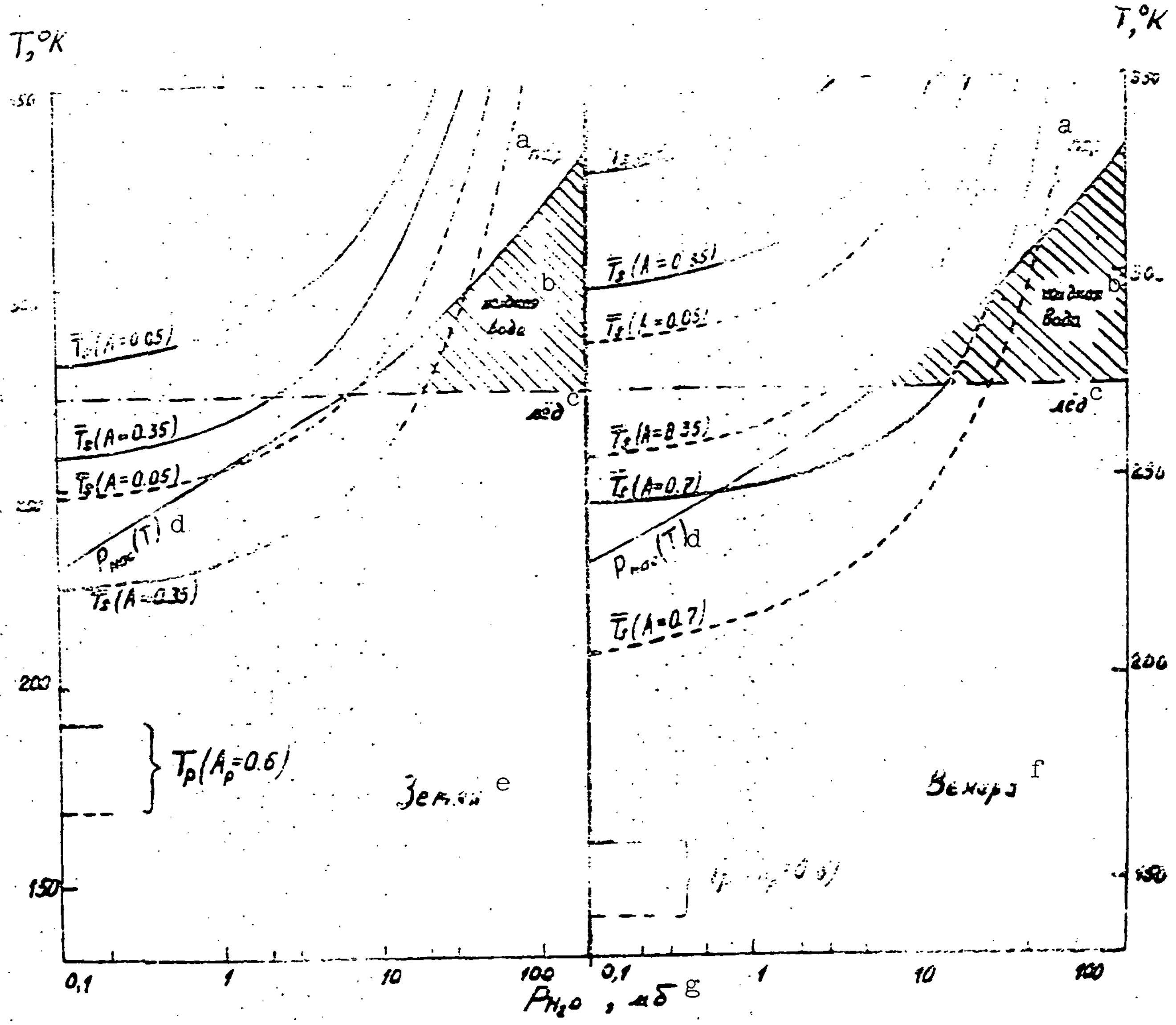

Fig. 4. Model of evolution of atmosphere with greenhouse instability: for the Earth on the left, for Venus on the right; amount of H_2O released from interior on abscissa (simultaneous release of CO_2 in 1:6 ratio assumed in partial pressure units; surface temperature T_s calculated on assumption that all water remains in gas phase, on ordinate; solid curves correspond to present value of solar constant and dashed, to 40% less; if it is assumed that temperature T_s is the same for all points on the planet and curve T_s (P_{H_2O}, P_{CO_2}) goes above the saturation level (curve T_{sat}), this assumption is justified and, then, unstable greenhouse effect develops and surface temperature increases irreversibly in proportion to outgassing; "cold traps" in polar regions prevent development of greenhouse instability (their temperature T_p shown at lower left).

Key:
- a. Vapor
- b. Liquid water
- c. Ice
- d. $P_{sat}(T)$
- e. Earth
- f. Venus
- g. P_{H_2O}, mbar

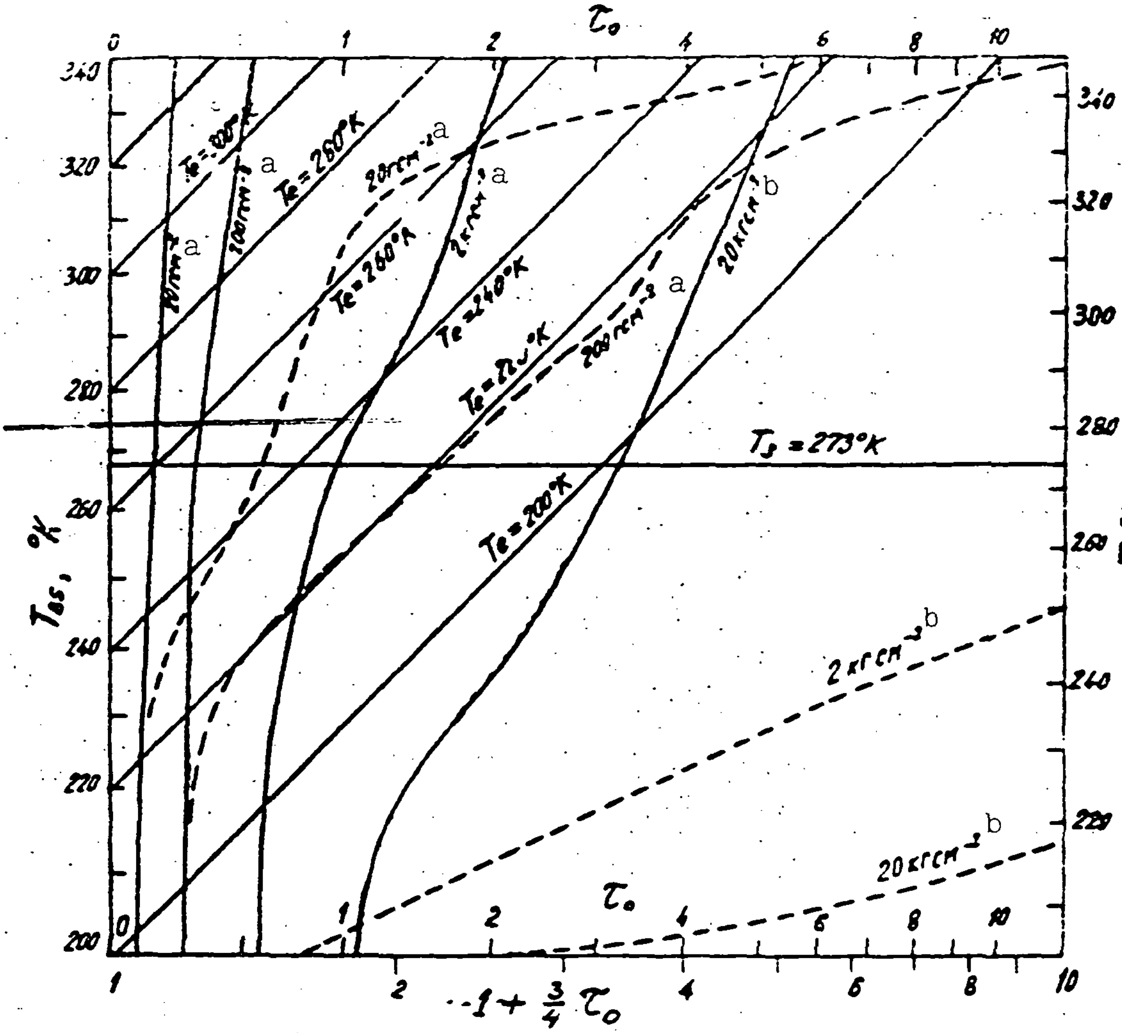

Fig. 5. Illustration of calculation of surface temperature with greenhouse effect: quantity $1+(3/4)\tau_0$, right side of equation (3), on abscissa in logarithmic scale ; brightness temperature T_{B_S} given on left of ordinate, kinetic temperature of surface T_S on the right (it is assumed that $\varepsilon=0.9$), also in logarithmic scale; straight lines at 45° angle give T_{B_S} and T_S as a function of τ_0, with various values of effective temperature T_e; family of solid curves going from bottom to top and deviating to the right are quantities τ_0 (T_S, u_{CO_2}) for the dry version (see text); family of dashed curves, for wet version of greenhouse effect model; figures around these curves are amount of CO_2 in 1 cm² cross section column (u_{CO_2}); equilibrium temperature with given values of T_e and u_{CO_2} are determined by intersection of corresponding T_S (τ_0 , T_e) and τ_0 (T_S, u_{CO_2}) curves.

Key: a. g·cm^{-2} b. kg·cm^{-2}

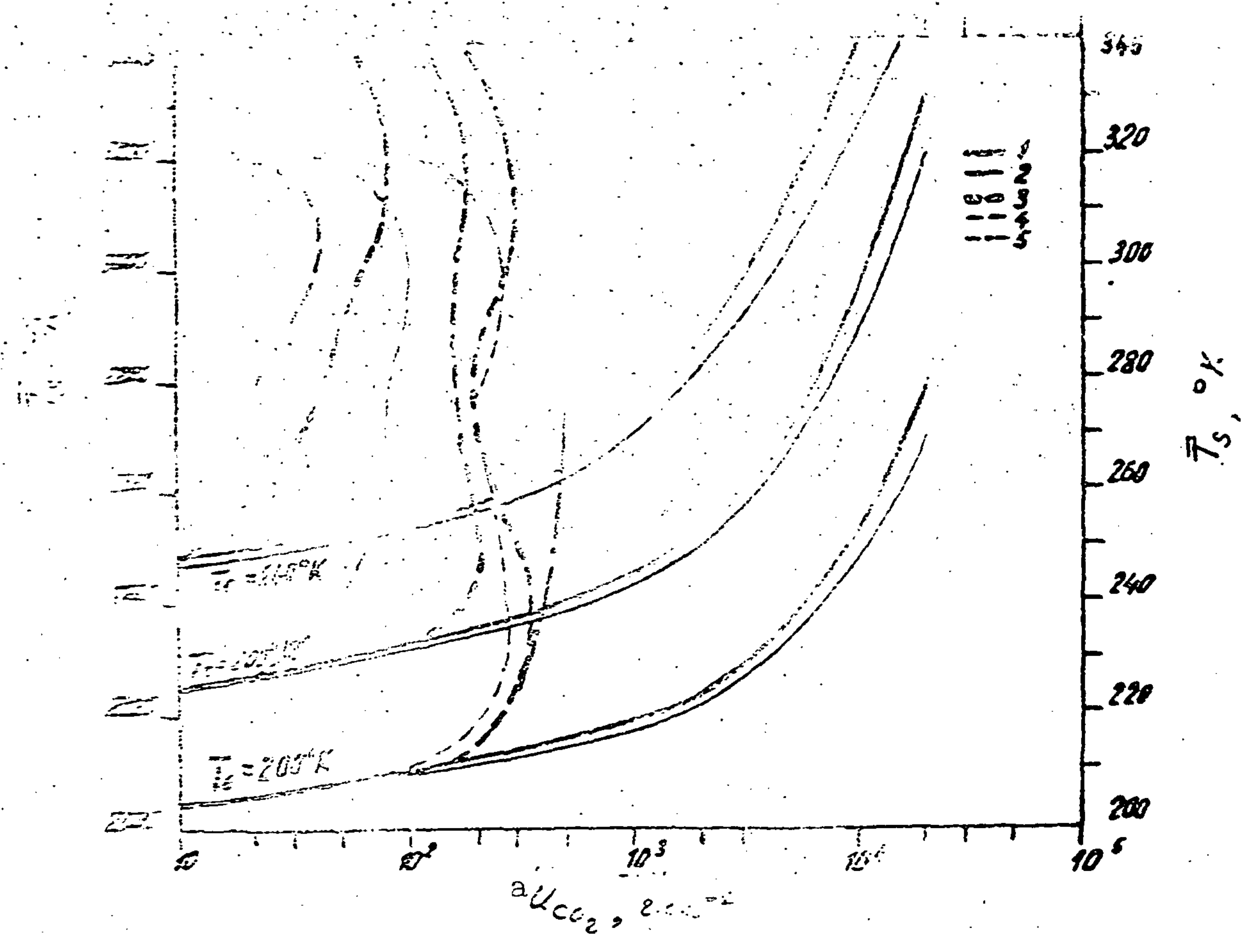

Fig. 6. Average surface temperature of planet $\bar{T}_s$ with allowance for greenhouse effect: u_{CO_2}, amount of CO_2, on abscissa; $\bar{T}_s$ on ordinate; 1. Earth, dry model; 2. Mars, dry model; 3. Earth, wet model; 4. Mars, wet model; 5. Earth, convective model (curves 1-4 calculated with allowance only for radiant transport).

Key: a. u_{CO_2}, g·cm^{-2}

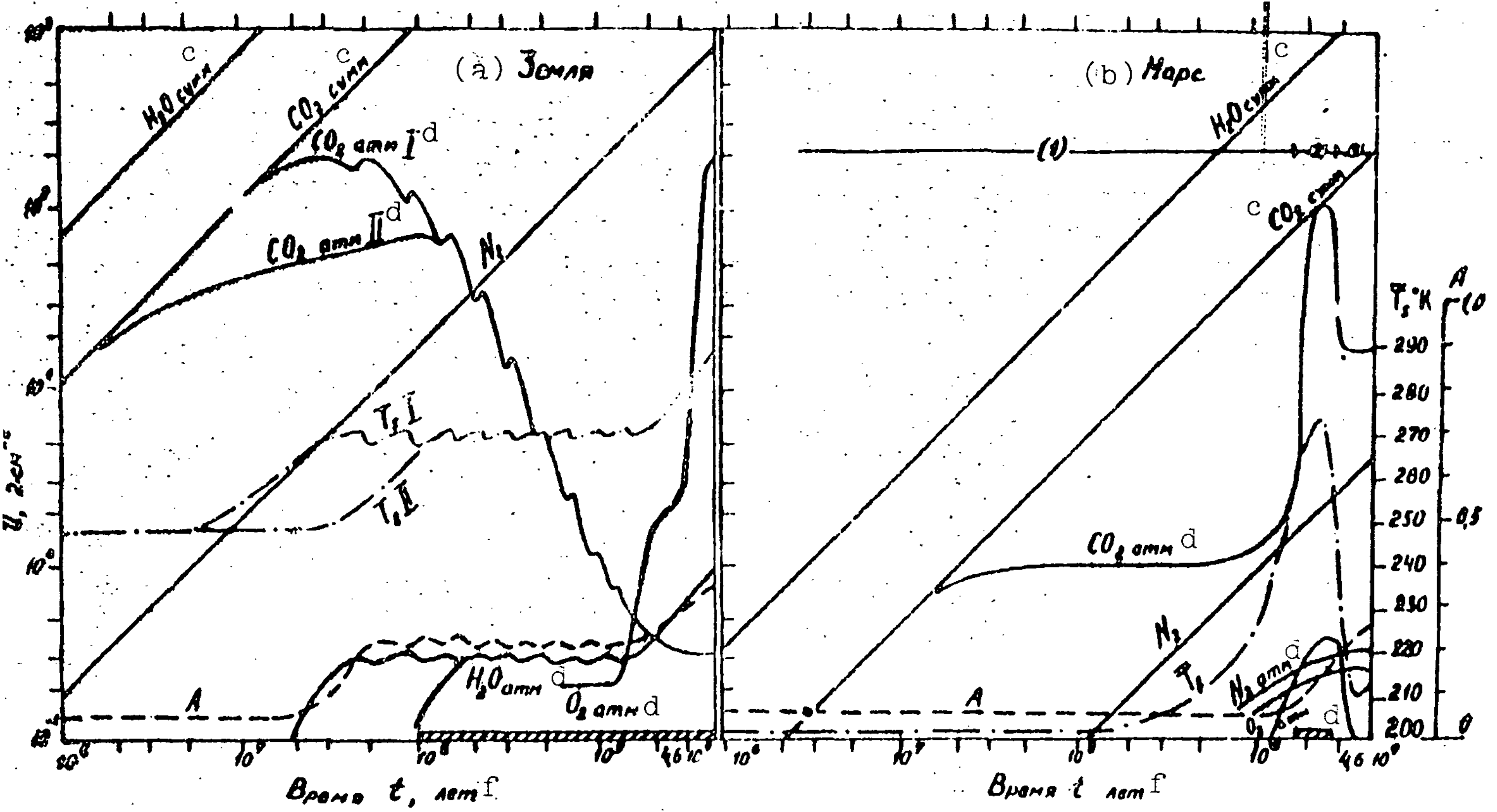

Fig. 7. Models of evolution of atmosphere and climate of the Earth (a) and Mars (b): on abscissa, time (from arbitrary time of completion of accretion); amount of volatiles released during outgassing on ordinate; total amount (atmosphere + lithosphere + hydrosphere) and abundance in atmosphere given separately; for Earth, version 1 assumes initial accumulation of only H_2O in polar caps, version 2, condensed carbon dioxide also; cyclic changes during period Earth was at melting point shown provisionally by wavy line (see Section 3d); how average surface temperature $\bar{T}_s$ and spherical albedo A changed is shown; O_2 accumulation pattern after Rutteh [30]; on Mars, during first approximately 2 billion years, main bulk of CO_2 was concentrated in polar caps, then, relatively brief "paradise" followed (hydrosphere, comparatively dense atmosphere and warm climate) and, then, the present cold period began (see text); three periods in the history of Mars are designated by arabic numbers in the upper part of the figure; time interval during which hydrosphere existed on surface noted by dashed strip at bottom.

Key: a. Earth	d. Atmosphere (atm)
b. Mars	e. u, g·cm^{-2}
c. Total	f. Time t, years

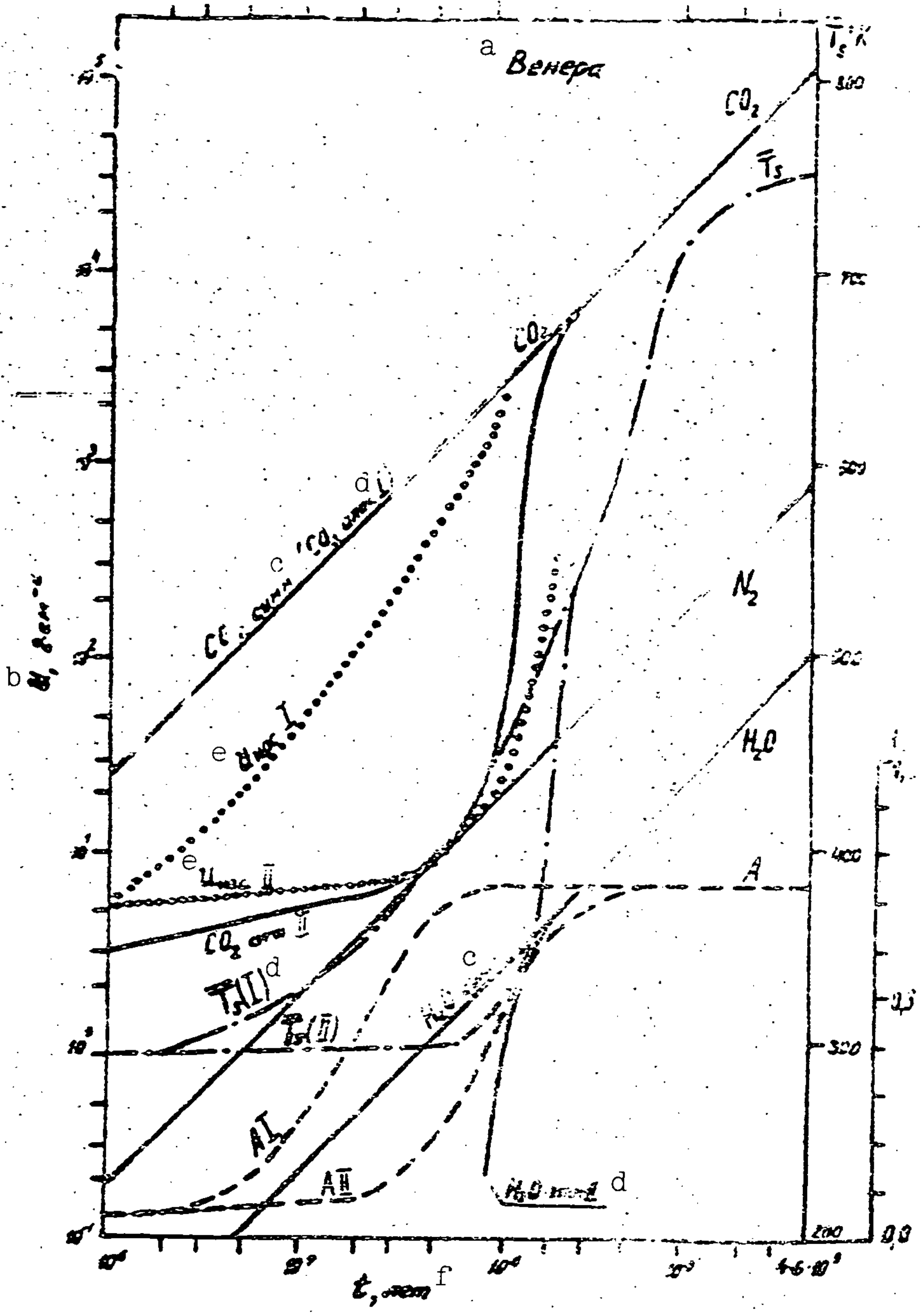

Fig. 8. Model of evolution of atmosphere and climate of Venus; designations same as in Fig. 7; version 1 assumes initial accumulation of CO_2 condensate in polar regions, version 2, without accumulation; course of evolution differs sharply from that of earth (Fig. 7); reason evidently is H_2O deficiency.

Key:
- a. Venus
- b. u, $g \cdot cm^{-2}$
- c. Total
- d. Atmosphere
- e. u_{sat}
- f. t, years

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