

GEOCHEMICAL PROBLEMS IN THE PRODUCTION OF THE VENUS CLOUDS

GODFREY T. SILL

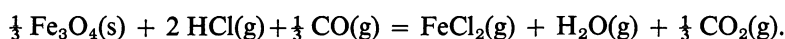
Lunar and Planetary Laboratory, University of Arizona, Tucson, Ariz., U.S.A.

Abstract. Spectroscopic evidence is strong that the clouds of Venus are composed of ferrous chloride hydrate. At the surface of the planet it appears as though the vapor pressure of ferrous chloride may be quite low (10^{-6} atm), especially if such vapor is allowed to come to equilibrium with the other constituents of the Venus atmosphere. The formation of magnetite (Fe_3O_4) may be favored, and the spectrum of magnetite is shown in relation to the spectrum of the Venus cloud cover. The presence of ferrous chloride in the upper atmosphere may be due to a non-equilibrium condition.

The spectrum of volatiles, such as the halides of mercury, are considered vs the albedo of Venus. The presence of these volatiles seems incompatible with the spectroscopic evidence. It is suggested that the planet has been depleted of its volatiles, as it has been depleted of its water.

1. Spectroscopic evidence in the region of 0.2μ to 4.0μ indicates that the clouds of Venus are composed of hydrated ferrous chloride (Kuiper, 1969, *Comm. LPL*, no. 101; cf. also this symposium). The clouds of Venus accessible to observation in the near UV, visible, and near IR are those of the upper atmosphere at a height of 60 km and a temperature of about 250 K. Any cloud material must be influenced by production rates of the material near the surface of the planet, just as the water vapor clouds of earth are dependent on evaporation rates near the surface.

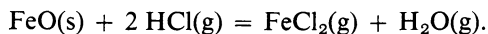
Anhydrous ferrous chloride is not known for its high volatility, even at the surface temperature of Venus, 700 K. Extrapolation along the modified Clausius-Clapeyron equation of vapor pressure of FeCl_2 yields a vapor pressure of approximately 10^{-5} atm at 700 K. Using more recent vapor pressure and thermodynamical data, Brewer *et al.* (1963) calculate that the vapor pressure of FeCl_2 would be 10^{-6} atm at 700 K. This low vapor pressure causes problems in creating an abundant Venus cloud cover, especially if the vapor of FeCl_2 is allowed to come to equilibrium with the surface rocks of Venus. Using the thermodynamic data of Brewer *et al.* (1963) and Lewis and Randall (1961), the author has calculated the equilibrium pressure of FeCl_2 as a very low $10^{-7.5}$ atm in the reaction:



where $\text{Fe}_3\text{O}_4(\text{s})$ would be magnetite on the surface of Venus, or perhaps granular sized in the atmosphere, and where $\text{FeCl}_2(\text{g})$ would be the quantity of ferrous chloride produced by the constituents of the Venus atmosphere. The abundances used in the calculations were:

$$\begin{aligned} P_{\text{H}_2\text{O}} &= 10^{-4} \text{ atm (from mixing ratio of } 10^{-6}) \\ P_{\text{HCl}} &= 10^{-4.2} \text{ atm} \\ P_{\text{CO}} &= 10^{-2.3} \text{ atm} \\ P_{\text{CO}_2} &= 10^2 \text{ atm} \end{aligned}$$

With the same abundances, the equilibrium vapor pressure of $\text{FeCl}_2(\text{g})$ in the following reaction yielded a pressure of 10^{-6} atm.



In any case, if FeCl_2 is produced through the reaction of HCl on the surface rocks of Venus, the quantity of vapor so produced is quite small, and seems to be unable to account for a Venus cloud or haze layer at the observed level of 60 km.

The thermodynamic data used is not completely certain; the calculated FeCl_2 vapor could differ from the above by, perhaps, an order of magnitude or so. In any case the vapors of FeCl_2 may not necessarily be produced by reaction with surface rock. If the vapor is liberated into the Venus atmosphere the above reactions may not specify the true state of affairs. If the oxide is produced by the reaction of ferrous chloride vapor and water vapor, then the oxide should initially be treated as a vapor and not as a solid, or perhaps microcrystalline aggregates of oxide analogous to a vapor. This state of the oxide would undoubtedly favor the production of FeCl_2 vapor, instead of decreasing it. In any case the author intends to investigate this problem in the laboratory.

As quoted by Kuiper (1969) FeCl_3 is a common volcanic emanation, especially in the Hawaiian group. Any FeCl_3 , if not already decomposed into FeCl_2 and chlorine, would soon be reduced in the Venus atmosphere to FeCl_2 . The high vapor pressure of FeCl_3 at 700° , converted to FeCl_2 would yield virtually all solid FeCl_2 with a minor amount present as vapor. The solid FeCl_2 would be quite stable in the Venus atmosphere and with any vertical transport mechanism the FeCl_2 particles should be easily raised to higher altitudes. Admittedly the explanation is contrived, but does not seem unreasonable. At the higher elevations and cooler temperatures, the FeCl_2 would become hydrated, and may perhaps be the dominant influence in controlling the pressure of $\text{H}_2\text{O}(\text{g})$ in the Venus atmosphere.

If any oxides of iron are produced in the Venus atmosphere, and are of sufficiently small particle size to be buoyed up to the upper atmosphere, they do not seem to show themselves spectroscopically. The spectral reflectances of several oxides of iron are shown in Figure 1. These do not match the Bond albedo of Venus, and Fe_3O_4 as a matter of fact, would serve to uniformly decrease the albedo of the planet. (FeO spectral reflectivity was not measured, but being a black solid like Fe_3O_4 is presumed to have a similar reflectivity.)

2. It has been suggested by Lewis (1969) that the cloud layers of Venus could be composed of various compounds of mercury and elemental mercury itself, each of the cloud materials condensing at a level where their concentration exceeds their vapor pressure. The lowest level is formed from HgS , then succeeded at higher levels by Hg_2Br_2 , Hg_2I_2 , Hg , and the uppermost haze level of 240 K composed of Hg_2Cl_2 overlying a deep cloud of liquid mercury droplets. Figure 2, g and h, shows the spectral reflectivity of the chlorides of mercury and Figure 3 the bromides and iodides of mercury. They all show the same type of reflectivity – low in the near UV (and blue for some), with a sharp rise to around 100% reflectivity, which then continues out to

9--P.A.

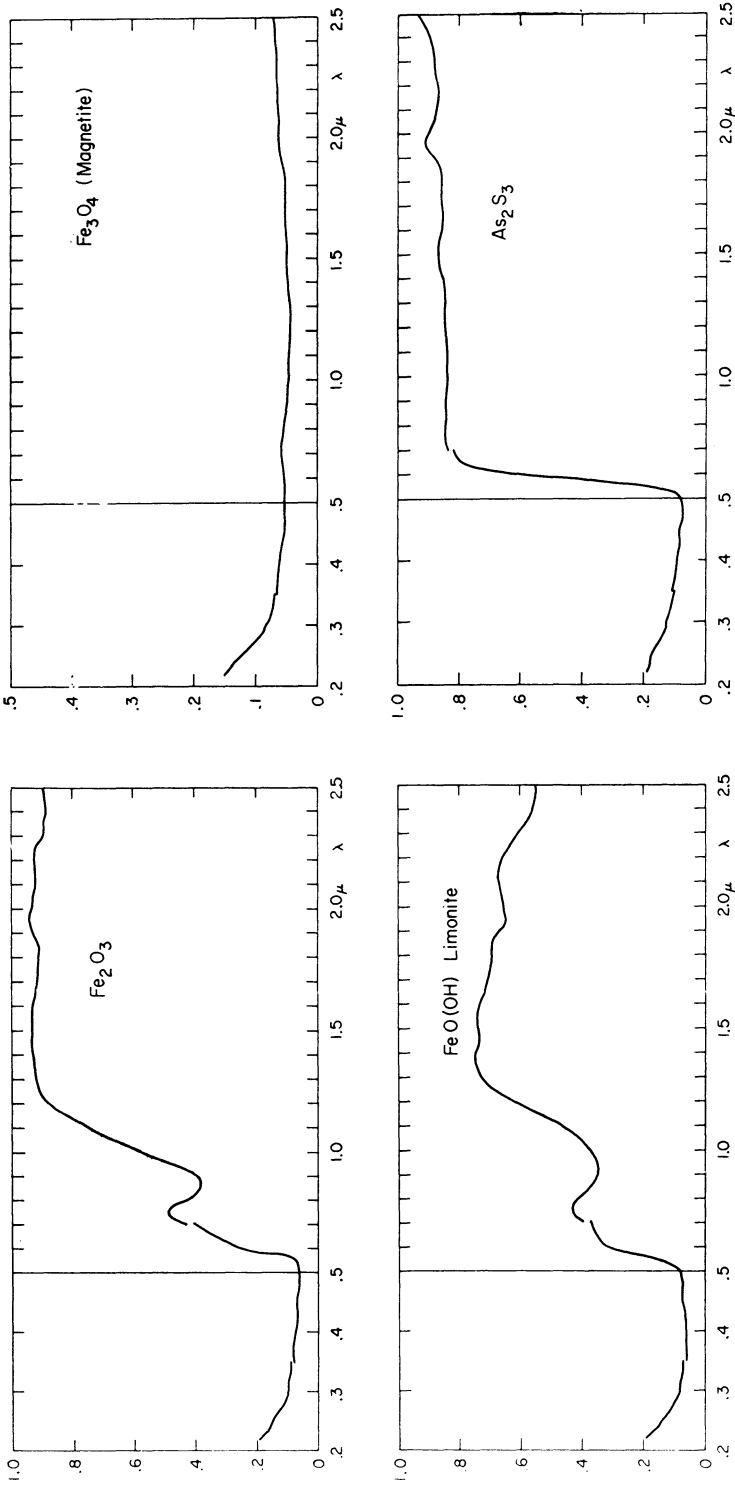


Fig. 1. Spectral reflectivities of oxides of iron, from 0.2 to 2.5 μ . All measurements are vs a white standard, LiF.

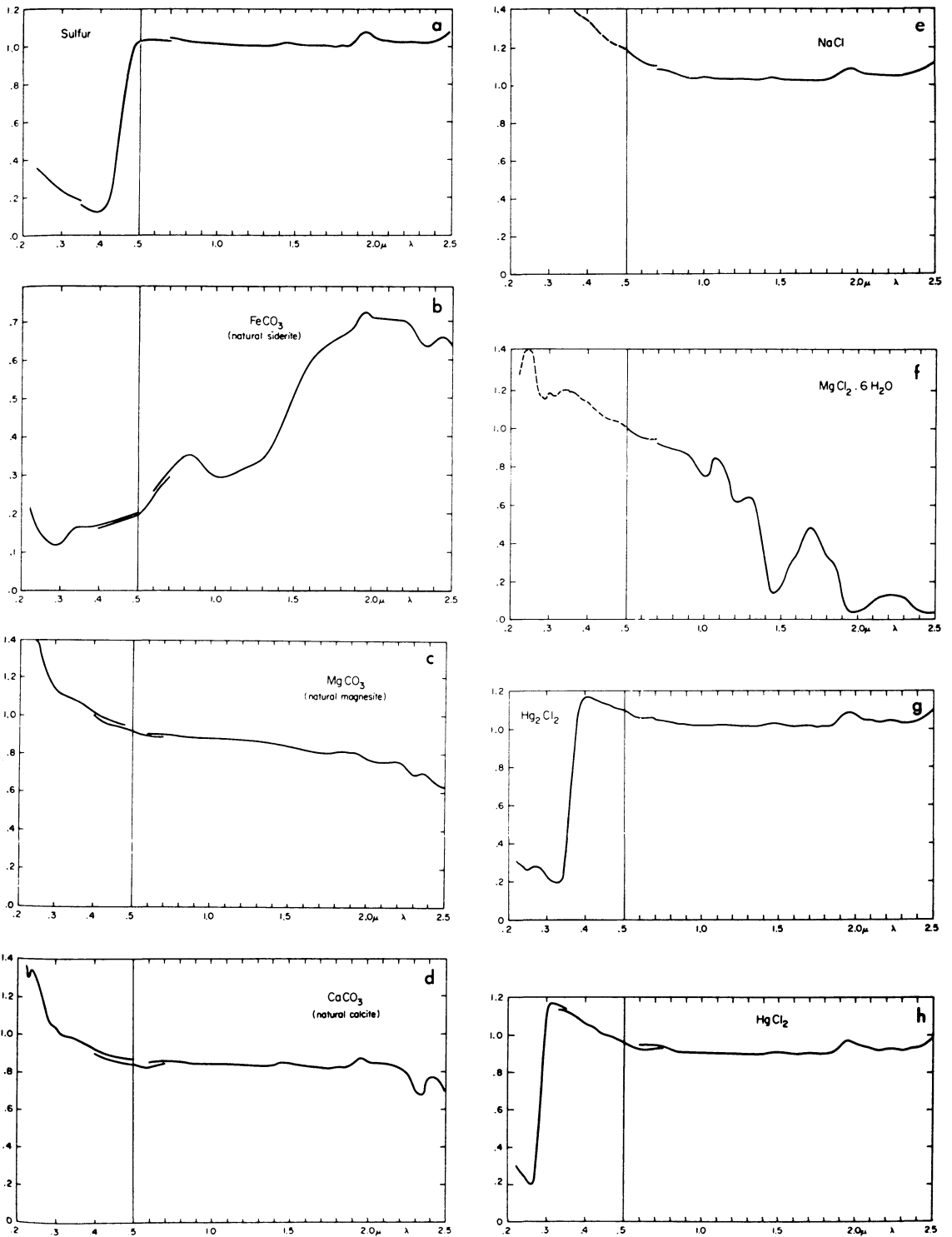


Fig. 2. Spectral reflectivities of the chlorides of Mercury. g and h.

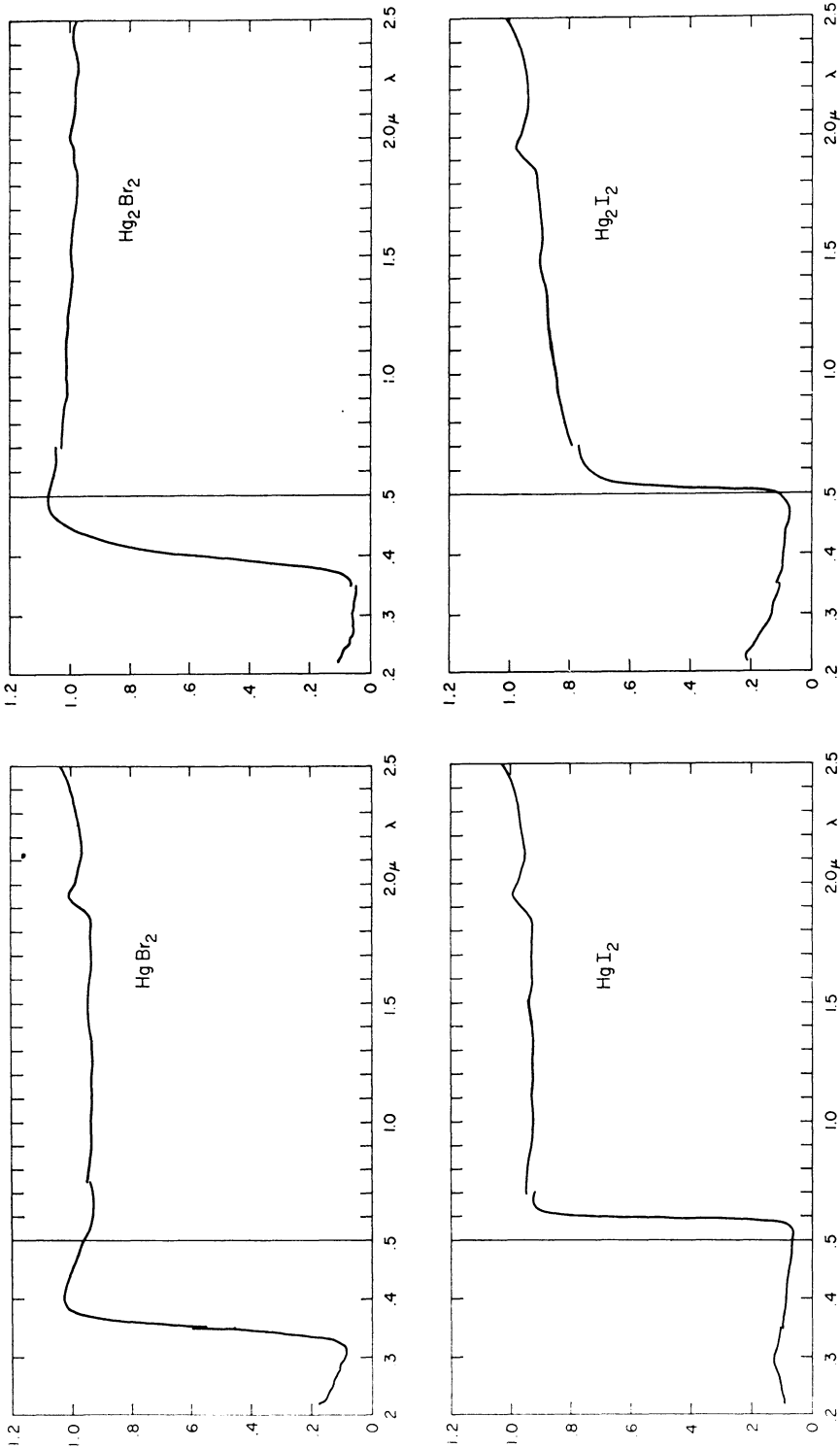


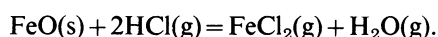
Fig. 3. Spectral reflectivities of the bromides and iodides of Mercury.

2.5 μ in the near IR. None of these has the characteristic features of the Venus Bond albedo, and it would seem that their presence is not proven observationally.

As Anders (1968) points out, Venus might have passed through a thermal history quite different from the earth. If, as he notes, Venus in its accreting stages did not fall below 400 K until late in its formation interval, then the planet would have been depleted of many volatiles, such as the H₂O he mentions. The same could quite easily be applied to the element mercury. Therefore it may not be valid to take the abundance of Hg from the earth's crust and apply it to Venus. There may not be clouds of Hg compounds in the atmosphere of Venus simply because there is too little Hg available.

In conclusion, there do seem to be difficulties in producing clouds of ferrous chloride hydrate in the atmosphere of Venus, but these problems can be eased if vertical mixing is fairly rapid in the atmosphere of Venus, and if the whole atmosphere is not in equilibrium with the planetary surface. Other more volatile compounds seem at first sight, to be more favorable constituents of the clouds of Venus, but elemental abundances and depletion factors must be taken into account, as well as the primary evidence of spectroscopic observation of the planet.

Note Added in Proof. A reaction similar to the first one described in this article was tested in the laboratory. Ferrous oxide was treated with vapors of hydrogen chloride at 700 K to see whether ferrous chloride would be produced according to the reaction:



Nitrogen gas was bubbled through concentrated hydrochloric acid at a rate of 10 cc/min, and passed over FeO in a furnace at 700 K. The cool glass outlet tubing, where it left the furnace, began to show traces of green FeCl₂ · 4H₂O within one hour's time. Despite the unfavorable thermodynamics of the reaction, the reaction did go, undoubtedly due to the fact that equilibrium conditions did not prevail: evidently the FeCl₂ sublimed out of the reaction vessel as soon as it was formed. However, this may also be the case on Venus with a wind blowing across the surface. Equilibrium conditions may not prevail between the surface of the planet and a moving atmosphere.

References

- Anders, Edward: 1968, 'Chemical Processes in the Early Solar System, as Inferred from Meteorites', *Act. Chem. Res.* **1**, 289–298.
- Brewer, Leo, Somayajulu, G. R., and Brackett, E.: 1963, 'Thermodynamic Properties of Gaseous Metal Dihalides', *Chem. Rev.* **63**, 111–121.
- Kuiper, G. P.: 1969, 'Identification of the Venus Cloud Layers', no. 101, *Commun. Lunar Planetary Lab.* **6**, 4.
- Lewis, G. N. and Randall, M.: 1961, *Thermodynamics*, 2nd ed., McGraw-Hill.
- Lewis, John S.: 1969, 'Geochemistry of the Volatile Elements on Venus', *Icarus*, in press.