

## NO. 171 SULFURIC ACID IN THE VENUS CLOUDS

by GODFREY T. SILL, O. CARM.

December 15, 1972

### ABSTRACT

The extremely dry nature of the Venus upper atmosphere appears to demand the presence of an efficient desiccating agent as the chief constituent of the clouds of Venus. On the basis of polarization measures one would expect this substance to be present as spherical droplets, 1-2 $\mu$  in diameter, with a refractive index  $n$  of  $1.46 \pm 0.02$  at 3500Å in the observed region of the atmosphere, with  $T \sim 235^\circ\text{K}$ . This substance must have ultraviolet, visible and infrared reflection properties not inconsistent with the observed spectrum of Venus. Sulfuric acid, of about 86% by weight composition, roughly fulfills the first of these properties. The visible and ultraviolet transmission features of a thin layer of elemental bromine and hydrobromic acid dissolved in sulfuric acid somewhat resemble the Venus spectrum, up to 14 $\mu$ . The chemical process postulated for forming sulfuric acid involves the oxidation of sulfur and its compounds to sulfuric acid through the agency of elemental bromine, produced by the photolytic decomposition of hydrogen bromide.

### 1. Current data on the Venus Clouds

Substantial data exist on the spectroscopic and polarimetric properties of the Venus clouds. Yet the identity of the clouds is still uncertain. Venus shows high reflection of visible light, with an albedo approaching 100%. There are strong absorption features in the ultraviolet and infrared, independent of the atmospheric absorptions caused by CO<sub>2</sub>. Ultraviolet photography of the planet shows regions of variable darkness, attributed to different cloud layers on the planet, revealing a dynamic system of

production and destruction of a strong ultraviolet absorber, produced photolytically in the upper atmosphere. It is important to remember that the high resolution UV spectroscopy of the planet utilizes the average reflection of the whole planet in the ultraviolet. Figure 1 shows the albedo of Venus from 0.2 to 4.0 $\mu$ , as taken from Kuiper's 1969 article on the clouds of Venus, with the UV region modified by Wallace *et al.* (1972), and the 3-4 $\mu$  region to allow for the CO<sub>2</sub> absorption 3.7-4.0 $\mu$  observed by Beer *et al.* (1972). A double absorption near 3.8 $\mu$ ,

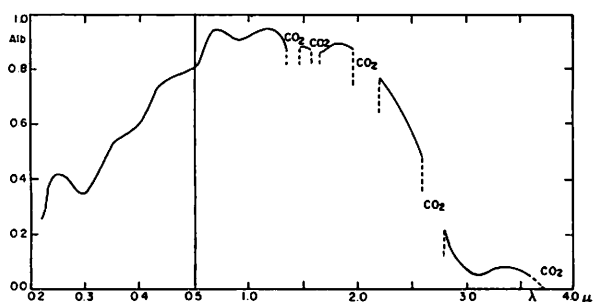


Fig. 1 Venus Bond albedos vs. wavelength, 0.2-4  $\mu$ .

assumed by these authors to be due to solid particles, is actually due to  $\text{CO}_2$  gas (Kuiper 1972).

Polarization studies by Coffeen (1968) led him to conclude that the particles in the clouds were probably spherical, with a refractive index  $n$  of 1.43-1.60 and a mean particle size of  $2.5\mu$ . Further work by Hansen and Arking (1971) and Coffeen and Hansen (1972) give a mean particle size of  $1.1\mu$  and  $n$  of  $1.46 \pm 0.02$  at  $0.35\mu$  decreasing to 1.43 at  $1.0\mu$ . The particles are spherical, and show other properties of spheres, the rainbow and possibly the glory.

Another important property of the Venus atmosphere at the level of the clouds, namely at 50 mb pressure ( $10^{-1.30}\text{atm}$ ) and  $235^\circ\text{K}$ , is the extremely low water vapor mixing ratio of  $10^{-6.0}$  ( $P_{\text{H}_2\text{O}} = 10^{-4.30}\text{mb}$ ). The vapor pressure of ice is higher than this value by orders of magnitude. If  $\text{H}_2\text{O}$  is a constituent of the clouds, it must be present with a strong desiccating agent. Kuiper (1969) in suggesting  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$  as a constituent of the Venus clouds made the cogent observation that the vapor pressure of water in  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$  at  $250^\circ\text{K}$  was compatible with the observed vapor pressure of water. This property is not unique to  $\text{FeCl}_2$ , however. Other possible desiccating agents can fulfill this function.

Is there any one substance that can account for all the above properties of the clouds as well as being compatible with the albedo of Venus over the spectrum?  $\text{FeCl}_2$  does a creditable job for some parts of the spectrum, but not all.  $\text{FeCl}_2$  does not satisfy the polarimetric properties because it tends to form hexagonal platy crystals, not spheres.

The author was intrigued by the fact that  $\text{FeSO}_4$  hydrate, as well as other hydrated sulfates, showed low reflectivity between  $3.0$  to  $4.0\mu$  in the infrared. No other hydrates did as well in satisfying the low reflectivity of Venus in this region. An obvious candidate for consideration as a cloud constituent was

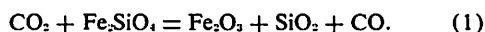
$\text{H}_2\text{SO}_4$ , which also showed strong absorption in the  $3$  to  $4\mu$  region.

The above considerations led to an interim report dated 24 March 1972, sent to NASA and scientific colleagues, prepared by Dr. Kuiper, from which we quote:

"Mr. Sill found that elemental sulfur may form a cloud layer in the deeper atmosphere. In any case, sulfur-dioxide will penetrate into the upper atmosphere, where it could be oxidized to sulfuric acid by free halogens, particularly iodine; and there possibly form small cloud particles in the upper Venus atmosphere composed of sulfuric acid, of 88% concentration. This concentration would be consistent with the observed  $\text{H}_2\text{O}$  mixing ratio. The refractive index of this sulfuric acid solution would be about 1.45 at  $240^\circ\text{K}$ , in agreement with the polarization data. This material would supercool into spheres, as also indicated by the observed polarization properties of the planet. This explanation for the Venus clouds could be either an alternative to the  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$  explanation advanced in *LPL Comm. No. 101* or possibly apply to the UV cloud layer only and thus be in addition to the ferrous-chloride explanation for the yellow lower clouds. In either case, the reflection spectra should be obtained next year of sulfuric acid fogs produced in the laboratory, both with and without dissolved halogens."

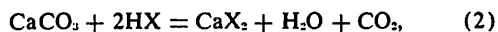
Another section of this report is also quoted:

"Mr. Sill found that the observed  $\text{CO}/\text{CO}_2$  ratio of about  $10^{-4.3}$  may be explained as due to an equilibrium reaction involving the weathering of iron-bearing olivines and pyroxenes by carbon dioxide:



At  $T_s = 750^\circ\text{K}$  and  $P_s = 100$  atm. the  $\text{CO}/\text{CO}_2$  ratio according to thermodynamics should indeed be about  $10^{-4.3}$ .

"Mr. Sill found that the abundances of the acid halides ( $\text{HF}$  and  $\text{HCl}$ ) may be explicable if one considers an equilibrium with a surface deposit of calcite, the latter being called upon to explain the abundance of  $\text{CO}_2$ . Carbonates are attacked by acid halides,



where  $X = \text{F}, \text{Cl}, \text{Br},$  or  $\text{I}$ . With the ratio  $\text{H}_2\text{O}/\text{CO}_2 = 10^{-6}$  found in the upper atmosphere,  $\text{HCl}$  and  $\text{HF}$  would indeed have the mixing ratios of  $10^{-6}$  and  $10^{-8}$ , as observed. If on the other hand, elemental abundances were solely responsible one would expect  $\text{HCl}$  to be only 5 times more abundant than  $\text{HF}$ . Therefore, it would follow that the process of eq. (2), rather than the abundance ratios, determines the relative amounts of  $\text{HCl}$  and  $\text{HF}$ . If the  $\text{H}_2\text{O}/\text{CO}_2$  ratio in the lower atmosphere is well in excess of  $10^{-6}$ , this could imply that the acid halides also would be more abundant there.

"If  $\text{HBr}$  and  $\text{HI}$  are used in eq. (2), then the equilibrium amounts of  $\text{HBr}$  and  $\text{HI}$  are found to be an order of magnitude more than  $\text{HCl}$ ; though here elemental abundances may affect the total bromine and iodine availability. Furthermore,  $\text{HBr}$  and  $\text{HI}$  are less stable than  $\text{HCl}$ , and tend to break down upon exposure to UV (sun) light around  $2500\text{\AA}$ .

"An observational program was therefore initiated for the detection of  $\text{Br}_2$  or  $\text{HBr}$  on Venus. The strong  $\text{HBr}$  absorption at  $2.0$  lies in the middle of very intense Venus  $\text{CO}_2$  absorptions. However,  $\text{Br}_2$  has a strong electronic band in the accessible region,  $3600$ - $5500\text{\AA}$ , with a maximum absorption at  $4100\text{\AA}$ . This absorption causes the gas to be strongly colored visually. The band structure of  $\text{Br}_2$  is most readily seen between  $5300$ -

5400Å, since the absorption is nearly continuous near its maximum. If the yellow tint of Venus were due to gaseous Br<sub>2</sub>, only ½ mm atm. would be required. This amount would just be detectable on Venus with an existing LPL spectrograph having 4Å/mm dispersion, as observed between the sun's Fraunhofer lines. Spectra of Venus were obtained with this instrument on the 61-inch telescope, Catalina Observatory. No detectable Br<sub>2</sub> absorptions were found between 5100-5400Å. However, the Br<sub>2</sub> absorptions are so numerous and sharp that high resolution on Venus is called for. This problem is being pursued."

The present publication updates these preliminary results.

The first property to verify was the vapor pressure of water in equilibrium with various H<sub>2</sub>SO<sub>4</sub> solutions at 235°K. The INTERNATIONAL CRITICAL TABLES give values of P<sub>H<sub>2</sub>O</sub> over H<sub>2</sub>SO<sub>4</sub> solutions from 10 to 95% H<sub>2</sub>SO<sub>4</sub>. The appropriate values seemed to be in the high H<sub>2</sub>SO<sub>4</sub> concentrations. At 235°K the following were calculated:

% (wt) H <sub>2</sub> SO <sub>4</sub>	Log P <sub>H<sub>2</sub>O</sub> of soln. (mb)
90	-5.03
85	-4.14
80	-3.56

Since log P<sub>H<sub>2</sub>O</sub> (mb) at the cloud level is -4.3, the 85% H<sub>2</sub>SO<sub>4</sub> solution is close to the observed value, with 86% solution a good fit. More exhaustive analysis of water vapor regulated by H<sub>2</sub>SO<sub>4</sub> was performed by Fink, Larson, *et al.* (1972). They found H<sub>2</sub>SO<sub>4</sub> of about 80% composition can dry the upper atmosphere to give good agreement with the measured abundance of H<sub>2</sub>O.

The second property to consider is refractive index *n*. The INTERNATIONAL CRITICAL TABLES list refractive index for H<sub>2</sub>SO<sub>4</sub> solutions (particularly 95-96% solutions) at various temperatures and wavelengths. From 301 to 387°K the refractive index decreases linearly with temperature increase. Extrapolating back to 235°K, and correcting for wavelength, *n* for 95-96% H<sub>2</sub>SO<sub>4</sub> at 3500Å is 1.440. With the *n* value of 1.405 for H<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O (73%) at 20°C (HANDBOOK OF CHEMISTRY AND PHYSICS), the 235°K *n* value should be 1.419. The 86% H<sub>2</sub>SO<sub>4</sub> solution would therefore be calculated as *n* = 1.431 at 235°K. This value is close to the 1.46 ± 0.02 of Coffeen and Hansen, but somewhat outside the limit. Solutions of H<sub>2</sub>SO<sub>4</sub> > 95% are compatible with the polarization measurements. It well might be that the spherical droplets are actually frozen. This would raise the refractive index of 86% H<sub>2</sub>SO<sub>4</sub> to about 1.453, well within the acceptable limits. H<sub>2</sub>SO<sub>4</sub> freezes in a com-

plex manner, with various eutectics (H<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>·4H<sub>2</sub>O) freezing at various temperatures, and mixtures of them freezing at lower temperatures. Pure H<sub>2</sub>SO<sub>4</sub> freezes at 10.5°C, the monohydrate at 8.6, the dihydrate at -38.9°, the tetrahydrate at -24.5°.

The author has observed in the laboratory the freezing and melting properties of an 88% H<sub>2</sub>SO<sub>4</sub> solution. The frozen H<sub>2</sub>SO<sub>4</sub> seemed to have an ill-defined melting point, it appeared to just become less viscous as it melted, behaving almost like a glass. A thin layer of the acid was frozen in dry ice and was perfectly transparent. The surface looked glassy. A cold metal spatula seemed to dent the surface; no fractures were observed as is common with water ice. The cloud particles of Venus could therefore be of this "glassy" type H<sub>2</sub>SO<sub>4</sub>, the droplets frozen into spheres, with a refractive index indicative of this denser state, namely about 1.45.

The third property of H<sub>2</sub>SO<sub>4</sub> to compare with the clouds of Venus is spectral reflectivity. As of this time it has not been possible to obtain reflection spectra from fogs of H<sub>2</sub>SO<sub>4</sub>. As a second best choice, *transmission spectra* of thin layers of H<sub>2</sub>SO<sub>4</sub> might simulate to a degree the complex absorption and scattering occurring in a fog of droplets. The thin layer of H<sub>2</sub>SO<sub>4</sub> was obtained by putting a drop of the acid between two plates and letting them seal together. Excess acid was usually squeezed out around the edges of the plates. It is estimated that the layer of acid is approximately 0.05 mm thick. Two plates of optical quartz, each 2 mm thick were used in the transmission spectra from 0.2 to 3.5μ. AgCl plates, ground and polished, were utilized in the spectral region 2.5 to 15.0μ. Also used in this region, with less success, were drops of H<sub>2</sub>SO<sub>4</sub> sandwiched between layers of polyethylene and Saran. The absorptions of the plastics were added to H<sub>2</sub>SO<sub>4</sub>, of course. This was partially cancelled in the dual beam spectrophotometer by placing two layers of plastic in the reference beam, but complete cancellation of the plastic film does not appear to be possible. Instrumental effects near the strong and sharp absorption features of the plastic film produce spurious features in the H<sub>2</sub>SO<sub>4</sub> spectrum. The 0.2 to 3.5μ spectra were obtained from a Beckman DK-2A dual-beam quartz spectrophotometer, and the 2.5 to 15.0μ spectra from a Perkin-Elmer 137 NaCl spectrophotometer, both used by courtesy of Dr. B. Nagy of the University of Arizona's Department of Organic Geochemistry.

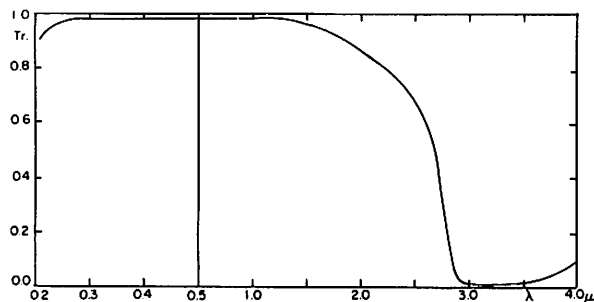


Fig. 2 Transmission spectrum of 88%  $\text{H}_2\text{SO}_4$ , 0.05 mm thick.

Figure 2 shows the spectral transmittance of a thin layer of 88%  $\text{H}_2\text{SO}_4$ . The two quartz plates were used with an acid layer about 0.05 mm thickness between the two plates. The reference beam was the air path. The spectrum needed only very small correction for the absorption of the two quartz plates. By comparison with the Venus spectrum, Figure 1, it can be seen that there is a good match from about 1-3 $\mu$ . Obviously the ultraviolet and visible spectral region must be explained by some other substance(s). Among possible candidates for ultraviolet absorptivity is  $\text{SO}_2$  dissolved in cold  $\text{H}_2\text{SO}_4$ . Since S is oxidized to the 6+ oxidation state in  $\text{H}_2\text{SO}_4$ , the intermediate oxidation state of 4+ in  $\text{SO}_2$  should be expected. The visible yellow color of the Venus clouds presents a problem as well. There are not too many gaseous substances which have a yellow tint. One is brown-yellow  $\text{NO}_2$ . But at the temperature of the Venus clouds the dimmer  $\text{N}_2\text{O}_4$  is highly favored, with a consequent drastic lessening of color intensity. Furthermore, it may be extremely difficult to oxidize N in the atmosphere of Venus. A better candidate is  $\text{Br}_2$ ; a red-brown liquid or gas, which if diluted and dissolved in  $\text{H}_2\text{SO}_4$  to a moderate degree produces a yellow solution; higher concentrations give a red-brown solution. The intensity of the color of  $\text{Br}_2$  varies with temperature.  $\text{Br}_2$  saturated in 88%

$\text{H}_2\text{SO}_4$  solution at room temperature produces a red-brown solution; when cooled to dry ice temperatures, the frozen solid is yellow. The chemical aspects of  $\text{Br}_2$  and  $\text{H}_2\text{SO}_4$  will be discussed below.

Figure 3 shows the inferred Bond albedo of Venus in expanded scale from 0.2 to 0.6 $\mu$ . Wallace (personal communication), from his geometric albedo in the rocket UV, estimates that the Bond albedo of Venus is about 0.4 at 2500 $\text{\AA}$ . Figure 4 shows the transmittance of  $\text{Br}_2$  and  $\text{HBr}$  dissolved in  $\text{H}_2\text{SO}_4$ ;  $\text{HBr}$  was added to the  $\text{Br}_2$  to dissolve more  $\text{Br}_2$  than water alone would dissolve. The  $\text{HBr} + \text{Br}_2$  solution was added to cold concentrated  $\text{H}_2\text{SO}_4$  to obtain a solution of 88%  $\text{H}_2\text{SO}_4$ . Outgassing of  $\text{HBr}$  from the solution was rather vigorous. Solution B was more concentrated than A in  $\text{Br}_2$  and showed more yellow color. Evidently even more coloring agent ( $\text{Br}_2$ ) could be present than in solution B to match Venus 0.3-0.5 $\mu$ ; while the higher UV reflectance of Venus could be due to scattering. However, Venus has a UV peak near 2500 $\text{\AA}$ , whereas the  $\text{Br}_2$  solution peaks at 2200 $\text{\AA}$  and the UV scattering would tend to displace it shortward. The Venus spectrum shows a dip at about 2900 $\text{\AA}$ , whereas  $\text{Br}_2$  solution dips at 2700 $\text{\AA}$ , which would also be slightly displaced shortward by UV scattering.

The  $\text{SO}_2$  spectrum is shown in Figure 5. In curve A,  $\text{SO}_2$  gas was bubbled into cold 88%  $\text{H}_2\text{SO}_4$  and a layer about 0.1 mm thick was observed through the quartz plates. The  $\text{SO}_2$  does show a peak at 2400 $\text{\AA}$  and a dip centered at 2800 $\text{\AA}$ , somewhat closer to the Venus absorption and reflection. To observe the effect of a greater amount of dissolved  $\text{SO}_2$  than could be held by the  $\text{H}_2\text{SO}_4$  at room temperature, a cell of 88%  $\text{H}_2\text{SO}_4$ , 1 cm thick, was utilized with the  $\text{SO}_2$  at about 1/200 of saturation. A similar cell with pure 88%  $\text{H}_2\text{SO}_4$  was used in the reference beam of the Beckman DK-2A.

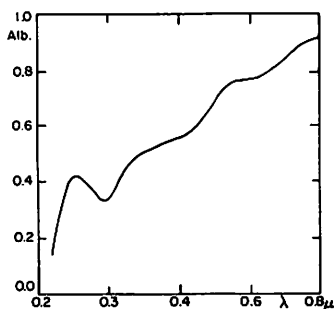


Fig. 3 Venus Bond albedo vs. wavelength, 0.2-0.6  $\mu$ .

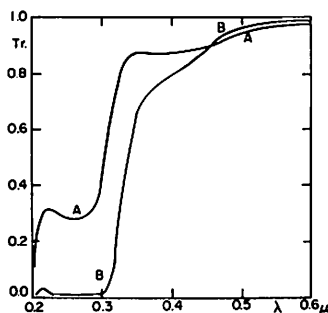


Fig. 4  $\text{HBr} + \text{Br}_2$  dissolved in 88%  $\text{H}_2\text{SO}_4$  (two concentrations).

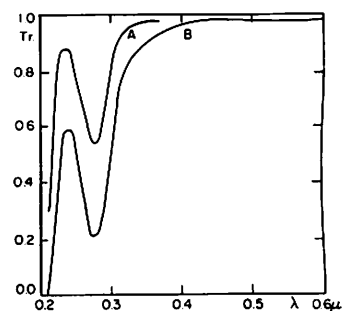


Fig. 5  $\text{SO}_2$  dissolved in 88%  $\text{H}_2\text{SO}_4$  (two concentrations).

When  $\text{Br}_2$  vapor is poured onto a  $\text{SO}_2\text{-H}_2\text{SO}_4$  solution, immediate bleaching of the  $\text{Br}_2$  is observed, as well as a diminution of the absorption features of  $\text{SO}_2$ . Depending on which constituent survives, the spectrum either resembles the  $\text{SO}_2$  or the  $\text{Br}_2$  spectrum more closely. Evidently the  $\text{Br}_2$  oxidizes the  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  and the  $\text{Br}_2$  is reduced to  $\text{HBr}$ .

Figure 6 shows the infrared spectrum from 4.0 to  $15.0\mu$  of 88%  $\text{H}_2\text{SO}_4$  (solid line) with the left hand ordinate of transmittance. The sample was one drop of acid squeezed between  $\text{AgCl}$  plates, with similar plates in the reference beam. The dashed spectrum of Venus is that of Gillett, Low, and Stein (1968) with the right-hand ordinate of log power at the detector. The dotted lines are, first, the reflection of sunlight from a body of unit albedo, and second, the black-body radiation curve at  $225^\circ\text{K}$ . If there is  $\text{H}_2\text{SO}_4$  in the clouds cooler than the emitting surface, then indeed  $\text{H}_2\text{SO}_4$  should show in absorption. There are some similarities between the absorptions of the Venus spectrum 7- $12\mu$  and the absorptions of 88%  $\text{H}_2\text{SO}_4$ , especially in the absorption feature centered at  $11.2\mu$ , prominent in Hanel's Venus spectrum (1968).

## 2. Chemical Production of the $\text{H}_2\text{SO}_4$ Clouds

The mode of production of  $\text{H}_2\text{SO}_4$  in the Venus atmosphere poses a complex problem. First of all no S compounds have been detected on Venus as gases. Upper limits to the mixing ratio of S compounds are available, and the values are (Kuiper 1969):  $\text{SO}_2 < 10^{-7.5}$ ,  $\text{COS} < 10^{-8}$ ,  $\text{H}_2\text{S} < 10^{-3.7}$ . Two of these compounds can probably be ruled out because of their instability to ultraviolet radiation in the upper atmosphere of Venus.  $\text{H}_2\text{S}$  was exposed to the UV radiation of a quartz mercury penlight (most effective radiation at the  $\text{Hg } 2536.5\text{\AA}$ ). Within minutes, noticeable deposition of S particles on the walls of the flask was observed as well as a fine smoke of S in the gas. Within an hour decomposition was virtually complete.  $\text{COS}$  is almost as unstable to UV as  $\text{H}_2\text{S}$ , decomposing into  $\text{CO}$  and S. This decomposition also approaches 100% in hours. Since the upper Venus atmosphere appears transparent to  $\lambda > 2000\text{\AA}$ ,  $\text{H}_2\text{S}$  and  $\text{COS}$  can be ruled out. This leaves one with  $\text{SO}_2$  and S as the most likely carriers of S to the upper atmosphere.

$\text{SO}_2$  has S in the 4+ oxidation state; in order to produce  $\text{H}_2\text{SO}_4$  it is necessary to oxidize S to the 6+ state, as found in  $\text{H}_2\text{SO}_4$ , or in the anhydride of  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_3$ . (The  $\text{SO}_3$  would quickly absorb water

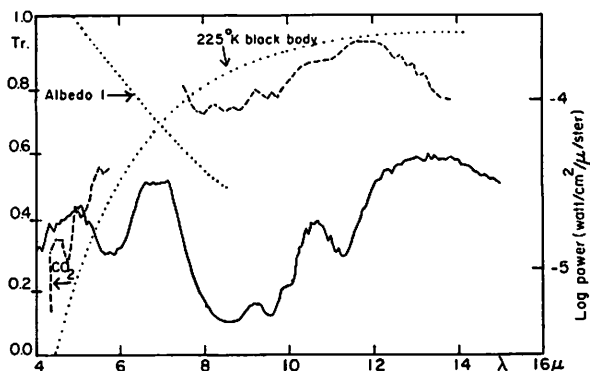
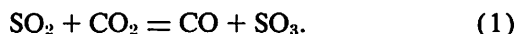


Fig. 6 Solid line: Transmission spectrum with 88%  $\text{H}_2\text{SO}_4$  solution (left ordinates). Dashed line: Infrared spectrum of Venus with black body and unit albedo references (right ordinates).

and form  $\text{H}_2\text{SO}_4$ ). Is it possible to produce  $\text{SO}_3$  in the Venus atmosphere? The process would be:



The resulting log  $K$  values are  $-32.64$ ,  $-24.43$ ,  $-16.40$ , and  $-13.14$  for the temperatures of  $298^\circ$ ,  $400^\circ$ ,  $600^\circ$ ,  $750^\circ\text{K}$ , respectively. The thermodynamic data for calculating the equilibrium constant,  $K$ , are from Robie and Waldbaum (1968). With the  $\text{CO}_2/\text{CO}$  ratio of  $10^{4.34}$  of Venus, presumed to be constant throughout the atmosphere, it is possible to calculate the  $\text{SO}_2/\text{SO}_3$  ratio for the lower atmosphere ( $T > 400^\circ\text{K}$ ) where thermodynamics can furnish valid information. The ratios for  $298^\circ\text{K}$  are included simply to show the trend:

Temp. $^\circ\text{K}$	298	400	600	750
$\text{SO}_2/\text{SO}_3$ ratio	$10^{28.32}$	$10^{25.09}$	$10^{12.06}$	$10^{8.80}$

The ratio is *unfavorable* for  $\text{SO}_3$  production at any level, let alone the upper atmosphere. In the lower hotter atmosphere it appears that the most abundant S species would be  $\text{COS}$ ,  $\text{SO}_2$ , and  $\text{S}_2$ , in that order. It is impossible to give accurate ratios of the S compounds without knowing what the total S abundance is, and whether or not the  $\text{CO}_2/\text{CO}$  ratio remains constant. One possible surface reaction which might determine the abundance of atmospheric  $\text{SO}_2$  involves the equilibrium decomposition of anhydrite,  $\text{CaSO}_4$ , in a  $\text{CO}_2\text{-CO}$  atmosphere:



At a surface temperature of  $750^\circ\text{K}$ , thermodynamics predicts a  $\text{CO}/\text{SO}_2$  ratio of 10. The  $\text{CaSO}_4\text{-CaCO}_3$  equilibrium was chosen because  $\text{CaCO}_3$  is often considered as the major weathered mineral in a  $\text{CO}_2$

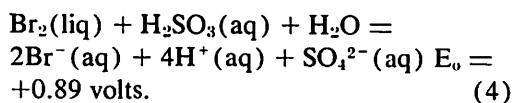
atmosphere. Furthermore  $\text{CaSO}_4$  is often found as a principal S compound in geothermal regions, indicating its ability to survive under moderately high temperature conditions. If the  $\text{CO}/\text{SO}_2$  ratio of 10 should survive to the upper atmosphere there would be an abundant supply of  $\text{SO}_2$  for forming  $\text{H}_2\text{SO}_4$ , provided there is a mechanism for further oxidizing the S to  $\text{SO}_3$ - $\text{H}_2\text{SO}_4$ .

The oxidizing agent in the earth's atmosphere for converting  $\text{SO}_2$  to  $\text{SO}_3$  is  $\text{O}_2$ . On Venus this is ruled out, and the most likely agents are molecular halogens, namely  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$ .  $\text{F}_2$  can be rejected because of the extreme chemical stability of HF. Likewise  $\text{Cl}_2$  gas must be rejected because HCl does not photolytically dissociate for  $\lambda > 2000\text{\AA}$ . The spectra of HCl solutions show no notable absorptions in the ultraviolet between 2000-4000 $\text{\AA}$ . HBr and HI are strong absorbers. Both gases are readily dissociated into hydrogen gas and the molecular halogen under Hg vapor irradiation, and a few hour's radiation brings about equilibrium. In the case of HBr:

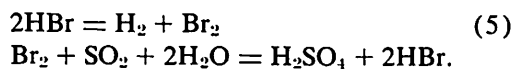


equilibrium quantities of the gases indicate that 7% of HBr is decomposed in the gas-gas equilibrium. The aqueous solution of HBr also shows a noticeable darkening due to formation of  $\text{Br}_2$  under UV exposure.

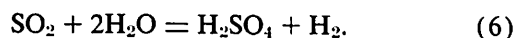
Mention was made of the bleaching effect of  $\text{SO}_2$  gas dissolved in  $\text{H}_2\text{SO}_4$  when  $\text{Br}_2$  fumes were poured onto the surface of the acid- $\text{SO}_2$  solution. This apparently shows the ease at which  $\text{Br}_2$  will oxidize  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  in an acid medium. The thermodynamics also indicate a favorable reaction (Lattimer 1952):



With a positive potential of 0.89 v, the reaction should and does proceed rapidly at room temperature. The two reactions can be summarized as:



The HBr is reconstituted in the process, and in effect serves as a carrier catalyst for the reaction. The overall reaction therefore involves destruction of  $\text{H}_2\text{O}$  into  $\text{H}_2(\text{g})$ , which presumably escapes from Venus, and oxygen incorporated into  $\text{H}_2\text{SO}_4$ :

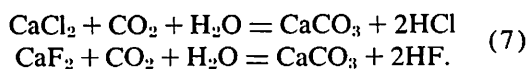


Reaction (6) is not favored thermodynamically and could never occur at the low temperature of the Venus clouds, but the intermediate reaction with  $\text{Br}_2$  (and presumably the other halogen,  $\text{I}_2$ ) make the process possible. None of the intermediate substances has been identified in the atmosphere of Venus, namely  $\text{SO}_2$ , HBr and  $\text{Br}_2$ . HBr is a difficult problem spectroscopically because its absorption bands at 2 and 4 microns fall into the heavy  $\text{CO}_2$  bands.  $\text{Br}_2$  (gas) was examined at our laboratory with the helpful assistance of Allen Thomson and Thomas N. Gautier. Moderately strong absorption bands were found in the region of 5364 $\text{\AA}$ . Sill, Gautier, and Kuiper attempted to detect gaseous  $\text{Br}_2$  in the atmosphere of Venus first with the 61-inch telescope of the Catalina Observatory, then with the 107-inch telescope of the McDonald Observatory. Edwin S. Barker of the University of Texas graciously aided us in obtaining high resolution spectra at the Coudé focus of the 107-inch telescope with its attendant echelle grating spectrograph. Spectra of Venus, the sun, and the sun +  $\text{Br}_2$  (gas) were obtained in the region of 5364 $\text{\AA}$ . The results were negative. From the spectra it is estimated that the smallest quantity of  $\text{Br}_2$  that could be seen in Venus is about 0.13 mm-atm. *An upper limit to the Venus mixing ratio*  $\text{Br}_2/\text{CO}_2$  can be set at  $< 10^{-7.3}$ . This implies a very small quantity of  $\text{Br}_2$  vapor, much less than the 4 mb vapor pressure of elemental  $\text{Br}_2$  at 235°K. On the other hand  $\text{Br}_2$  is very soluble in cold  $\text{H}_2\text{SO}_4$ , especially in the presence of HBr.

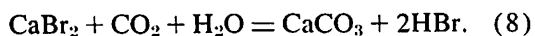
Both  $\text{Br}_2$  and  $\text{SO}_2$  have mixing ratios with upper limits  $< 10^{-7}$ . This may simply be a sign of their high reactivity with each other. The reaction is fast and involves reconstituting HBr. Since no upper limit on HBr has been established, the whole postulated mechanism cannot be proven at this time. The empirical data discussed above indicate that the visible and UV albedos of Venus may be consistent with  $\text{Br}_2$  dissolved in  $\text{H}_2\text{SO}_4$ . The highly sensitive test for gaseous  $\text{Br}_2$  is not applicable to dissolved  $\text{Br}_2$  as the sharp lines of the gas are smeared into the broad band of a liquid.

Chemical considerations would lead one to suspect that HBr is a gaseous constituent of the atmosphere of Venus, chiefly because HF and HCl are present. In general one halogen implies the presence of the others, taking due account of their chemical activity. A perfect case in point is the relative abun-

dance of HCl and HF in the Venus atmosphere, with mixing ratios of  $10^{-6.0}$  and  $10^{-8.0}$  respectively. The Cl/F ratio in the atmosphere is 100, whereas the cosmic elemental abundance ratio of Cl/F is 5.5 (Suess-Urey) or 1.8 (Cameron) according to the HANDBOOK OF PHYSICAL CONSTANTS. Something is making F less abundant in the atmosphere. Sea water on earth shows a similar disparity with a Cl/F ratio of 7000. In this latter case the explanation is due to the higher solubility of chlorides vs fluorides, plus the relative stability of fluoride micaceous minerals versus the chloride. As far as Venus is concerned, the relative solubilities of chlorides and fluorides in water have no bearing on the case, but rather the chemical stability of chloride and fluoride minerals in the presence of a hot  $\text{CO}_2$  atmosphere. Pertinent reactions might be:



At  $750^\circ\text{K}$ , with  $P_{\text{CO}_2}$  at 100 atm, the relative amounts of gaseous hydrogen halides, HCl/HF, is about 100, which is the observed ratio in the upper atmosphere. The simple cosmic abundance ratio is not valid. The same argument can be applied to the equivalent bromide:



The ratio HCl/HBr is less than 1. It is possible that HBr might be more abundant than HCl in the Venus atmosphere if the surface reactions are the dominant influence in atmospheric abundance. This may be the case, otherwise HCl should be more abundant than the observed mixing ratio of  $10^{-6.0}$ . Cl in the earth's oceans amounts to  $8.6 \times 10^{22}$  moles, whereas in Venus' atmosphere there is about  $1.3 \times 10^{16}$  moles. Unless severe depletion of Cl occurred on Venus vs earth, the excess Cl on Venus should be locked in the surface rocks in a way similar to equation (7). When one considers Br on Venus, there might appear to be a problem of the absolute abundance of Br. The Cl/Br ratio in the earth's oceans is 660, which ratio is the one assumed by Suess-Urey as the relative cosmic abundance. If the absolute abundance of Br on Venus matches that in the earth, there is more than enough Br to make the equilibrium of equation (8) applicable, namely HBr would be more abundant in the atmosphere than HCl. Similar arguments can be applied to I, and HI would be thermally unstable and decompose.

### 3. Forming $\text{H}_2\text{SO}_4$ Synthetically in the Laboratory

Tests were conducted in the laboratory to see if  $\text{H}_2\text{SO}_4$  could be formed by the irradiation of HBr and S compounds. Acid solutions of HBr and various S gases, particularly  $\text{SO}_2$  and COS were irradiated with the quartz Hg lamp. COS vigorously decomposed, producing large quantities of S. Some  $\text{H}_2\text{SO}_4$  was produced, which was analyzed by precipitating  $\text{BaSO}_4$  on the addition of  $\text{BaCl}_2$  solution. The conversion of COS to  $\text{H}_2\text{SO}_4$  was about 3%.  $\text{SO}_2$  showed slightly more conversion to  $\text{H}_2\text{SO}_4$ . In one day's irradiation about 5% converted. Without HBr, conversion to  $\text{H}_2\text{SO}_4$  by  $\text{SO}_2$  was negligible. The amount of  $\text{BaSO}_4$  precipitated was minute. Even elemental  $\text{Br}_2$  and S, mixed together in water solution showed a high conversion to  $\text{H}_2\text{SO}_4$ , but since this reaction occurred in the open air undoubtedly dissolved  $\text{O}_2$  facilitated the reaction. Therefore,  $\text{H}_2\text{SO}_4$  is readily produced under postulated Venus atmospheric conditions.

### 4. Conclusion

The lack of detectable S compounds in the atmosphere of Venus has always been a problem. Whereas the atmosphere of Earth is dominated by  $\text{O}_2$  and  $\text{H}_2\text{O}$ , the Venus atmosphere could be dominated by the halogens. The lack of S is explained by postulating that the clouds of Venus are frozen droplets of 86%  $\text{H}_2\text{SO}_4$ , formed by the oxidation of  $\text{SO}_2$  by elemental  $\text{Br}_2$  in the upper atmosphere of Venus.

*Acknowledgments.* The work described in this paper was carried out under NASA Grant Nr. NGL-03-002-002.

### REFERENCES

- Beer, R., Norton, R. H., and Martonchik, J. V. 1971, "Absorption by Venus in the 3-4 Micron Region," *Ap. J. Letters*, 168, L121-L124.
- Coffeen, D. 1968, "A Polarimetric Study of the Atmosphere of Venus," Ph.D. dissertation, University of Arizona.
- Coffeen, D. and Hansen, J. E. 1972, "Polarization Studies of Planetary Atmospheres," a contributed paper to IAU Colloquium 23 on Polarization, University of Arizona.
- Fink, U., Larson, H., Kuiper, G. P., and Poppen, R. F. 1972, "Water Vapor in the Atmosphere of Venus," *Icarus*, 17, 617-631.
- Gillett, F. C., Low, F. J., and Stein, W. A. 1968,

- "Absolute Spectrum of Venus from 2.8 to 14 Microns," *J. Atmos. Sci.*, **25**, 594,595.
- Hanel, R., Forman, M. and Stambach, G. 1968, "Preliminary Results of Venus Observations between 8 and 13 Microns," *J. Atmos. Sci.*, **25**, 586-593.
- Hansen, J. E. and Arking, A. 1971, "Clouds of Venus: Evidence for their Nature," *Science*, **171**, 669-672.
- Kuiper, G. P. 1969, "Identification of the Venus Cloud Layers," *LPL Comm.*, **6**, No. 101, 229-250.
- . 1972. Personal communication; Burch, D. E., Grynak, D. A., Patty, R. R., and Bartky, C. E. 1969, "Absorption of Infrared Radiant Energy by CO<sub>2</sub> and H<sub>2</sub>O. IV. Shapes of Collision-Broadened CO<sub>2</sub> Lines," *Jour. Opt. Soc. Amer.*, **59**, 267-280.
- Latimer, W. L. 1952, *The Oxidation States of the Elements and their Potentials in Aqueous Solutions*, Prentice-Hall, New York.
- Robie, R. A. and Waldbaum, D. R. 1968, *Thermodynamic Properties of Minerals and Related Substances*, G.S.B. 1259, U.S. Govt. Printing Office, Washington.
- Wallace, L., Caldwell, J. J. and Savage, B. D. 1972, "Ultraviolet Photometry from the Orbiting Astronomical Observatory. III, Observations of Venus, Mars, Jupiter and Saturn Longward of 2000Å," *Ap. J.*, **172**, 755-769.



#### TABLE OF CONTENTS

No. 166	Arizona-NASA Atlas of the Infrared Solar Spectrum, Report X.....	155
	by D. C. Benner, G. P. Kuiper, L. Randić, and A. B. Thomson	
No. 167	Narrow-Band Photometry of the Galilean Satellites.....	171
	by Willem Wamsteker	
No. 168	Spectral Albedos of the Galilean Satellites.....	179
	by Thomas Lee	
No. 169	Map of the Galactic Nucleus at $10\mu$ .....	181
	by G. H. Rieke and F. J. Low	
No. 170	Preliminary Report on Optical Seeing Tests at Mt. Lemmon.....	185
	March-June, 1971	
	by George V. Coyne, S. J.	
No. 171	Sulfuric Acid in the Venus Clouds.....	191
	by Godfrey T. Sill, O. Carm.	