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Abstract

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DETERMINATION OF THE CHEMICAL COMPOSITION OF THE ATMOSPHERE OF VENUS BY THE VENERA-4 INTERPLANE- TARY STATION

Introduction. After the discovery of Venus' s powerful atmosphere, made in 1761 by M. V. Lomonosov, numerous attempts were made to study its characteristics by ground-based observational means. By infrared spectrometry, the presence only of CO₂ was determined with sufficient reliability; its content, however, was supposed by different authors to range from several percent to 100%. Existing indications of the presence of other gases (H₂O, N₂, O₂, etc.) were disputed until recently ⁽¹⁾. The lack of factual material led to the appearance of numerous models of the atmosphere of Venus, constructed on arbitrarily chosen characteristics. The flyby of the Mariner-2 spacecraft near Venus in 1962 did not bring substantial clarity to the state of the problem. It became obvious that only direct measurements of the principal parameters of the atmosphere could provide a reliable basis for interpreting ground-based observations and for the geochemical characterization of the planet' s surface.

1. Experimental setup. On 12 VI 1967, the Soviet interplanetary station Venera-4 was launched; after 128 days of flight it approached the planet and, passing through its atmosphere, made the first soft landing on its night-side surface. For the first time, by means of direct measurement, the almost linear course of the temperature of Venus' s atmosphere was determined, beginning at an altitude of approximately 26 km and down to the planet' s surface. Over this interval the temperature varied from $25 \pm 10^\circ$ to $270 \pm 10^\circ$. The corresponding change in pressure was from 0.7 to 20 atm; its course is very close to adiabatic ⁽²⁾.

The main scientific task of the Venera-4 station was the study of the physico-chemical characteristics of the atmosphere of Venus. The station consisted of two main parts—the orbital compartment and the descent apparatus. The descent apparatus had a mass of 383 kg and a shape close to a sphere, with a diameter of about 1 m. Instruments for determining the temperature, pressure, and chemical composition of the planet' s atmosphere were installed on it. All

measurements were carried out in the planet's atmosphere during the parachute descent of the descent apparatus.

The chemical composition of the atmosphere of Venus was determined by gas analyzers specially developed by us for this purpose. On the descent apparatus there were 11 gas analyzers, which were assembled into two groups—the first consisted of 5 analyzing cells, the second of 6. The gas analyzers were actuated by commands from a program-timing device. The first batch of gas analyzers operated in the atmosphere of Venus at a pressure of about 550 mm, the second at about 1500 mm. The temperature of the medium in which the measurements were made was respectively $25 \pm 10^\circ$ and $90 \pm 10^\circ$.

2. Apparatus and methods for determining the chemical composition of the atmosphere. Of the many possible methods of determining composition, we used the simplest and most reliable physicochemical methods, based on well-studied reactions possessing sufficient selectivity. To increase reliability

the results, both threshold and amplitude sensors with duplicate determinations were installed. Each gas analyzer was a cylinder of a definite volume, divided into two compartments by a membrane. In one of the compartments there was a chemical absorbent that absorbed the specified component. Until the moment of measurement both compartments were evacuated and sealed. During analysis the atmosphere was admitted simultaneously into both compartments, which were then sealed again. To determine the principal components of the atmosphere, the difference in pressures arising in the compartments as a result of absorption of one of the components was recorded. For analysis of components present in the atmosphere in small quantities, more sensitive physicochemical methods were used (based on measurement of the difference in resistance arising in different cells of specially selected chemical absorbents, the difference in heat transfer of special current-conducting elements, etc.). Using the data from the gas analyzers, the contents of CO_2 , N_2 , O_2 , and H_2O in the atmosphere of Venus were determined. The determinations were carried out over a wide interval of their possible concentrations because of the large scatter and uncertainty of the initial data from ground-based observations. In the present article the results of preliminary processing of the information obtained are considered.

3. Measurement results. The results of determining the chemical composition of the atmosphere of Venus are given in Table 1. As can be seen from the tab—

Table 1

Analysis conditions	Component determined	Sensor type	Principle of operation of the sensor	Measurement limit or threshold	Measurement results
1st group of analyzers	1st group of analyzers	1st group of analyzers	1st group of analyzers	1st group of analyzers	1st group of analyzers
$H 26 \pm 1$ $kmP \sim 550$ $mmt \sim 25 \pm 10^\circ$	CO ₂	Threshold	Thermal conductivity	Threshold 1%	More than 1%
$H 26 \pm 1$ $kmP \sim 550$ $mmt \sim 25 \pm 10^\circ$	CO ₂	Amplitude	Absorption by KOH	7-100%	90 ± 10%
$H 26 \pm 1$ $kmP \sim 550$ $mmt \sim 25 \pm 10^\circ$	N ₂	Amplitude	After absorption of CO ₂ and O ₂ – absorption of N ₂ → Zr at 1000°	7-100%	Less than 7%
$H 26 \pm 1$ $kmP \sim 550$ $mmt \sim 25 \pm 10^\circ$	O ₂	Threshold	W (overheating of the filament at 800°)	Threshold 0.4%	More than 0.4%
$H 26 \pm 1$ $kmP \sim 550$ $mmt \sim 25 \pm 10^\circ$	H ₂ O	Threshold	Absorption by P ₂ O ₅ , measurement of electrical conductivity	Threshold 0.1%	More than 0.1%
2nd group of analyzers	2nd group of analyzers	2nd group of analyzers	2nd group of analyzers	2nd group of analyzers	2nd group of analyzers

Analysis conditions	Component determined	Sensor type	Principle of operation of the sensor	Measurement limit or threshold	Measurement results
$H \sim 19 \pm 1$ $kmP \sim 1500$ $mmt \sim 90 \pm 10^\circ$	CO ₂	Amplitude	Absorption by KOH	2-30%	More than 30%
$H \sim 19 \pm 1$ $kmP \sim 1500$ $mmt \sim 90 \pm 10^\circ$	CO ₂	Threshold	Absorption by KOH	Threshold 1%	More than 1%
$H \sim 19 \pm 1$ $kmP \sim 1500$ $mmt \sim 90 \pm 10^\circ$	N ₂	Amplitude	After absorption of CO ₂ and O ₂ – absorption of N ₂ → Zr at 1000°	2.5-50%	Less than 2.5%
$H \sim 19 \pm 1$ $kmP \sim 1500$ $mmt \sim 90 \pm 10^\circ$	O ₂ (±H ₂ O)	Threshold	Phosphor source	Threshold 1.6%	Less than 1.6%
$H \sim 19 \pm 1$ $kmP \sim 1500$ $mmt \sim 90 \pm 10^\circ$	H ₂ O	Threshold	Absorption by P ₂ O ₅ , measurement of electrical conductivity	Threshold 0.05%	More than 0.05%
$H \sim 19 \pm 1$ $kmP \sim 1500$ $mmt \sim 90 \pm 10^\circ$	H ₂ O	Amplitude	Absorption by CaCl ₂	Threshold 0.7%	Less than 0.7%

le, the presence of CO₂ was confirmed by 4 sensors, whose readings are distributed as follows: more than 1%, more than 1%, more than 30%, and 90 ± 10%. Although for the amplitude sensor the error in determining CO₂ reached

$\pm 10\%$ in the atmosphere of Venus is not less than 90% (acid vapors of HCl, etc., previously detected in the atmosphere of Venus by ground-based observations in amounts less than 0.01%, could not affect the measurement results).

The nitrogen sensors twice indicated the absence of appreciable quantities of it in the atmosphere of Venus. One negative value was obtained at the nominal threshold sensitivity of the sensor of 7%, the other at a threshold value of 2.5%. Taking into account that the second determination had a larger relative error (though not overlapping the threshold of the first measurement), the threshold for nitrogen content of less than 7% may be regarded as reliably established by these two measurements.

The content of O_2 proved to lie between two threshold values of sensors operating on different principles. In one sensor a tungsten filament instantly burned out (at a temperature of about 800°), calculated for a threshold of about 3 mm partial pressure of O_2 in the sensor volume, which corresponds to 0.5% of the gas at a pressure of 550 mm. The other sensor is based on absorption of O_2 by sublimating phosphorus vapors; the P_2O_5 formed in this process is capable of absorbing water vapor. The sensor, calculated for a threshold value of the absorbed mixture $H_2O + O_2$ of 1.6%, gave a negative indication. From the data of the joint determination of the $H_2O + O_2$ mixture, as we shall see below, the O_2 content cannot be higher than 1-1.5%.

Water was determined by three sensors. At the upper point ($H \sim 26$ km) the sensor with P_2O_5 , determining the sum of vaporous and condensed water, gave an H_2O content greater than 0.65 mg/l, which corresponds to a value greater than 0.1% or to a condensation temperature above -22° . At the lower point ($H \sim 20$ km) the content of water vapor according to the sensor with P_2O_5 also proved to be greater than 0.65 mg/l (greater than 0.05%), while according to the pressure sensor with a $CaCl_2$ absorber it was less than 11 mm (less than 0.7%), which corresponds to a condensation temperature below 15° . Since the instrument at this time had a temperature of not less than 25° , the pressure loss due to condensation of vapor in the instrument should be regarded as entirely negligible, and it may be considered that the true upper limit of the vapor pressure of H_2O was determined.

Thus, the possible interval of vapor pressure in different layers of the atmosphere of Venus lies 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, since the conditions at the surface of Venus (temperature 270° and pressure ~ 20 atm.) lie far outside the field of existence of liquid water.

4. **Discussion of results.** Summarizing the overall result of the analyses, the following composition of the atmosphere of Venus may be adopted:
 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 is evident from all the data, the content of O_2 in the atmosphere of Venus

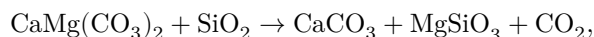
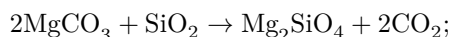
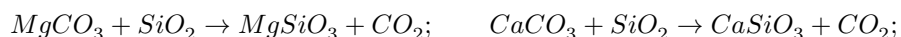
is less than 1%, and N_2 is below 7% and probably does not reach 2-4%. This composition excludes any significant role of other gases that had been assumed by some investigators. At the same time, the presence of argon and other inert gases in the atmosphere of Venus is not excluded. The Ar content can be estimated from the N_2 content. Knowledge of the complete composition of the atmosphere makes it possible to calculate certain possible equilibrium impurities arising as a result of photochemical reactions. On the whole, the atmosphere of Venus proved to be oxidizing and most consistent with the greenhouse model.

The data presented may be somewhat refined after complete processing of the experimental results and allowance for all possible effects.

If one compares the modern atmospheres of Venus and Earth, extremely interesting results are obtained: the total amount of degassed products for both planets lies within one half-order of magnitude, except for the hydrogen lost by Venus.

Carbon in the Earth's crust is bound with the carbonates of sedimentary rocks and amounts to about $2 \cdot 10^{23}$ g CO_2 (3). If all CO_2 is released from the carbonates and hydrosphere of the Earth into the atmosphere, the mass ($5 \cdot 10^{21}$ g) of the atmosphere will increase by ~ 40 times, i.e., roughly speaking, the gas pressure will be about 40 atm. Complete quantitative agreement with the Earth is achieved under the condition that $\sim 1/2$ of the possible CO_2 content is assumed to be on Venus in sedimentary rocks in a bound state, and the other part in the atmosphere.

If the pressure of CO_2 on Venus is taken to be ~ 20 atm., then the conditions of carbonate-silicate equilibrium are such that the carbonates of magnesium and calcium should begin to decompose at a temperature of about 300° . The conditions of this equilibrium have been studied repeatedly (for example, (4)), in various variants of reactions of the type



and so on, and were proposed to explain the increased quantity of CO_2 in planetary atmospheres. It is quite beyond doubt that, on the surface of Venus, all these reactions are sharply 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 of NH_4Cl , which sublimes at a temperature of $\sim 350^\circ$. On Venus, because of the enormous amount of CO_2 , it should occur

in the form $(\text{NH}_4)_2\text{CO}_3$. However, $(\text{NH}_4)_2\text{CO}_3$ decomposes at a temperature of 58° . In other words, ammonia may be present in the atmosphere of Venus. NH_4Cl is a stable molecule, while NH_3 is readily oxidized by O_2 to N_2 .

If we take as probable a nitrogen content of about 3–4%, and O_2 less than 1%, then simple multiplication by a pressure of 20 atm gives the same amount of nitrogen and oxygen in the atmosphere of Venus as the content of these gases in the Earth's atmosphere (78 and 21%, respectively). It is unlikely that all these coincidences can be accidental. Most likely they indicate that endogenous processes—namely, the melting out of crustal material and the processes of planetary degassing for planets of equal size—proceed along the same path, and only the subsequent history of the atmospheres changes their appearance depending on proximity to the Sun, the mass of the planet, which determines the degree of dissipation of the atmosphere, and other exogenous factors ⁽³⁾.

Because Venus is closer to the Sun, its equilibrium temperature is more than 50° higher. This, independently of other factors, caused water and carbon dioxide to pass in significant quantities into the atmosphere of Venus. The appearance of water and carbon dioxide in the atmosphere in considerable amounts, in turn, caused enormous absorption of solar heat by the atmosphere and, along with this, significant photodissociation of water and carbon dioxide in the absence of a sufficient protective action of nitrogen and oxygen in the atmosphere and at its high temperature; moreover, the oxygen formed was absorbed by the rocks of the surface of Venus. CO—the product of photodissociation of carbon dioxide—was not preserved and recombined into CO_2 owing to the presence of oxygen from the coupled reaction, the photodissociation of water. Under these conditions, and at the high temperature of the surface of Venus, hydrogen dissipated. All this led to self-heating of the atmosphere, the formation of a greenhouse effect. Probably some portion of heat was contributed from the planet's interior. When the temperature of the surface of Venus reached approximately $250\text{--}300^\circ$, very many carbonates reacted with silicates, releasing into the atmosphere an enormous quantity of carbon dioxide. From the obtained data on the temperature and pressure of the atmosphere on Venus it follows that water must boil at a temperature above 200° .

Thus, in terms of endogenous processes, Earth and Venus are very close. At the same time, exogenous processes, which depend first of all on the surface temperature (i.e., proximity to the Sun), led to the formation of different atmospheres. The conditions that arose on the surface of Venus 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 undergone profound destruction. The existence of such an aggressive atmosphere under conditions of its intense motion probably led to the leveling of the planet's surface.

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