Reports

Vertical Distribution of Water in the Atmosphere of Venus: A Simple Thermochemical Explanation

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Several lines of evidence concerning the vertical abundance profile of water in the atmosphere of Venus lead to strikingly unusual distributions (the water vapor abundance decreases sharply in the immediate vicinity of the surface) or to serious conflicts in the profiles (different infrared bands suggest water abundances that are discrepant by a factor of 2.5 to 10). These data sets can be reconciled if (i) water molecules associate with carbon dioxide and sulfur trioxide to make gaseous carbonic acid and sulfuric acid in the lower atmosphere, and (ii) the discrepant 0.94-micrometer water measurements are due to gaseous sulfuric acid, requiring it to be a somewhat stronger absorber than water vapor in this wavelength region. A mean total water abundance of 50 ± 20 parts per million and a near-surface free water vapor abundance of 10 ± 4 parts per million are derived.

HE SURFACE TEMPERATURE OF VEnus is roughly 750 K, far too high for the presence of liquid water: any water present would at once boil away and exist as water vapor in the atmosphere. But it is also well established that the atmosphere of Venus is extremely dry: whereas heating Earth to the temperature of Venus would produce a very wet atmosphere with a surface partial pressure of water vapor of about 300 atm, typical estimates of the water partial pressure on Venus are near 3×10^{-3} atm, fully 10^{-5} as much. But almost as interesting as the extraordinary aridity of Venus is the serious disagreement among the results of the several experiments that have attempted to measure the water abundance below the clouds. This problem is reviewed in detail by von Zahn et al. (1).

Very high water concentrations of several thousand parts per million were reported as a result of the Pioneer Venus gas chromatograph (PVGC) experiment (2), whereas all other direct measurements of the water content lie in the range from 20 to 200 ppm. The PVGC experimenters pointed out, however, that their high value could be caused by the slow evaporation of sulfuric acid (H_2SO_4) droplets ingested during passage through the clouds. Another, less direct, measurement was carried out by the infrared net flux radiometers on the four Pioneer Venus (PV IR) entry probes (3). The absolute fluxes measured below the clouds were much too large to be reasonable and increased with depth. Large corrections were applied to the data on the basis of a proposed error source, but even the corrected data show many cases in which the flux increases with depth. The results for the four probes were found to be extremely discordant, suggesting water-mixing ratios from 10 to over 1000 ppm. For these reasons, we shall attempt no quantitative explanation of the PVGC or PV IR radiometer data.

The most sensitive measurements bearing on the water abundance in the lower atmosphere of Venus, infrared spectra returned by the Soviet Venera 11 entry probe (4), cover a spectral region (0.7 to 1.25 µm) within which one weak (0.82 μ m) and two strong (0.94 and 1.13 µm) water bands are found. The intensity of transmitted sunlight was measured from an altitude of over 61 km down to the planetary surface. Below an altitude of about 44 km, just below the base of the H₂SO₄ cloud layer, we would normally expect the mole fraction of water vapor to be independent of altitude. Preliminary interpretation of these bands (4), however, showed clearly that such homogeneous models did only a poor job of explaining the data. Models in which the water mole fraction increased with altitude, from about 20 ppm at the surface to about 200 ppm at the cloud base, gave an improved but not convincing fit. The water vapor profiles that fitted the 0.94-µm data best had the unfortunate property that they seemed quite unphysical. In a search for "hydrogen-hiding" reactions with other known or suspected atmospheric constituents (C, N, O, S, F, Cl, As, Sb, and P compounds), no explanation for such a strange water distribution could be found.

A much more thorough interpretation of the Venera 11 data (5) refined the dilemma. It was found that (i) if it was assumed that all the opacity in the Venera 11 spectral region was due to carbon dioxide (CO2) and H₂O, the data for the 0.94-µm band required a vertical variation in the water abundance from about 20 ppm at the surface to a peak value of about 200 ppm near the cloud base at 44 km, with the abundance dropping off again above the clouds to below 30 ppm near 60 km (Fig. 1); (ii) the 0.84- and 1.13µm bands, although not analyzable with the same precision, were compatible with average water abundances of about 20 ppm, an amount insufficient to provide even half the equivalent width of the 0.94-µm band. This result clearly implied a contribution from an absorber other than water in the 0.94-µm band, but no such species could be identified: however, the correlation of the gaseous absorption maximum with the cloud base suggested the possibility of a gaseous absorber formed by evaporation of H₂SO₄ cloud droplets (5). If, rather unreasonably, we ignore the estimate of 20 ppm given by the 0.84- and 1.13- μ m bands and attribute all of the 0.94-µm opacity to water vapor, then the average water abundance (integrated over the altitude range from 0 to 70 km) would be 43 ppm. A lower limit on the water abundance would be set by attributing the excess (discordant) opacity in the 0.94µm band near an altitude of 44 km to some other species besides water. Then the altitude-averaged water abundance required to explain the rest of the 0.94-µm opacity is near 24 ppm.

We have developed a model of the chemical behavior of water on Venus (6), based on laboratory data for the thermodynamics of the gas-phase reaction

$$H_2O + SO_3 = H_2SO_4 \tag{1}$$

on the vapor pressure of H_2SO_4 (7, 8), and on the stability of the gaseous carbonic acid (H_2CO_3) molecule,

$$H_2O + CO_2 = H_2CO_3$$
 (2)

which has recently been characterized (9). We use a standard enthalpy change of $\Delta H_{298}^0 = -22.7$ kcal mol⁻¹ and an entropy change of $\Delta S^0 = -34.42$ cal mol⁻¹ K⁻¹ for reaction 1 (6), and $\Delta H_{298}^{0} = 6$ kcal mol⁻¹ and $\Delta S^0 = 2$ cal mol⁻¹ K⁻¹ for reaction 2 (10).

Venus atmospheric models were calculated for water-mixing ratios ranging from 20

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Fig. 1. Vertical distribution of water on Venus inferred from the Venera 11 and 12 infrared scanning photometer for a ten-layer model atmosphere (5). The Venera data (4, 5) show a wide variation from layer to layer, with a striking minimum at the surface and a strong 'spike" near an altitude of 45 km. Calculated profiles of the gases H₂CO₃, H₂O, and H₂SO₄ are shown (assuming a total of 90 ppm water) for the model described in the text. The



smoothed cloud density is given for reference on the left side of the diagram (20).

to 200 ppm. In our first models we made the simplifying assumption that in the vicinity of the clouds the abundances of both water and sulfur trioxide (SO₃) were derived from the evaporation and dissociation of H_2SO_4 and hence were equal (an excess of water is more probable). The results of such a calculation for a water abundance of 90 ppm are shown in Fig. 1.

Several generalizations emerge from this and other calculated models. First, the depletion of water vapor near the ground can be ascribed to the formation of gaseous H₂CO₃. Second, SO₃ and water vapor have negligible affinity near the surface, and thus H₂SO₄ vapor reaches 1 ppm only near an altitude of 21 km. Third, gaseous H₂SO₄ is extremely stable in the vicinity of the cloud base, reaching 63 ppm (versus 27 ppm for water vapor) near 44 km. The anomalous (excess) 0.94-µm absorption peak corresponds almost perfectly with the calculated profile of gaseous H₂SO₄. This finding strongly suggests that H₂SO₄ vapor, or some other gas derived directly from it, is responsible for the very high spike in the 0.94-µm absorption. Fourth, the columnaverage free water vapor abundance for this model is 36 ppm, compared to the assumed total water abundance of 90 ppm: 60% of the total water is bound to CO_2 or SO_3 (principally the former). The percentage of free water is model-independent because the equilibrium expressions for reaction 2 gives a H₂O:H₂CO₃ ratio that is independent of the total water abundance. Therefore, the lower limit on free water set above by omitting the 45-km "spike" then suggests a minimum total water abundance of 24/0.6 = 40 ppm, and the free water abundance of 20 ppm deduced from the 0.82- and 1.13-µm bands implies a total water abundance of 20/0.6 = 33 ppm. Precisely at the surface, fully 80% of the total water is bound to CO₂. All these results are extremely insensitive to plausible errors in the thermodynamic data used (11). Finally,

the falloff of the water abundance above the clouds is governed by the vapor pressure of water over concentrated H_2SO_4 , as has been long accepted (1), and no new modeling of this familiar phenomenon was attempted.

The altitude at which H_2SO_4 saturates to make constant-boiling (98% by weight) H_2SO_4 droplets is a sensitive function of the gaseous H_2SO_4 abundance. Steffes (8) has shown from vapor pressure arguments that 15 to 30 ppm H_2SO_4 would not only provide saturation above altitudes of 46 to 48 km, but that this amount of H_2SO_4 vapor would also account for the microwave absorption seen in spacecraft occultation experiments.

In light of the present model, it is interesting to reexamine the other sources of data on the water abundance below the Venus clouds. Figure 2 summarizes the results from the Venera 11 and 12 mass spectrometers (12), the Venera 12 gas chromatograph (13), the Pioneer Venus Large Probe Mass Spectrometer (LMS) (14), and, for comparison, the Venera 11 and 12 infrared photometer data for the same altitudes (4, 5). Our model suggests that the striking discordance between these experimental results is due to the complex and unexpected altitude-dependent speciation of water. Our

Fig. 2. Comparison of water abundance determinations for the atmosphere of Venus beneath the main cloud layer. The Venera 11 (V11) and Venera 12 (V12) entry probe experiments that provided these data are the infrared photometer (ϕ) (4, 5), the mass spectrometer (MS) (12), and the gas chromatograph (GC) (13) experiments. The Pioneer Venus LMS data are given with the original authors' error bars (14). Because of the unanticipated complexity of the speciation of water, these experiments yielded highly discordant results. However, the

model predicts that there should be an altitude interval (19 to 35 km) within which at least 70% of the total water is in the form of free H₂O vapor. It is satisfying to find that the data from these six experiments are concordant within (and only within) this altitude interval. We therefore use the four reported detections of water in this region, plus the lower limits discussed above, to estimate a total water content in the range from 30 to 70 ppm.

At the surface the nominal percentage of total water bound in gaseous H₂CO₃ is 80%. Allowing an uncertainty of a factor of 3 in the equilibrium constant for reaction 2 [in accord with the estimates of gaseous H_2CO_3 abundance given in (9)], the fraction of total water bound as H₂CO₃ at the surface of Venus must lie in the range 80^{+13}_{-20} %. The correct water partial pressure to use in equilibrium treatments of the chemical interaction of atmospheric gases with crustal minerals is then $10^{+10}_{-6.5}$ ppm. Discussions with Donahue (15) have revealed that the Pioneer Venus LMS experiment did not provide direct evidence for the $H_2CO_3^+$ ion near the surface of Venus, but the speciation of gaseous H₂CO₃ in the LMS inlet system and ionization region is quite unknown. The abundance of free hydrogen seen by the LMS varies rapidly and (apparently) inexplicably with altitude in the same altitude range where we predict abundant H₂CO₃ vapor. These data remain unpublished.

We conclude that the 0.94-µm band measures opacity due not only to CO₂ and water vapor but also to some other cloud-related species such as gaseous H₂SO₄. The general trends evident in the Venera 11 infrared data, including both the complex altitude dependence of opacity and the impossibility of reconciling the 0.84- and 1.13-µm data with free water abundances much larger than 20 ppm, are all readily comprehensible when formation of gaseous H₂SO₄ and H₂CO₃ is considered. Laboratory study of the near-infrared absorption spectrum of



region from 19 to 35 km, where free water vapor dominates and complexes are minor, yielded concordant estimates of the water abundance.

H₂SO₄ vapor and related compounds could permit a quantitative interpretation of the Venus spectrum, and is strongly encouraged. The near-surface association of CO2 and water vapor is a direct result of our acceptance of the data of Terlouw et al. (9). It is critically important that the equilibrium behavior of this system be confirmed by further experiments. One can also directly test this model by using Venus water profiles to be measured by the Near Infrared Mapping Spectrometer experiment on the Galileo spacecraft (16). Further, the conditions of temperature and pressure and the high CO2 and water vapor abundances conducive to extensive gaseous H₂CO₃ formation are closely similar to those hypothesized for early Earth. An improved understanding of the thermochemical and optical properties of this species may permit substantial improvement of these models.

REFERENCES AND NOTES

1. U. von Zahn, S. Kumar, H. Niemann, R. Prinn, in

Venus, D. M. Hunten, L. Colin, T. M. Donahue, V. I. Moroz, Eds. (Univ. of Arizona Press, Tucson, 1983), pp. 299-430.

- V. I. Oyama et al., J. Geophys. Res. 85, 7891 (1980). 3. H. E. Revercomb, L. A. Sromovsky, V. E. Suomi,
- Icarus 61, 521 (1985). V. I. Moroz, N. A. Parfent'ev, N. F. San'ko, Cosmic
- Res. (U.S.S.R.) 17, 601 (1979). 5. L. D. G. Young, A. T. Young, L. V. Zasova, Icarus
- **60**, 138 (1984). 6. J. I. Gmitro and T. Vermeulen, Am. Inst. Chem. Eng. J. 10, 740 (1964).
- 7. G. P. Ayers, R. W. Gillett, J. L. Gras, Geophys. Res. Lett. 7, 433 (1980).
- 8. P. G. Steffes, Icarus 64, 576 (1985).
- J. K. Terlouw, C. B. Lebrilla, H. Schwartz, Angew. Chem. Int. Ed. Engl. 26, 354 (1987).
- 10 Terlouw et al. (9) found in the mass spectrum of NH₄HCO₃ vapor (at 120 K) a peak for H₂CO₃ with a peak area somewhat less than 1% of that for CO_2 . Vapor pressure data on NH_4HCO_3 (17) give a Gibbs free energy of vaporization to NH3, H2O, and CO2 of -4600 cal mol⁻¹ at 120 K. Because of the very large theoretical activation energy of at least 40 kcal mol⁻¹ for dissociation of gaseous H₂CO₃ into water vapor and CO₂ (18), we assume that the CO₂:H₂CO₃ ratio was fixed at about 5×10^{-3} in the evaporation chamber rather than in the mass spectrometer. In combination with a ΔH_{298}^0 of -146.1 kcal mol⁻¹ for formation of H₂CO₃ from the elements (9) and a ΔH_{400}^{0} of -152.1 kcal mol⁻¹ for gaseous CO₂ plus H₂O from the JANAF tables (19), we deduce an enthalpy change at 400 K of 6

kcal mol^{-1} and an entropy change of 2 cal mol^{-1} K⁻¹ for reaction 2.

- 11. As a sensitivity test, we calculated a large number of models without using laboratory thermodynamic data on $\rm H_2CO_3$ and $\rm H_2SO_4$ vapors. Instead, grids of enthalpy and entropy values for both reactions were systematically explored to see which values could give a satisfactory fit to the Venus water profile. We found that the ranges of best-fit thermodynamic properties required to fit the Venus observations were extremely close to the published laboratory data.
- V. G. Istomin, K. V. Grechev, V. A. Kochnev, Space 12. Res. 20, 215 (1980).
- B. G. Gel'man *et al.*, *ibid.*, p. 219.
 J. H. Hoffman, R. R. Hodges, Jr., T. M. Donahue, M. B. McElroy, J. Geophys. Res. 85, 7882 (1980).
 T. M. Donahue, personal communications.
- 16. J. B. Pollack, personal communication.
- 17. W. K. Hutchison, J. Chem. Soc. 1931, 410 (1931); W. K. Huthison, J. Chem. Soc. 1931, 410 (1931), T. Stobiecki, A. Baranski, Z. Kowalski, *Chem. Sto-sow.* 1, 81 (1957).
 See, for example, M. T. Nguyen and T.-K. Ha, *J. Am. Chem. Soc.* 106, 599 (1984).
- JANAF (Joint Army-Navy-Air Force) Thermochemical Tables (Dow Chemical Company, Midland,
- MI, 1973).
 L. W. Esposito, R. G. Knollenberg, M. Ya. Marov, O. B. Toon, R. P. Turco, in *Venus*, D. M. Hunten, L. Colin, T. M. Donahue, V. I. Moroz, Eds. (Univ. of Arizona Press, Tucson, 1983), pp. 484–564. 21. We thank K. Vemulapalli, D. M. Hunten, A. T.
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Negative Pressure-Temperature Slopes for Reactions Forming MgSiO₃ Perovskite from Calorimetry

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A new and sensitive differential drop solution calorimetric technique was developed for very small samples. A single experiment using one 5.18-milligram sample of perovskite, synthesized at 25 gigapascals and 1873 Kelvin, gave 110.1 ± 4.1 kilojoules per mole for the enthalpy of the ilmenite-perovskite transition in MgSiO₃. The thermodynamics of the reaction of MgSiO₃ (ilmenite) to MgSiO₃ (perovskite) and of Mg₂SiO₄ (spinel) to MgSiO₃ (perovskite) and MgO (periclase) were assessed. Despite uncertainties in heat capacity and molar volume at high pressure and temperature, both reactions clearly have negative pressure-temperature slopes, -0.005 ± 0.002 and -0.004 ± 0.002 gigapascals per Kelvin, respectively. The latter may be insufficiently negative to preclude whole-mantle convection.

GSIO₃-rich perovskite is thought to dominate the earth's \blacktriangle lower mantle (1). Knowing its stability is crucial for understanding the seismic discontinuity near 650 km and for predicting lower mantle properties. The pressure-temperature (P-T) slope (dP/dT) of reactions forming perovskite may help determine whether the mantle is compositionally layered or whether whole mantle con-

vection can occur; a strongly negative slope would inhibit convection across the boundary (2, 3). The nature of convection has important implications for the evolution of the earth, its heat budget, and the coupling of convection in the core to processes in the mantle and crust.

Ito and Yamada (4) first demonstrated that for the transformations of MgSiO₃ ilmenite to perovskite and of Mg₂SiO₄ spinel to perovskite and periclase, have negative slopes (dP/dT < 0) and that both reactions occur at similar pressures and temperatures. Ito and Takahashi (5) refined these observations. They concluded that the pronounced sharpness of the 650-km discontinuity can be reasonably interpreted as the dissociation of silicate spinel into perovskite plus magnesiowustite. Although their data suggest that dP/dT is negative, pressure and temperature determinations in multianvil devices still have considerable uncertainties, and phase boundary reversals are difficult. Thus, the slope of the perovskite-forming reaction has remained somewhat uncertain. Because of the importance of this slope in considerations of whole mantle convection, it is desirable to determine dP/dT by a different and independent method, in order to test whether the phase synthesis runs were indeed close to equilibrium, to confirm that the slope is negative, and to obtain a reliable value for dP/dT.

High-temperature oxide melt solution calorimetry (6) offers a means of obtaining thermochemical data for high-pressure silicates (7-9). However, in order to apply this technique to the very small amounts of MgSiO₃ perovskite obtainable by synthesis at 25 GPa in a multianvil apparatus, its sensitivity had to be improved. In this report, we describe a new differential dropsolution technique and report a calorimetric determination, using 5 mg of perovskite, of the enthalpy difference between MgSiO₃ pyroxene and perovskite. Combination with earlier thermodynamic data (7-10) allows calculation of the stability fields of MgSiO3 perovskite and comparison with high-pressure studies.

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