

NO. 171 SULFURIC ACID IN THE VENUS CLOUDS

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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 μ in diameter, with a refractive index n of 1.46 ± 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 μ . 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 CO₂. 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 μ , 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 μ region to allow for the CO₂ absorption 3.7-4.0 μ observed by Beer *et al.* (1972). A double absorption near 3.8 μ ,

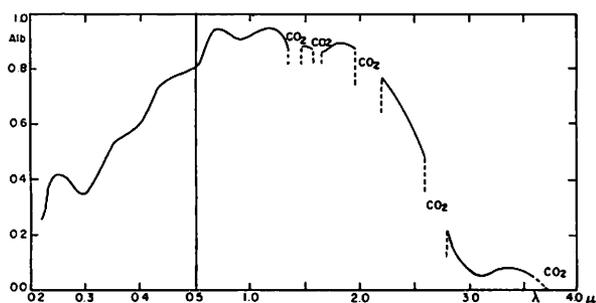


Fig. 1 Venus Bond albedos vs. wavelength, 0.2-4 μ .

assumed by these authors to be due to solid particles, is actually due to 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 2.5μ . Further work by Hansen and Arking (1971) and Coffeen and Hansen (1972) give a mean particle size of 1.1μ and n of 1.46 ± 0.02 at 0.35μ decreasing to 1.43 at 1.0μ . 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°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 H_2O 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°K was compatible with the observed vapor pressure of water. This property is not unique to 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? FeCl_2 does a creditable job for some parts of the spectrum, but not all. 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 FeSO_4 hydrate, as well as other hydrated sulfates, showed low reflectivity between 3.0 to 4.0μ 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

H_2SO_4 , which also showed strong absorption in the 3 to 4μ 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 H_2O mixing ratio. The refractive index of this sulfuric acid solution would be about 1.45 at 240°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."

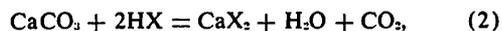
Another section of this report is also quoted:

"Mr. Sill found that the observed CO/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 CO/CO_2 ratio according to thermodynamics should indeed be about $10^{-4.3}$.

"Mr. Sill found that the abundances of the acid halides (HF and 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 CO_2 . Carbonates are attacked by acid halides,



where $X = \text{F}, \text{Cl}, \text{Br},$ or I . With the ratio $\text{H}_2\text{O}/\text{CO}_2 = 10^{-6}$ found in the upper atmosphere, HCl and 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 HCl to be only 5 times more abundant than HF . Therefore, it would follow that the process of eq. (2), rather than the abundance ratios, determines the relative amounts of HCl and 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 HBr and HI are used in eq. (2), then the equilibrium amounts of HBr and HI are found to be an order of magnitude more than HCl ; though here elemental abundances may affect the total bromine and iodine availability. Furthermore, HBr and HI are less stable than HCl , and tend to break down upon exposure to UV (sun) light around 2500\AA .

"An observational program was therefore initiated for the detection of Br_2 or HBr on Venus. The strong HBr absorption at 2.0 lies in the middle of very intense Venus CO_2 absorptions. However, Br_2 has a strong electronic band in the accessible region, 3600 - 5500\AA , with a maximum absorption at 4100\AA . This absorption causes the gas to be strongly colored visually. The band structure of 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 Br₂, 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 Br₂ absorptions were found between 5100-5400Å. However, the Br₂ 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 H₂SO₄ solutions at 235°K. The INTERNATIONAL CRITICAL TABLES give values of P_{H₂O} over H₂SO₄ solutions from 10 to 95% H₂SO₄. The appropriate values seemed to be in the high H₂SO₄ concentrations. At 235°K the following were calculated:

% (wt) H ₂ SO ₄	Log P _{H₂O} of soln. (mb)
90	-5.03
85	-4.14
80	-3.56

Since log P_{H₂O} (mb) at the cloud level is -4.3, the 85% H₂SO₄ solution is close to the observed value, with 86% solution a good fit. More exhaustive analysis of water vapor regulated by H₂SO₄ was performed by Fink, Larson, *et al.* (1972). They found H₂SO₄ of about 80% composition can dry the upper atmosphere to give good agreement with the measured abundance of H₂O.

The second property to consider is refractive index *n*. The INTERNATIONAL CRITICAL TABLES list refractive index for H₂SO₄ 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% H₂SO₄ at 3500Å is 1.440. With the *n* value of 1.405 for H₂SO₄·2H₂O (73%) at 20°C (HANDBOOK OF CHEMISTRY AND PHYSICS), the 235°K *n* value should be 1.419. The 86% H₂SO₄ 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 H₂SO₄ > 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% H₂SO₄ to about 1.453, well within the acceptable limits. H₂SO₄ freezes in a com-

plex manner, with various eutectics (H₂SO₄·H₂O, H₂SO₄·2H₂O, H₂SO₄·4H₂O) freezing at various temperatures, and mixtures of them freezing at lower temperatures. Pure H₂SO₄ 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% H₂SO₄ solution. The frozen H₂SO₄ 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 H₂SO₄, the droplets frozen into spheres, with a refractive index indicative of this denser state, namely about 1.45.

The third property of H₂SO₄ 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 H₂SO₄. As a second best choice, *transmission spectra* of thin layers of H₂SO₄ might simulate to a degree the complex absorption and scattering occurring in a fog of droplets. The thin layer of H₂SO₄ 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 H₂SO₄ sandwiched between layers of polyethylene and Saran. The absorptions of the plastics were added to H₂SO₄, 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 H₂SO₄ 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.

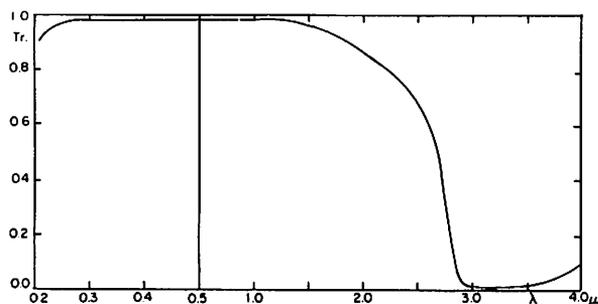


Fig. 2 Transmission spectrum of 88% H_2SO_4 , 0.05 mm thick.

Figure 2 shows the spectral transmittance of a thin layer of 88% H_2SO_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 μ . Obviously the ultraviolet and visible spectral region must be explained by some other substance(s). Among possible candidates for ultraviolet absorptivity is SO_2 dissolved in cold H_2SO_4 . Since S is oxidized to the 6+ oxidation state in H_2SO_4 , the intermediate oxidation state of 4+ in 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 NO_2 . But at the temperature of the Venus clouds the dimmer N_2O_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 Br_2 ; a red-brown liquid or gas, which if diluted and dissolved in H_2SO_4 to a moderate degree produces a yellow solution; higher concentrations give a red-brown solution. The intensity of the color of Br_2 varies with temperature. Br_2 saturated in 88%

H_2SO_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 Br_2 and H_2SO_4 will be discussed below.

Figure 3 shows the inferred Bond albedo of Venus in expanded scale from 0.2 to 0.6 μ . Wallace (personal communication), from his geometric albedo in the rocket UV, estimates that the Bond albedo of Venus is about 0.4 at 2500 \AA . Figure 4 shows the transmittance of Br_2 and HBr dissolved in H_2SO_4 ; HBr was added to the Br_2 to dissolve more Br_2 than water alone would dissolve. The $\text{HBr} + \text{Br}_2$ solution was added to cold concentrated H_2SO_4 to obtain a solution of 88% H_2SO_4 . Outgassing of HBr from the solution was rather vigorous. Solution B was more concentrated than A in Br_2 and showed more yellow color. Evidently even more coloring agent (Br_2) could be present than in solution B to match Venus 0.3-0.5 μ ; while the higher UV reflectance of Venus could be due to scattering. However, Venus has a UV peak near 2500 \AA , whereas the Br_2 solution peaks at 2200 \AA and the UV scattering would tend to displace it shortward. The Venus spectrum shows a dip at about 2900 \AA , whereas Br_2 solution dips at 2700 \AA , which would also be slightly displaced shortward by UV scattering.

The SO_2 spectrum is shown in Figure 5. In curve A, SO_2 gas was bubbled into cold 88% H_2SO_4 and a layer about 0.1 mm thick was observed through the quartz plates. The SO_2 does show a peak at 2400 \AA and a dip centered at 2800 \AA , somewhat closer to the Venus absorption and reflection. To observe the effect of a greater amount of dissolved SO_2 than could be held by the H_2SO_4 at room temperature, a cell of 88% H_2SO_4 , 1 cm thick, was utilized with the SO_2 at about 1/200 of saturation. A similar cell with pure 88% H_2SO_4 was used in the reference beam of the Beckman DK-2A.

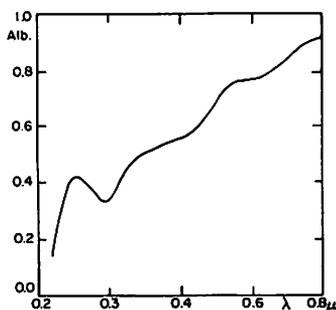


Fig. 3 Venus Bond albedo vs. wavelength, 0.2-0.6 μ .

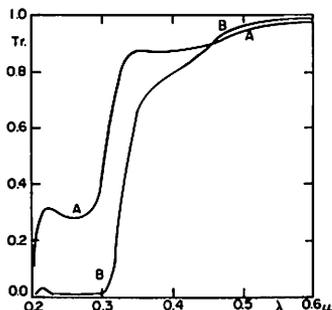


Fig. 4 $\text{HBr} + \text{Br}_2$ dissolved in 88% H_2SO_4 (two concentrations).

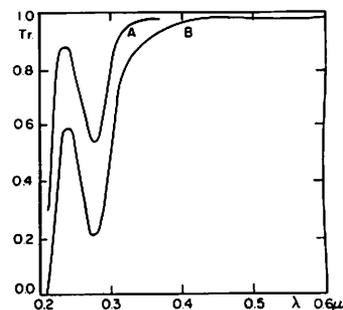


Fig. 5 SO_2 dissolved in 88% H_2SO_4 (two concentrations).

When Br_2 vapor is poured onto a $\text{SO}_2\text{-H}_2\text{SO}_4$ solution, immediate bleaching of the Br_2 is observed, as well as a diminution of the absorption features of SO_2 . Depending on which constituent survives, the spectrum either resembles the SO_2 or the Br_2 spectrum more closely. Evidently the Br_2 oxidizes the SO_2 to H_2SO_4 and the Br_2 is reduced to HBr .

Figure 6 shows the infrared spectrum from 4.0 to 15.0μ of 88% H_2SO_4 (solid line) with the left hand ordinate of transmittance. The sample was one drop of acid squeezed between 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°K . If there is H_2SO_4 in the clouds cooler than the emitting surface, then indeed H_2SO_4 should show in absorption. There are some similarities between the absorptions of the Venus spectrum 7- 12μ and the absorptions of 88% H_2SO_4 , especially in the absorption feature centered at 11.2μ , prominent in Hanel's Venus spectrum (1968).

2. Chemical Production of the H_2SO_4 Clouds

The mode of production of H_2SO_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. H_2S 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. COS is almost as unstable to UV as H_2S , decomposing into CO and S. This decomposition also approaches 100% in hours. Since the upper Venus atmosphere appears transparent to $\lambda > 2000\text{\AA}$, H_2S and COS can be ruled out. This leaves one with SO_2 and S as the most likely carriers of S to the upper atmosphere.

SO_2 has S in the 4+ oxidation state; in order to produce H_2SO_4 it is necessary to oxidize S to the 6+ state, as found in H_2SO_4 , or in the anhydride of H_2SO_4 , SO_3 . (The SO_3 would quickly absorb water

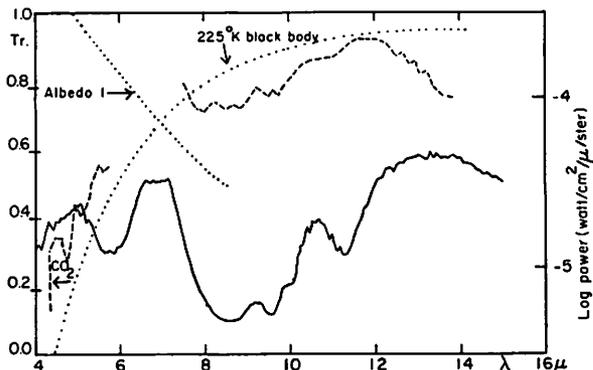


Fig. 6 Solid line: Transmission spectrum with 88% H_2SO_4 solution (left ordinates). Dashed line: Infrared spectrum of Venus with black body and unit albedo references (right ordinates).

and form H_2SO_4). Is it possible to produce 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° , 400° , 600° , 750°K , respectively. The thermodynamic data for calculating the equilibrium constant, K , are from Robie and Waldbaum (1968). With the CO_2/CO ratio of $10^{4.34}$ of Venus, presumed to be constant throughout the atmosphere, it is possible to calculate the SO_2/SO_3 ratio for the lower atmosphere ($T > 400^\circ\text{K}$) where thermodynamics can furnish valid information. The ratios for 298°K are included simply to show the trend:

Temp. $^\circ\text{K}$	298	400	600	750
SO_2/SO_3 ratio	$10^{28.32}$	$10^{25.09}$	$10^{12.06}$	$10^{8.80}$

The ratio is *unfavorable* for 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 COS , SO_2 , and 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 CO_2/CO ratio remains constant. One possible surface reaction which might determine the abundance of atmospheric SO_2 involves the equilibrium decomposition of anhydrite, CaSO_4 , in a $\text{CO}_2\text{-CO}$ atmosphere:



At a surface temperature of 750°K , thermodynamics predicts a CO/SO_2 ratio of 10. The $\text{CaSO}_4\text{-CaCO}_3$ equilibrium was chosen because CaCO_3 is often considered as the major weathered mineral in a CO_2

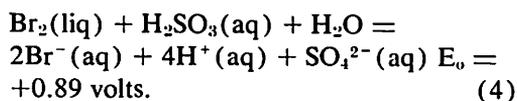
atmosphere. Furthermore CaSO_4 is often found as a principal S compound in geothermal regions, indicating its ability to survive under moderately high temperature conditions. If the CO/SO_2 ratio of 10 should survive to the upper atmosphere there would be an abundant supply of SO_2 for forming H_2SO_4 , provided there is a mechanism for further oxidizing the S to SO_3 - H_2SO_4 .

The oxidizing agent in the earth's atmosphere for converting SO_2 to SO_3 is O_2 . On Venus this is ruled out, and the most likely agents are molecular halogens, namely F_2 , Cl_2 , Br_2 and I_2 . F_2 can be rejected because of the extreme chemical stability of HF. Likewise 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 \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:

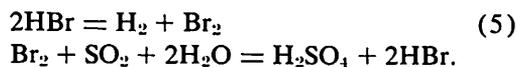


equilibrium quantities of the gases indicate that 7% of HBr is decomposed in the gas-gas equilibrium. The aqueous solution of HBr also shows a noticeable darkening due to formation of Br_2 under UV exposure.

Mention was made of the bleaching effect of SO_2 gas dissolved in H_2SO_4 when Br_2 fumes were poured onto the surface of the acid- SO_2 solution. This apparently shows the ease at which Br_2 will oxidize SO_2 to H_2SO_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 H_2O into $\text{H}_2(\text{g})$, which presumably escapes from Venus, and oxygen incorporated into H_2SO_4 :

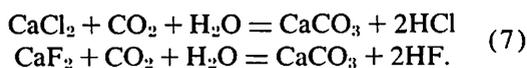


Reaction (6) is not favored thermodynamically and could never occur at the low temperature of the Venus clouds, but the intermediate reaction with Br_2 (and presumably the other halogen, I_2) make the process possible. None of the intermediate substances has been identified in the atmosphere of Venus, namely SO_2 , HBr and Br_2 . HBr is a difficult problem spectroscopically because its absorption bands at 2 and 4 microns fall into the heavy CO_2 bands. 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 \AA . Sill, Gautier, and Kuiper attempted to detect gaseous 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 + Br_2 (gas) were obtained in the region of 5364 \AA . The results were negative. From the spectra it is estimated that the smallest quantity of Br_2 that could be seen in Venus is about 0.13 mm-atm. *An upper limit to the Venus mixing ratio* Br_2/CO_2 can be set at $< 10^{-7.3}$. This implies a very small quantity of Br_2 vapor, much less than the 4 mb vapor pressure of elemental Br_2 at 235°K. On the other hand Br_2 is very soluble in cold H_2SO_4 , especially in the presence of HBr.

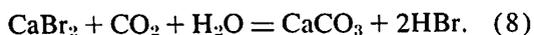
Both Br_2 and SO_2 have mixing ratios with upper limits $< 10^{-7}$. This may simply be a sign of their high reactivity with each other. The reaction is fast and involves reconstituting HBr. Since no upper limit on HBr has been established, the whole postulated mechanism cannot be proven at this time. The empirical data discussed above indicate that the visible and UV albedos of Venus may be consistent with Br_2 dissolved in H_2SO_4 . The highly sensitive test for gaseous Br_2 is not applicable to dissolved 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 CO_2 atmosphere. Pertinent reactions might be:



At 750°K , with P_{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 8.6×10^{22} moles, whereas in Venus' atmosphere there is about 1.3×10^{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 H_2SO_4 Synthetically in the Laboratory

Tests were conducted in the laboratory to see if H_2SO_4 could be formed by the irradiation of HBr and S compounds. Acid solutions of HBr and various S gases, particularly SO_2 and COS were irradiated with the quartz Hg lamp. COS vigorously decomposed, producing large quantities of S. Some H_2SO_4 was produced, which was analyzed by precipitating BaSO_4 on the addition of BaCl_2 solution. The conversion of COS to H_2SO_4 was about 3%. SO_2 showed slightly more conversion to H_2SO_4 . In one day's irradiation about 5% converted. Without HBr, conversion to H_2SO_4 by SO_2 was negligible. The amount of BaSO_4 precipitated was minute. Even elemental Br_2 and S, mixed together in water solution showed a high conversion to H_2SO_4 , but since this reaction occurred in the open air undoubtedly dissolved O_2 facilitated the reaction. Therefore, H_2SO_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 O_2 and H_2O , 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% H_2SO_4 , formed by the oxidation of SO_2 by elemental Br_2 in the upper atmosphere of Venus.

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