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DETERMINATION OF CHEMICAL COMPOSITION OF THE ATMOSPHERE
OF VENUS BY THE INTERPLANETARY STATION "VENERA-4"

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DETERMINATION OF CHEMICAL COMPOSITION OF THE ATMOSPHERE
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SUMMARY

The preliminary results of measurements on AIS VENERA-4 of Venus' atmosphere composition are as follows: CO_2 : 90 ± 10 percent; $0.4\% < \text{O}_2 < 1.5\%$; $\text{N}_2 < 7$ percent; H_2O content is 1 to 8 mg l. The contemporary atmospheres of the Earth and Venus are compared and their various chemical reactions are discussed. It is concluded that endogenous processes are very close for both planets, while exogenous processes led to formation of quite different atmospheres. The deep rock erosion and surface leveling on Venus are explained by the heavy and "aggressive" atmosphere of the planet and its intense motion.

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INTRODUCTION. After the discovery of powerful Venus' atmosphere, made in 1761 by M. G. Lomonosov, numerous attempts were conducted with the view of studying its characteristics with the aid of ground observation means. Applying the method of infrared spectroscopy only CO_2 content could be reliably established, the content of which being, however, assumed by various authors to be between a few to 100 percent. The existence of indications on the presence of other gases, such as H_2O , N_2 , O_2 , and others, was up to now the object of controversy.[1]. The scarcity of factual material led to the appearance of numerous model atmospheres of Venus, generally constructed on the basis of arbitrarily chosen characteristics. The flight by Venus of spacecraft "Mariner-2" in 1962 contributed no significant clarity to the state of the question. It became obvious that only direct measurements of the basic parameters of the atmosphere could provide a reliable foundation for the interpretation of ground observations and of the geochemical characteristic of planet's surface.

(*) OPREDELENIYE KHIMICHESKOGO SOSTAVA ATMOSFERY VENERY MEZHPLANETNOY STANTSIIY VENERA-4

1. STATEMENT OF THE PROBLEM. On 12 June 1967 took place the launching of the Soviet interplanetary station "VENERA-4", which approached the planet after 128 days of flight and, having passed its atmosphere, effected the first soft landing on its night side surface. The nearly linear course of temperature of Venus' atmosphere, beginning from an altitude of about 26 km to the surface, was measured for the first time directly. Over this portion the temperature varied from $25 \pm 10^\circ$ to $270 \pm 10^\circ$. The corresponding pressure variation constituted from 0.7 to 20 atm, its course being close to adiabatic [2].

The basic scientific problem of Venera-4 was the study of physico-chemical characteristic of Venus' atmosphere. The station (probe) consisted of two basic parts: an orbital compartment and a descending capsule. The latter weighed 383 kg and had a shape close to a sphere of about 1 meter in diameter. The devices for the determination of temperature, pressure and chemical composition of planet's atmosphere were installed on it. All measurements were conducted within the atmosphere of the planet during the parachute descent of the capsule.

The chemical composition of Venus' atmosphere was determined by a gas analyzer, especially worked out by us for that objective. 11 such gas analyzers were installed on the capsule; they were assembled into two groups: the first group consisted of 5 analyzing cells and the second one of 6 such cells. The gas analyzers operated on command of the program-temporal device. The first "team" of gas analyzers operated in Venus' atmosphere at pressure of about 550 mm, and the second one at pressure of about 1500 mm. The temperature of the medium where measurements were conducted was respectively $25 \pm 10^\circ$ and $90 \pm 10^\circ$.

2. APPARATUS AND METHODS OF DETERMINATION OF CHEMICAL COMPOSITION. Of the numerous possible methods of determination of the composition we utilized the simplest and most reliable physico-chemical methods based upon well studied reactions of sufficient selectivity. In order to improve the reliability of the results, we established threshold, as well as amplitude sensors with duplicating determinations. Each gas analyzer constituted a cylinder of specific volume, divided in two compartments by a membrane. A chemical absorber, designed to absorb the assigned component, was placed in one of the compartments. Both compartments were evacuated and hermetized prior to the measurement time. During analysis, the atmosphere was introduced simultaneously in both compartments, which then were hermetized anew. In order to determine the basic components of the atmosphere, registrations of pressure differentials were made, these occurring as a result of absorption in the compartment of one of the components. For the analysis of the components present in the atmosphere in small amounts, more sensitive physico-chemical methods were applied; these methods were based on measurement of differences in the resistances occurring in especially assorted absorbers in various cells, and of the difference in heat transfer of especially heat-conducting elements, etc. Thus, CO_2 , N_2 , O_2 and H_2O content in the atmosphere of Venus was determined with the help of the above-described gas analyzers. These determinations were conducted in a broad interval of their possible concentrations in view of the large scattering and uncertainty of the initial data from ground observations. Considered here are the preliminary results of such a processing.

T A B L E 1

Conditions of Analysis	Component being determined	Type of Sensor	Principle of sensor's operation	Measurement limit or threshold	Results of measurement.
FIRST GROUP OF ANALYZERS					
H = 26 ± 1 km P ~ 550 mm t ~ 25 ± 10°	CO ₂	Threshold s.	Heat conductivity	Threshold 1%	> 1%
	CO ₂	Amplitude s.	KOH absorption	7 - 100%	90 ± 10
	N ₂	Amplitude s.	After absorption of CO ₂ and O ₂ → absorption N ₂ → Zr at 1000°	7 - 100%	< 7%
	O ₂	Threshold s.	W (burning of filament at 800°)	Threshold 0.4%	> 0.4%
	H ₂ O	Threshold	Absorption of P ₂ O ₅ , conductance measurement	Threshold 0.1%	> 0.1%
SECOND GROUP OF ANALYZERS					
H = 19 ± 1 km P ~ 1500 mm t ~ 90 ± 10°	CO ₂	Amplitude s.	Absorption of KOH	2 - 30%	> 30%
	CO ₂	Threshold s.	Absorption of KOH	Threshold 1%	> 1%
	N ₂	Amplitude s.	After absorption of CO ₂ and O ₂ → absorption N ₂ → Zr at 1000°	2.5 - 50%	< 2.5%
	O ₂ ± H ₂ O	Threshold	Phosphorus evaporation	Threshold 1.6%	< 1.6%
	H ₂ O	Threshold	P ₂ O ₅ absorption, measurement of conductance	Threshold 0.06%	> 0.05%
	H ₂ O	Amplitude	Absorption of CaCl ₂	Threshold 0.7%	< 0.7%

3. RESULTS OF MEASUREMENTS.

The results of determination of the chemical composition of Venus' atmosphere are compiled in Table 1 (page 3). As may be seen from it, the presence of CO_2 is corroborated by 4 sensors, whose readings are distributed as follows: more than 1%, more than 1%, more than 30% and $90 \pm 10\%$. Although the error in the determination of CO_2 for the amplitude sensor attained $\pm 10\%$ on account of superimposition of external inaccuracies, we are inclined to consider that the content of CO_2 in Venus' atmosphere constitutes no less than 90% (acid vapors of HCl and so forth, earlier detected in the atmosphere of Venus by way of ground observations in the amount less than 0.01%, could not have affected the results of measurements).

The nitrogen sensors have indicated twice the absence of notable amounts of that gas in the atmosphere of Venus. One negative value was obtained at time of nominal sensor's threshold response giving 7%, and the other, at threshold value, gave 2.5%. Taking into account that the second determination had a greater (though not overlapping the threshold of the first measurement) relative error, we may consider as reliably established that the threshold of nitrogen content is less than 7%.

The content in O_2 was found to be between the two threshold values of sensors operating on different principles. In one of them the wolfram filament burned out instantaneously (at about 800°), though it was calculated for a threshold of about 3 mm partial O_2 pressure in sensor's volume, which corresponds to 0.5% of the gas at 550 mm pressure. The other sensor was based upon absorption of O_2 by sublimating vapors of phosphorus; the P_2O_5 then forming is capable of absorbing water vapors. The sensor, computed for a threshold value of absorbed mixture $\text{H}_2\text{O} + \text{O}_2$ of 1.6%, gave a negative reading. As will be seen below from the data of concomitant determination of mixture $\text{H}_2\text{O} + \text{O}_2$, the content of O_2 can not be above 1 to 1.5 percent.

Water was determined by three sensors. At the upper point ($H \sim 26$ km) the sensor with P_2O_5 , determining the sum of vapor-like and condensed water, gave an H_2O content greater than 0.65 mg/l, which corresponds to a quantity greater than 0.1% or to condensation temperature above -22° . At the lower point ($H \sim 20$ km) the content in water vapor according to the sensor with P_2O_5 was also found to be greater than 0.65 mg/l (more than 0.05%), whereas according to pressure sensor with CaCl_2 absorber it was less than 11 mm (less than 0.7%), which corresponds to a condensation temperature of less than 15° . Since during that time the device had a temperature of no less than 25° , the pressure loss at the expense of vapor condensation in the device should be recognized as entirely insignificant and considered that the true upper threshold of water vapor pressure has been determined.

Thus, the possible water vapor pressure in various layers of Venus' atmosphere is comprised between 0.65 and 11 mm, which corresponds to condensation temperatures of -22° and $+15^\circ$, i. e. the existence of droplet-liquid water is possible only in the cloud layer, for the conditions of Venus' surface (270° temperature and pressure of ~ 20 atm.) lie far beyond the limits of the field of existence of liquid water.

4. DISCUSSION OF THE RESULTS

Summing up the general result of analyses, it is possible to assume the following composition of Venus' atmosphere: CO_2 : $90 \pm 10\%$; O_2 : more than 0.4% and less than 1.5%; N_2 : less than 7%; H_2O : 1–8 mg/l.

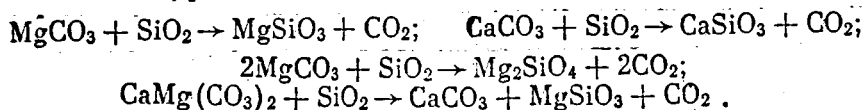
As may be seen from all data, the content of O_2 in the atmosphere of Venus is less than 1 percent, and N_2 is below 7 percent, probably not attaining 2 to 4 percent. This composition eliminates a significant role for other gases, which was assumed by some researchers. At the same time it is not excluded that argon and other inert gases may be present in the atmosphere of Venus. The Ar content may be estimated by the content in N_2 . The knowledge of the total composition of atmosphere allows us to compute also certain equilibrium admixtures, arising as a result of photochemical reactions. On the whole, the atmosphere of Venus was found to be oxidized and corresponding mostly to greenhouse model.

The data brought out may be made somewhat more precise after complete processing of the results of the experiment and the consideration of all possible effects.

If we compare the contemporary atmospheres of Venus and Earth, we shall obtain extremely interesting results: the total amount of degassed products for both planets is comprised within the limits of one half-order, with the exception of hydrogen lost by Venus.

Carbon in the Earth's crust is linked with carbonates of sedimentary rocks and constitutes about $2 \cdot 10^{23}$ g CO_2 [3]. If we separated all the CO_2 from carbonates and hydrosphere of the Earth into the atmosphere, the mass of the latter ($5 \cdot 10^{21}$ g) would increase ~ 40 times, i. e., roughly speaking, the gas pressure would be nearly 40 atm. The full quantitative correspondence with the Earth is attained at the condition to assume that more or less one half of possible CO_2 content is in Venus in sedimentary rocks in bound state, and the other is in the atmosphere.

If we assume on Venus a CO_2 pressure equal to ~ 20 atm, the conditions of carbonate-silicate equilibrium are such that Mg and Ca carbonates must begin to decompose at temperature of about 300° . The conditions of this equilibrium were studied more than once (for example, [4]), in various variants of reactions of the type



They were proposed for the explanation of increased amount of CO_2 in the planetary atmospheres. It is entirely beyond doubt that all these reactions on the surface of Venus are shifted to the right.

The source of N_2 in the atmosphere of Venus was NH_4 as on Earth, where it is degassed volcanically in the form NH_4Cl , which is sublimated at temperature of $\sim 350^\circ$. Because of the enormous amount of CO_2 on Venus, it must be in the form $(\text{NH}_4)_2\text{CO}_3$. However, $(\text{NH}_4)_2\text{CO}_3$ is decomposed at 58° . In other words, ammonia may be found in Venus' atmosphere. NH_4Cl is a stable molecule and NH_3 is easily oxidized by O_2 to N_2 .

If we assume the probable nitrogen content on Venus at about 3 to 4% and that of O_2 as less than 1 percent, a simple multiplication by the pressure of 20 atm gives for the atmosphere of Venus the same amount of nitrogen and oxygen as in the Earth's atmosphere (respectively 78 and 21%). These coincidences can hardly be casual, and they much rather speak in favor of the fact that endogenous processes, and namely, the melting of crust matter and the degassing processes of planets are proceeding along the same path, when of equal dimension, and only the subsequent history of atmospheres modifies their appearance as a function of closeness to the Sun, of planet's mass determining the degree of atmosphere dissipation and other exogenous factors [3].

Because of a closer position of Venus relative to the Sun, its equilibrium temperature is higher than 50° . Independently of other factors, this conditioned the transition into the atmosphere of Venus of water and carbon dioxide in substantial amounts. The appearance of water and of carbon dioxide in the atmosphere in substantial amounts induces in its turn an enormous solar heat absorption by the atmosphere and, at the same time, a significant water and carbon dioxide photodissociation in the absence of sufficient shielding action of nitrogen and oxygen in the atmosphere and its high temperature. The thus formed oxygen is absorbed by the rocks of Venus' surface. Owing to the presence of oxygen from the conjugate reaction — photodissociation of H_2O , the product of carbon dioxide photodissociation—CO, was not preserved and recombined into CO_2 . Under these conditions of high surface temperature of Venus, hydrogen dissipated. All this led to atmosphere self-heating and to formation of hothouse effect. Probably a certain heat equivalent was contributed by planet's interior. When Venus' surface temperature reached approximately 250 to 300° , a large number of carbonates reacted with silicates, liberating into the atmosphere enormous amounts of carbon dioxide. It follows from the obtained temperature and pressure data of Venus' atmosphere that water must boil at temperature above 200° .

Therefore, Venus and Earth are very close in endogenous processes. At the same time, exogenous processes, which are dependent on surface temperature in the first place (i.e. closeness to the Sun), have led to formation of different atmospheres. The conditions having arisen on the surface of Venus have led, as a result of self-regulation processes, to the formation of a heavy atmosphere. Under these conditions the surface rocks of Venus must have been subject to deep erosion. The very existence of such an "aggressive" atmosphere have probably led in conditions of its intense motion to planet surface leveling.

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