No. 101 IDENTIFICATION OF THE VENUS CLOUD LAYERS*

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ABSTRACT

Observations establish the existence of two well-separated cloud layers on Venus: (a) a patchy layer observed in photographs taken at $\lambda < 4200$ Å, apparently consisting of bright veils often thousands of km in size, which at times exhibit retrograde motions up to 100 meters/sec., composed of particles about 0.1 μ diameter; and (b) a yellowish, optically impenetrable layer exhibiting gross horizontal structure only rarely, but having a variable upper boundary situated well within the troposphere. New diameter measures of the planet, coupled with recent data on the atmospheric temperature profile (Fig. 5), indicate that the *UV layer occurs in the upper stratosphere,* near the mesopause; and confirm that the boundary of the *thick yellow haze layer* is just below the tropopause, *within the troposphere.* With the known mixing ratio H_2O/CO_2 for the upper Venus troposphere, the possibility of water or ice clouds in the visible layers can be dealt with definitively.

A compilation of published photometric data from 0.2–4.0 μ and new spectrophotometric data (Fig. 2), compared to new laboratory measures (Figs. 6, 8), show that *the chief constituent of the yellow haze layer* is incompletely-hydrated $FeCl_2$, $n \simeq 1.55$; three absorption bands observed on Venus are attributed to Fe^{2+} (d-d) and one each to Fe-H_2O, Fe-Cl and O-H. The vapor pressure of H_2O in the upper troposphere of Venus, derived from the NASA CV-990 results in *Comm. LPL* No. 100, is found to be essentially equal to *the equilibrium dissociation pressure of the Venus cloud particles* and is so interpreted. The published H_2O measurements by Venera 4–6 for the deeper layers are discussed but found to be incompatible with well-established results.

The upper UV haze layer is thereupon re-examined; it may be $NH_4Cl(s)$. The violet-blue haze can be simulated in the laboratory by adding $HCl(g)$ to $NH_3(g)$ in very low concentrations.

It is concluded that *Venus has a halide meteorology,* compared to a water meteorology on Earth, and an ammonia meteorology in Jupiter and Saturn. The near-absence of water on Venus must be a basic planetary property, apparently resulting from a protoplanet temperature being substantially higher than that of proto Earth, *which caused H_2O to be* in the vapor phase and *lost with the inert gases.* This must have been caused by Venus forming *later* in the solar development as well as closer to the Sun.

Hypotheses on the composition of the Venus clouds have proliferated in recent years. The Proceedings of the CalTech-JPL Lunar and Planetary Conference (1966) describes the following interpretations, held by different authors: small water droplets, small ice crystals, hail stones (at depth); derivatives of methane, ethane, and benzene; and dust. Other recent publications have considered snow flakes (at depth), NH_4Cl, an ice-HCl solution, volcanic products, a carboniferous swamp, a planetary oil field, and the "global-seltzer ocean" theory. A useful critical view of this curious assortment is

made in the NASA Handbook of Venus (1967). Of necessity, many questions had to be left open for lack of data.

With the very low, but finite, mixing ratio of H_2O/CO_2 now established from the NASA 990 Jet observations (*Comm. LPL* Nos. 95, 100), and with the reinterpretation of the 2 μ region of the Johns Hopkins balloon spectrum of Venus (*Comm. LPL* 95), coupled with the new polarization data of Venus by Coffeen (1968), the problem of water or ice clouds can be dealt with definitively. One of the arguments used in past years in support of the ice hypothesis, the low reflectivity of the planet between 3-4 μ, is reinterpreted on the basis of new spectrophotometric data and found to lead to a very different conclusion.

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1. Clouds Visible in Ultraviolet

Ross (1928) in his extensive photographic coverage of Venus in 1927, using the 60-inch Mt. Wilson telescope, established that the planet shows a variable cloud pattern in UV light (3600 Å ±); but that in yellow or red light no clear markings appear except possibly on rare occasions. Wright (1927) had previously taken a few photographs at the Lick Observatory with the same general result. The cloud pattern may show changes even in a few hours. Recently the French observers (Boyer and Camichel, 1961 and 1965; Boyer, 1965; Boyer and Guérin, 1966) noted that the cloud pattern at times moves across the disk in retrograde motion roughly 90° per day, corresponding to a pseudo-rotation period of 4-5 days. No strict periodicity exists, however, either in this motion of the upper atmospheric layers nor in the details of the cloud forms. The observed motion could obviously either be real or be a group velocity caused by atmospheric waves.

Dollfus (1967) summarizes as follows the collection at the IAU Planetary Data Center at Meudon, which shows:

"that large formations in the Venusian atmosphere can evolve quickly — sometimes in as little as a few hours. Such aspects may be explained by rapid apparitions and disappearances of clouds on the spot, accompanied sometimes by motions. Furthermore, motions of the whole cloud layer are sometimes observed, consistent with a retrograde rotation of a four days' period, although the above observations alone are not convincing enough to support definitely such a rotation as real. The changes recorded in the cloud patterns . . . imply that clouds are not likely to be composed of solid dust, for, in such case, the time of formation and dissipation would be too long. They should, then, be composed of particles capable of condensation and evaporation, such as water."

In view of the very small angular velocity of the planet itself (rotation period 243 days; Carpenter 1966, Evans *et al.* 1966, Shapiro 1967 a, b) the apparent motions of the cloud masses correspond to values up to 100 m/sec.

A Venus photograph taken at 3600 Å is reproduced in Fig. 1, together with the Surveyor III TV record of the earth (JPL 1967). The similarity between the images is remarkable but probably fortuitous. The earth was recorded in visual light and shows cloud masses which under higher resolution
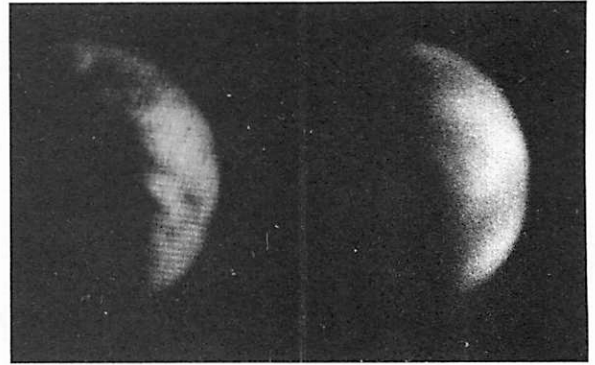

Fig. 1 Comparison of planets Venus and Earth with low resolution; Venus in UV, 61″ NASA telescope, June 13, 1967, 01ʰ57ᵐ20ˢ U.T.; Earth, visual light, Surveyor III, JPL, 1967.

are known to break up into hundreds or thousands of individual clouds and filaments. No high-resolution UV photographs of Venus have yet been taken; but we doubt on other grounds that with much higher resolution the close resemblance with the earth would remain.

Ross (1928) found that the UV clouds on Venus become gradually invisible at wavelengths substantially longer than 4000 Å:

"Details over the disk, interpreted as cloud formations, are found to be always present on photography taken with ultraviolet light. Photographs with blue-violet and with blue light show very weak details. Red and infrared exposures disclose no detail. This behavior for light of different colors is interpreted as follows: The outer atmospheric layer is assumed to be composed of a thin stratum of cirrus clouds, while the inner atmosphere is supposed to be exceedingly dense and yellowish. The details shown are atmospheric disturbances, visible either as dark areas, or as regions of enhanced brilliance, depending upon the character of the disturbance. . . . Measures of the relative values of the light from the dark and the adjoining bright areas give a maximum difference of 24 per cent for the negatives in ultraviolet light, and of 4 per cent for those in blue light."

In *Comm. LPL* No. 102 two series of recent UV photographs of the Venus clouds are presented, and also some additional evidence on the wavelength dependence of their visibility. Occasional delicate markings observed at $\lambda > 5000$ Å do not correlate well with the UV cloud pattern (Dollfus 1961).

Since the UV clouds are clearly visible around λ_U (~3600 Å), they are presumably composed of particles approximately 0.1 μ in diameter (λ_U/π).

At $\lambda \gg \lambda_U$ these particles will essentially be invisible. Since between 0.36 μ and 0.45 μ the Venus albedo increases by 1.4 $\times$ (Harris 1961, p. 307), the long-wave visibility cut-off is sharper than based on the scattering law of particles. *The large horizontal motions suggest that the UV clouds are located high* in the Venus atmosphere. Thus, if the particles were ice (H_2O or CO_2), or another sublimate, they would be more likely to exist in the *mesopause* than at the tropopause level. They would then be comparable to the *noctilucent clouds* on the earth (at 82 km elevation). We examine below whether this explanation is compatible with present information on the atmospheric composition and the dependence of measured planetary diameter vs. λ; also, whether H_2O, CO_2, or a halogen may be involved. A further possibility would be polymerized C_3O_2 formed in the upper strata of the Venus atmosphere (Kuiper 1957). In view of the near-absence of a magnetic field on Venus and therefore the presumed absence of a zonal distribution in the particle impacts as well as the solar UV radiation, it would be expected that polymerized C_3O_2 would be distributed nearly *uniformly* over the disk. The *patchy* appearance of the UV clouds on the other hand suggests that atmospheric circulation and resulting temperature differences play a role, and favors the assumption of condensation.

Yet another assumption would be that the UV clouds are extensions of the deeper thick haze (Sec. 2); but this appears improbable since their formation and disappearances are more rapid than corresponds to the fall time of particles of $d \simeq 0.1$ μ (a few meters per day). Finally, the UV clouds could be an *aerosol* of the type found in the terrestrial stratosphere. Junge (1963) thinks that these aerosol particles are formed in situ by oxidation of SO_2 or H_2S, trace constituents that may be present also on Venus; but it is not clear how this process would explain the UV cloud pattern and its changes. Presumably, therefore, the main constituent of the UV clouds is not photochemical, but a *temperature-dependent condensation*.

The planetary albedo from 2300-3000 Å, about 0.2 (cf. Fig. 2), is due in part (perhaps 20%) to the UV veils, as is true for Mars. A measure of the cloud contrast at 2300 Å (from balloon observations with 1 arc sec. resolution) would be informative. Some UV cloud contrast is also present on Mars (and, of course, in the terrestrial noctilucent clouds).

2. The Yellow Haze Layer

Penetration in visual light and in the infrared is limited by the yellow haze layer. This is most convincingly shown by the rotational temperatures
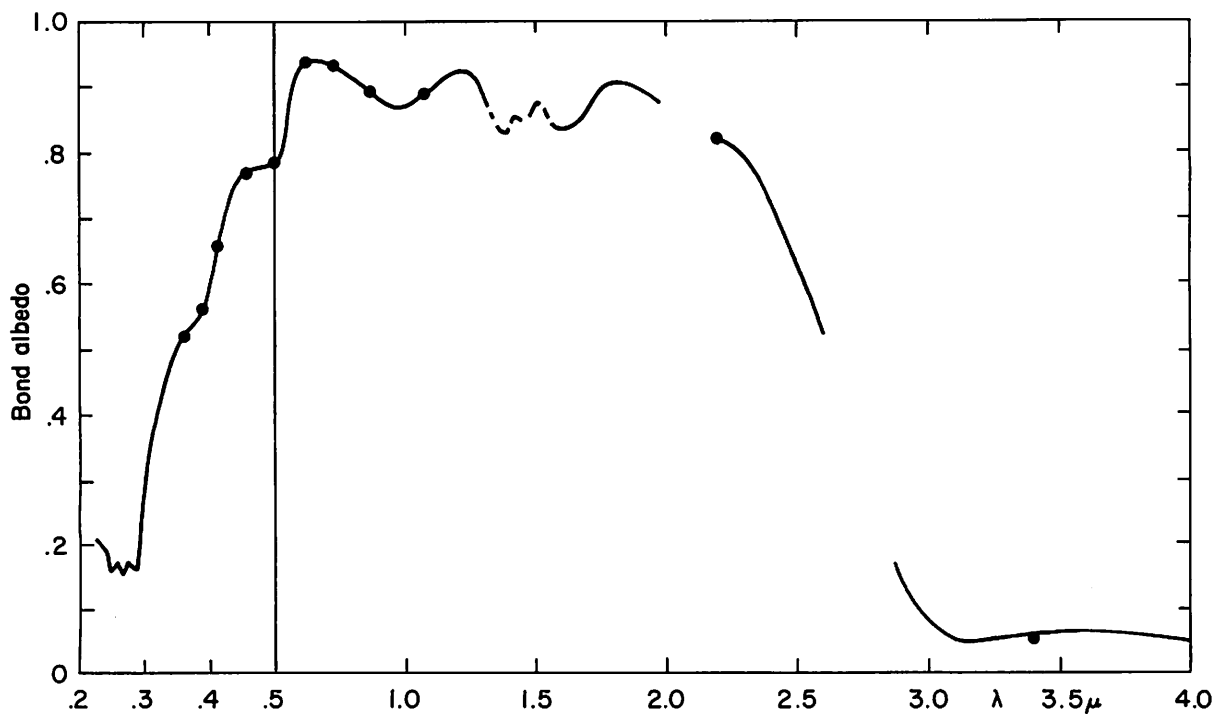

Fig. 2 Bond albedo vs. wavelength 0.2–4.0 μ. Sources described in text. Details near 1.5 μ somewhat uncertain.

derived from numerous CO_2 absorption bands from 0.87–3 μ, giving around 250° K, and beyond that from the thermal emission of the planet, found to be 220–230° K in the atmospheric window 8–14 μ. In the mm range the radiation temperatures are still low, about 300° K at $\lambda = 3$ mm and 380° K at $\lambda = 8$ mm. These low values are probably not produced by particles but by the rotational absorptions of the Venus atmosphere, as follows from the B values of the different constituents, with allowances for pressure broadening.

The effective top of the haze layer is not constant in altitude. Kuiper (1952) found from 80 spectra taken in 1944, 1948, and 1950 that the intensity of the 5 v_3 band of CO_2 at λ 8689 Å,

"varies systematically from about 0.05 of (the solar Ca II line) λ 8489 at phase angle 150° (near inferior conjunction) to 0.6 at phase angle 50° (near full phase); that day-to-day fluctuations of considerable magnitude occur; and that the observed distribution of CO_2 is often remarkably patchy over the disk. The patches are of such a size that they may correspond to the cloud features shown on ultra-violet photographs.

"Evidently, the Venus cloud layer is in violent motion. The light-yellow color of the cloud cover proves that it is not composed of water droplets; water clouds observed from above are white. This conclusion is consistent with the absence of water vapor from the Venus spectrum and the large abundance of CO_2 in its atmosphere. Possibly the cloud cover is composed of some oxide, say, silica, with a slight coloring due to iron oxide.

"Dr. H. Suess pointed out to the writer the interesting possibility that, alternatively, the cloud layer may be composed of salts (NaCl, $MgCl_2$). This case would apply if Venus initially did have ocean basins which later dried up. This could have happened if the water was lost by photodissociation in the upper atmosphere and the liberated oxygen was subsequently bound chemically. It is conceivable that photometric and polarimetric tests could decide between oxides and salts."

The *fluctuations in penetration level,* on a day-to-day basis, and also between areas at a given time, prove that the effective visibility limit is *situated within the Venus troposphere,* not the stratosphere where such motions would be absent. This is in accord with the average rotational temperature obtained from the CO_2 bands, approximately 250°

K, indicating that the 1-2 μ radiation observed is scattered by layers deeper than those responsible for the effective planetary radiation at 8-14 μ (220–230° K) and therefore situated 5-10 km below the tropopause. The observed CO_2 absorption is thus produced mostly in the Venus troposphere, and the *mixing ratios of the atmospheric constituents derived from the near-infrared spectrum will also refer to the troposphere,* not the stratosphere. This conclusion is important since some authors have assumed that the extremely low water-vapor content observed spectroscopically refers to the stratosphere. This latter view is definitely erroneous. Whether the tropospheric mixing ratio itself is constant with altitude is reviewed in Sec. 5.

The interpretation of a planetary spectrum may be illustrated by low-resolution spectra of the sunlit planet Earth, observed from 26 km elevation (cf. Fig. 3). The amount of water vapor corresponds, as expected, to the two complete slant paths (sun to earth surface, and back out to the balloon at 26 km) and is 10^3-10^4 times larger than for the stratosphere above the balloon.

Maximum penetration into the Venus troposphere will be recorded by the *hot bands* of CO_2 which favor the hotter and deeper layers. Spinrad (1966) observed the hot band of 5v_3 and derived a rotational temperature of 450° K, and a rough vibrational temperature of 400° K. This important but puzzling observation deserves to be repeated often for an atmosphere whose transparency varies so much.

The *particle size* of the upper layers of the yellow haze may be estimated variously. A rough value comes from analyses of the *planetary phase curve,* determined separately from different wavelengths. Sobolev (1964–1965) re-evaluated the scattering indicatrix from the phase curves by Müller and by Danjon for visual light. His results appear consistent with particles $d = 2$-3 μ, but Moroz (1968, p. 177) comments that: "V. V. Sobolev's method utilizes only the first two terms in the expansion of the indicatrix in Legendre polynomials. Checking this method against terrestrial aerosols shows that the indicatrices calculated in this manner may differ greatly from real indicatrices." Phase curves at 1.6-2.2 μ, closer to the presumed particle size, will probably be more instructive; such curves are currently being derived.

Other sources of information on the haze layer are the Venus *polarization curves,* derived separately for different wavelengths. The classical work by Lyot
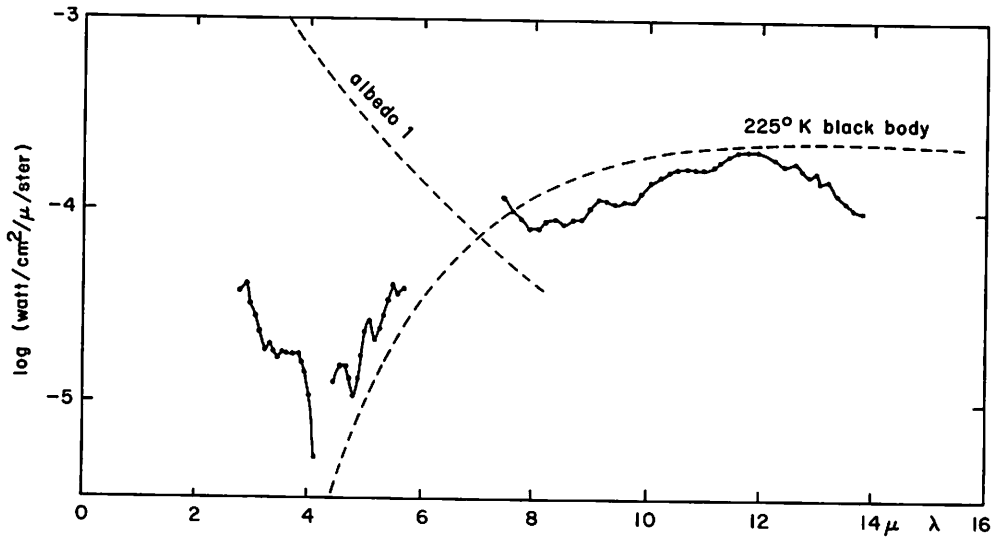
Fig. 2a   Spectrum of Venus taken at 105° phase angle and 0.37 of the disk illuminated (courtesy: Gillett, Low, and Stein, 1968).
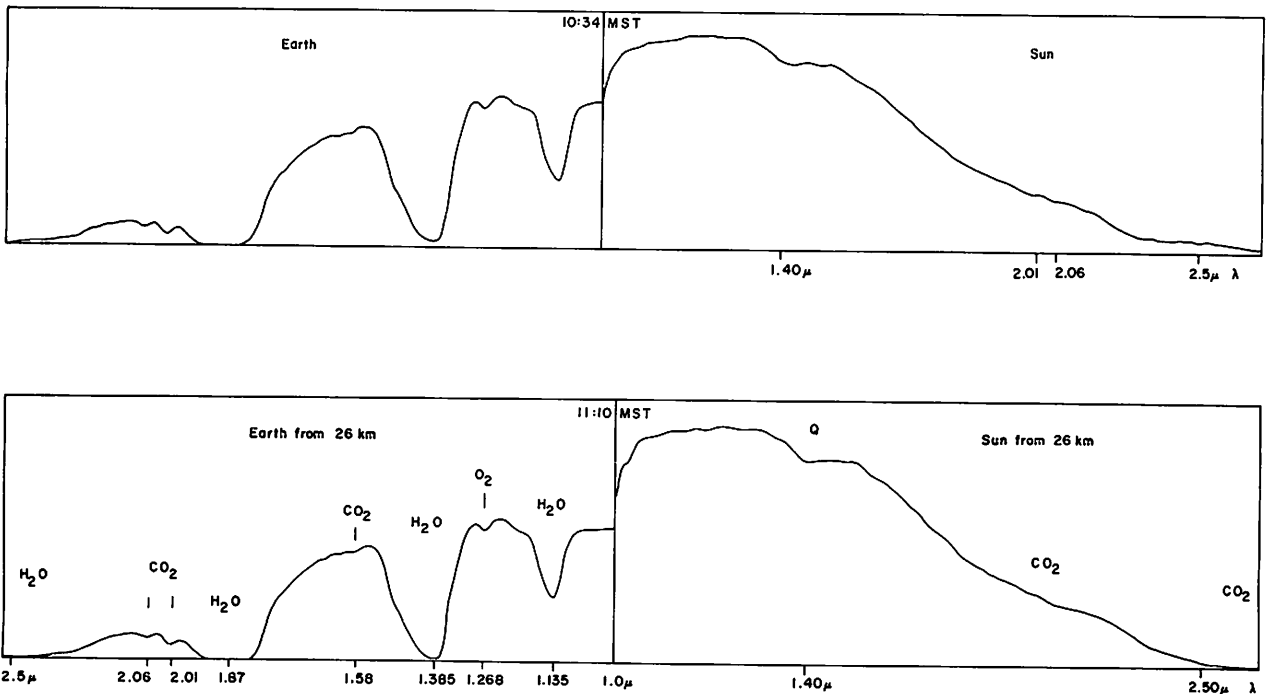

Fig. 3   Two spectra of Earth looking straight down, 1.0-2.5 μ, taken from 26 km height, at 37° N latitude, 11[h] a.m., November 19, 1963, showing H_2O bands of strength corresponding to total 2-way atmospheric path of reflected sunlight; with solar comparisons off MgO block. (Spectrometer used quartz prism having 10% absorption around 1.4 μ, indicated by Q in solar spectrum.) (NCAR-U. of A. spectra)

(1929) yielded the first polarization curve of modern accuracy, and he carried out important laboratory investigations in support. Lyot concluded that the Venus particles were water droplets about 2.2 μ in diameter; but in retrospect it is clear that from a single visual curve only *one* parameter, particle diameter *or* refractive index, can be derived with some assurance, not both. In other words, Lyot's curve can also be explained by adopting a larger refractive index and a different particle size (Kuiper 1957, p. 83–84). Polarization work done up to 1960 was reviewed by Dollfus (1961). A recent study by Coffeen (1968) extended the data to the UV and IR and allowed a good separation of n and particle size. On the basis of calculations of the scattering by spherical particles, Coffeen concluded that his polarization data restrict n to the range 1.43-1.60, and that the mean particle diameter is about 2.5 μ. Since these figures depend on the assumption of *spherical particles*, they definitely exclude water droplets, confirming earlier conclusions based, e.g., on the color of the planet (Kuiper 1952, p. 371), on the instability of a fog composed of micron-sized water droplets (which within seconds leads to the evaporation of the smaller particles and the growth of a small number of larger drops); and on polarization measures at 1 μ and 2 μ by Kuiper (1957, p. 85). The refractive indices of several chlorides are in the range set by Coffeen's result.

The *variation of albedo with wavelength* yields information on the particle composition, as is true for any colored solid. One must attempt, of course, to eliminate the absorptions of the overlying atmosphere, mostly by CO_2. Information now available is summarized in Fig. 2. For 0.35-1.1 μ it is based on the important study by Irvine et al. (1968, p. 820); for 0.23-0.35 μ, on the rocket observations by Evans (1967, p. 141) by reducing his geometric reflectivities for 90° phase angle to Bond albedos, taking the albedo at 3500 Å to be 0.51 (Irvine *et al.*), thus assuming the phase integrals to be the same within the interval 2300-3500 Å (which appears reasonable since the UV veils occur throughout this interval).* For 3.05-3.85 μ (average 3.4 μ) and 2.2 μ unpublished measures by Mr. R. I. Mitchell at LPL were used and adjusted to Irvine's albedo at 1.1 μ; for the interval 2.9-4.1 μ the curve derived by Gillett, Low, and Stein (1968) reproduced in our

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* More recent unpublished rocket data indicate a higher reflectivity 0.2-0.3 μ than reported by Evans; this will not basically affect the interpretations below.

Fig. 2a; and for intermediate parts, spectral observations. Among these are the CV-990 interferometer results and ratio spectra, Venus/Moon, published in *Comm.* 100; a ground-based interferometer spectrum of Venus, 1.2-4.0 μ obtained March 3, 1969, with lunar comparisons; and a short series of spectra obtained with the 61-inch NASA telescope between 0.3 and 2.5 μ in which Venus was compared to Mars and the Moon. The ratio spectra show no sharp dips or breaks in the Venus continuum; but there are varying slopes and of course the gaps due to heavy planetary CO_2 absorptions, left blank in Fig. 2.

Fig. 2 contains important clues to the composition of the yellow clouds, except that for $\lambda < 0.4$ μ the results must be used with caution because of the overlying veil of UV clouds. This veil may actually not contribute more than 0.1 or 0.2 of the total albedo since the maximum cloud contrast occurs around 0.35 μ and does not exceed 24% (Ross, 1928).

Parenthetically, the argument has been advanced (as quoted in NASA *Handbook* of Venus, Ch. 10) that the yellow color of the planet is *not* due to the clouds themselves, but to Rayleigh scattering of the overlying atmosphere, so that the clouds might actually be white. This conclusion is incorrect as is shown in Appendix 1.

The very low reflectivity from 3-4 μ has, in the past, often been attributed to *ice,* but this is incompatible both with the very low atmospheric H_2O content *(Comms. LPL* 95, 100, and Fig. 5 below) and the yellow color. The low IR reflectivity can, alternatively, be indicative of a *hydrated mineral.* It cannot be fully attributed to the small particle size of the Venus haze; Coffeen's (1968) mean diameter of 2.5 μ indicates that the particles will scatter effectively for $\lambda < 2.5\pi\mu$ or 8 μ. The yellow cloud material is therefore *nearly black from 3-4 μ and also dark in the UV* and shows characteristic features in between.

Before we discuss Fig. 2 for specific interpretations, we examine the gaseous composition of the Venus atmosphere.

3. Composition and Temperature Profile of the Venus Atmosphere

The Venus atmosphere is known to be overwhelmingly CO_2, based on direct measurements on Venera 4 (Pravda 1967) where the ratio, CO_2/total gas, was found to be in excess of 0.9; confirmed with increased precision (limits 0.93-0.97) by the Venera 5 and 6 probes (Pravda 1969). Nitrogen and inert

gases were found to be 0.02-0.05 of the total, oxygen < 0.004, and water vapor 0.004-0.011. The water-vapor content, about 10^{-6} according to the CV-990 flights, is re-examined in Sec. 5; the other results are entered in Table 1, which also lists the spectroscopic results, both positive and negative.

Table 1 is still very provisional since much more can be achieved at high altitudes both at $\lambda > 2.5\ \mu$ and $\lambda < 0.3\ \mu$; and even in the parts observed with high resolution by Connes et al. at the Haute Provence (1-2.5 μ). Fig. 4 shows that at $\lambda < 0.3\ \mu$ improved tests on SO_2 and NH_3 are possible between 1800-2200 Å. Below 1800 Å the absorption by CO_2 is very strong (Thompson, Harteck, and Reeves, 1963, p. 6432) and the planet will be almost black for λ 1200-1700 Å. The region 1800-2000 Å will be the best test for O_2 (op. cit., p. 6433), and 1850-2260 Å for NO (op. cit., p. 6435).

Fig. 5 collects the principal data on the atmospheric temperature profile. The full-drawn line and the two sets of ordinates (elevations and pressures) are taken from the Venera 4 data as presented at the May 1968 COSPAR meeting in Tokyo (Mikhnevitch and Sokolov, Fig. 7 and Table 3); supplemented and calibrated with the Venera 5 and 6 data just published (Pravda 1969). The dashed line represents the temperature profile, interpolated for 95% CO_2, of the Mariner V data published in Science (Kliore, Levy, Cain, 1967). It smoothes over the considerable fine structure shown in the original published profile, most of which is probably not real, though the indications of layering near the tropopause are interesting and deserve further analysis.

The U.S. and U.S.S.R. 1967 data are made to coincide at 300° K.

The Venera 5 and 6 data resolved the disturbing radius discrepancy discussed in the Mariner V Science article. The new radius, about 6052 km, accords well with the U.S. radar determinations published previously, 6056 ± 1 km (Ash, Shapiro, Smith, 1967), revised to 6050 ± 5 km (Ash, Campbell, Dyce, Ingalls, Jurgens, Pettengill, Shapiro, Slade, Thompson, 1968); and 6054 ± 2.2 km (Melbourne, Muhleman, O'Handley, 1968). This excellent agreement has also removed the discrepancy cited in the Mariner V Science article regarding the Venus surface temperature, now found by both research groups to be 700° K or slightly higher.

The positions of the haze layers in this temperature profile may now be estimated. Observations of the planet between 8 and 14 μ indicate a fairly constant "radiometric temperature" found by different authors to be between 210° and 250° K. We shall adopt 226° (Sinton and Strong, 1960; Sinton, 1961; Gillett, Low, and Stein 1968). A "gray-body" stratosphere then would be at 190° K. The dotted profile in Fig. 5 is based on a linear extrapolation of the Venera 4 temperatures, past the radiometric level to the 190° K value. It probably represents the *minimum* temperature of the tropopause; the Mariner value is some 40° higher.

We now examine whether H_2O and CO_2 can condense. The boundaries between the solid and vapor states are entered in Fig. 5 based on the mixing ratios of Table 1. It is seen that, as the temperature falls, H_2O will condense before CO_2; but

TABLE 1

COMPOSITION OF VENUS ATMOSPHERE

| GAS	MIXING RATIO	SOURCE
CO_2	0.95 ± 0.02	Venera 4, 5, 6 (Pravda, June 4, 1969)
N_2	0.035 ± 0.015	Venera 4, 5, 6 (Pravda, June 4, 1969)
CO	$10^{-4.34}$	Connes et al., Ap. J., 152, p. 741, 1968
HCl	$10^{-6.2}$	Connes et al., Ap. J., 147, pp. 1230–1237, 1967
HF	$10^{-8.2}$	Connes et al., Ap. J., 147, pp. 1230–1237, 1967
CH_4	$< 10^{-6}$	Connes et al., Ap. J., 147, p. 1235, 1967
CH_3Cl	$< 10^{-6}$	Connes et al., Ap. J., 147, p. 1235, 1967
CH_3F	$< 10^{-6}$	Connes et al., Ap. J., 147, p. 1235, 1967
C_2H_2	$< 10^{-6}$	Connes et al., Ap. J., 147, p. 1235, 1967
HCN	$< 10^{-6}$	Connes et al., Ap. J., 147, p. 1235, 1967
H_2O	$10^{-6.0}$	Kuiper et al., Comm. LPL No. 100
O_2	$< 10^{-5.0}$	Belton and Hunten, Ap. J., 153, p. 970, 1968
O_3	$< 10^{-8}$	Jenkins et al., Contrib. KPNO No. 421, 1969
SO_2	$< 10^{-7.5}$	Cruikshank and Kuiper, Comm. LPL No. 97
COS	$< 10^{-6}$	Cruikshank, Comm. LPL No. 98
COS	$< 10^{-8}$	Based on Comm. LPL No. 100
C_3O_2	$< 10^{-6.3}$	Based on Comm. LPL No. 100
H_2S	$< 10^{-3.7}$	Cruikshank, Comm. LPL No. 98
NH_3	$< 10^{-7.5}$	Based on Comm. LPL No. 100
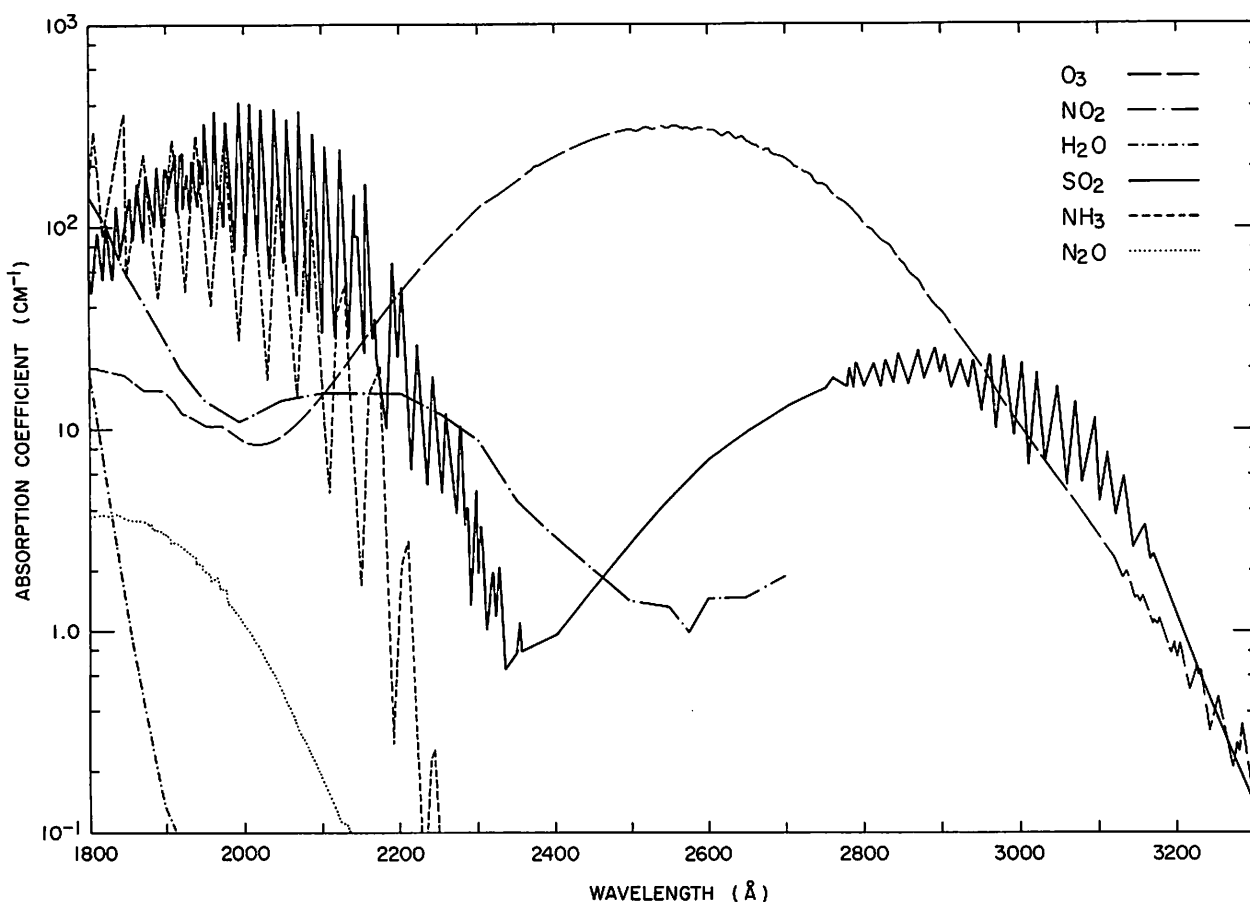
Fig. 4 Absorption coefficients of atmospheric gases in near-UV. (*after:* A.E.S. Green, ed. 1966. *The Middle Ultraviolet* [New York, Wiley], p. 63.)

that it is doubtful whether H_2O can condense anywhere. Also (cf. Lewis, 1968), the HCl present will shift the freezing line of H_2O in Fig. 5 somewhat to the left.

Fig. 5 shows the average top of the yellow haze layer, estimated as follows. The mean CO_2 rotational temperature deduced is about 250° K (Moroz 1968, Benedict 1968). In Fig. 5 this corresponds to a pressure of about 0.14 atm. Thus, at the bottom of the visible layer, p = 0.2–0.3 atm, consistent with the self pressure of the CO_2. Sinton, Low (Gillett *et al.*, 1968), and Hanel *et al.* (1968), among others, have noted that the CO_2 bands in the 8–14 μ region show little contrast with the continuum, though they found shallow depressions from 8–10 μ and at 11 μ (the former roughly coincides with the SiO_2 emission minimum but MgO and other substances have a similar dip). The near absence of CO_2 absorptions is consistent with (a) the "radiometric level" being situated within the gas zone observed; and (b) the observed gas zone being nearly isothermal. The

general radiative transfer problem for an atmosphere containing a dense cloud of micronsize particles has been treated by Samuelson (1967). Particles several microns in diameter have a strong forward scattering for $\lambda < 1$ μ and allow deep penetration; whereas they scatter nearly isotropically around 10 μ and may allow less penetration. Öpik (1961) had previously commented on this difference.

Water droplets or ice crystals cannot form in the Venus *troposphere* (cf. Fig. 5) and are ruled out also by Coffeen's (1968) study. According to Samuelson's (1967) analysis, any particles some microns in size will be capable of providing the necessary green-house effect and *maintain the near-adiabatic temperature gradient* required in a general way by the high surface temperature of the planet, and observed directly by the Venera 4, 5, and 6 probes.

The temperature profile for the Venus *stratosphere* has been derived theoretically by McElroy (1968). We have transferred his computed tem-
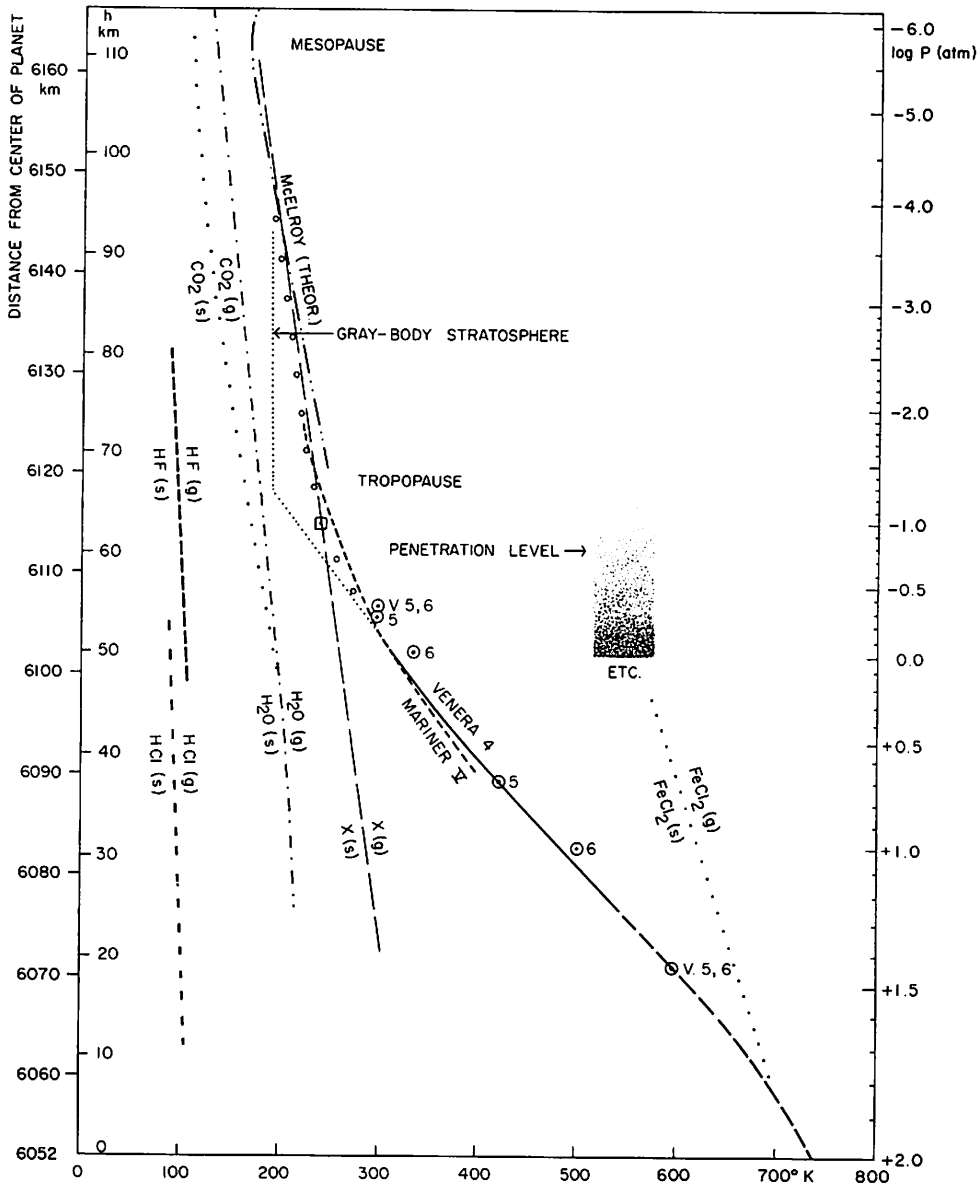
Fig. 5 Compilation of atmospheric pressure, temperature, and altitude relationships for planet Venus. Cf. Sec. 3 of text; dot in square, rotational temperature and pressure derived from CO (Connes *et al.*, 1968); small open circles: relationship adopted in computation of pressures.

perature curve (*op. cit.* Fig. 1) to our Fig. 5, which would suggest that H_2O condensation cannot quite occur at the mesopause level either. In Sec. 4 we shall find the UV haze to occur at or just below the mesopause level, which is suggestive of a condensation product; but photochemical processes will also favor the upper stratosphere.

4. Planetary Diameter and Cloud Level

The published measures of the optical diameter

of the planet are reviewed in the NASA *Handbook Venus* (Koenig *et al.*, 1967). The adopted mean value is that derived by de Vaucouleurs (1964), 12240 ± 15 km ($R = 6120 \pm 8$ km). This value coincides with the level of the tropopause in our Fig. 5 and should be, within the uncertainties, equivalent to the upper boundary of the dense haze layer expected to form the visible limb of the planet. Subsequent photographic measures by the writer on the Venus crescent near inferior conjunction have given

R = 6100 for red and near-infrared light; and R = 6145 km for the near UV (3600 A). This difference, of 0.7%, is regarded real and appears to establish the reality of the separation of the UV haze layer from the top of the dense yellow haze, inferred from its rapid horizontal motions.

From numerous observations of the occultation of Regulus by Venus on July 7, 1959, de Vaucouleurs and Menzel (1960) derived the altitude of the layer at which atmospheric refraction causes a factor 2 loss in the star light (as measured on Earth), to be 55 ±8 km above R = 6120 km (revised value). These results have been reanalyzed by Hunten and McElroy (1968), using the more detailed contract report by de Vaucouleurs and Menzel (1961), who find 6169 km radius for the occulting level. They also rederive the density at the occulting level which they find to be in good accord with the theoretical curve derived by McElroy (1968, 1969), entered in our Fig. 5.

5. Identification of the Venus Haze Layer

One notable property of the Venus haze layer is its great thickness, perhaps as much as 60 km (cf. Fig. 5 and the analysis by Samuelson, 1967). Only the upper parts can be observed optically, characterized by $d \simeq 2.5 \mu$, $n \simeq 1.5$-1.6 (Coffeen), and the reflection curve of Fig. 2.

Because Fig. 2 appears to be very different from the albedo curves of Mercury, the Moon, and Mars, at least in the region 0.35-0.8 μ (Harris 1961, pp. 308-310), one is tempted to exclude silicate materials from consideration of the Venus yellow haze. A small particle size, however, will markedly increase the albedo, and a comparison of Fig. 2 with reflection curves of *fine silicate dust* is not regarded superfluous. Adams and Filice (1967) published such curves for obsidian, rhyolite tuff, gabbro, and basalt for $0.4 < \lambda < 2.0 \mu$. There is no close resemblance with the Venus curve of Fig. 2. We have made supplementary checks of silicates for the interval $0.2 < \lambda < 2.5 \mu$ with the Zeiss Reflectance Spectrophotometer of the Chemistry Department through the courtesy of Dr. Feltham, in addition to more promising checks of *sublimates* to be discussed below. All spectral records were obtained by Godfrey Sill (O. Carm.), predoctoral student-assistant at LPL, to whom I am most indebted, not merely for the laboratory assistance, but for incisive discussions on the interpretation of the spectra. The new laboratory records are reproduced in Fig. 6. Records A-F show finely ground minerals and rock; records a-q,

the sublimates investigated. The curves are in reference to a (white) Li F standard. Unfortunately, this standard must have absorbed some water, with the result that completely anhydrous samples show slight positive features at 1.95 μ, and indications of a slight rise at 1.45 μ and 2.6μ. Also, the region 0.2-0.3 μ may be somewhat depressed, with the result that the ratio curves of Fig. 6 tend to show a rise in this interval. Otherwise the reflectance curves are reliable and consistent.

The silicates shown in Fig. 6A-F show no relationship to the Venus reflectance curve, Fig. 2, except for the iron dip at 1.05 μ in olivine. The very interesting question as to *which* surface materials would grind up into powder form and be able to be carried upward to the visible levels, is being pursued by Rev. Sill. He points out that quartz sand would *not* be among them! In any case, we have so far found no indications of aeolian materials in the Venus haze layer.

We next turn to *sublimate* particles possibly resulting from volcanic exhalations. The long list of conceivable sublimates may be shortened, first, by the observation that no sublimates will be visible on Venus whose vapor pressures at T $\cong$ 250° K are p > 1 mm; because this would imply atmospheric mixing ratios in excess of 10^{-2}, which, for chemically-active gases, would have led to their discovery (cf. Table 1). An incomplete list of substances so excluded is found in Table 2. (In addition, there are chemical reasons for excluding several entries in Table 2).

Of the sublimates whose vapor pressures at T = 250° K are below 1 mm, a substantial group can further be excluded on spectroscopic grounds if we are attempting to explain the characteristic absorptions of the planet shown in Fig. 2. The writer is indebted to Rev. G. Sill for the following formulation: "compounds of all non-transition metals may be excluded by the absorptions shown in Fig. 2 (except possibly their hydrates) because they lack transitions in the near-UV, visible or near-IR, and as a result are completely *white*." This does not mean

TABLE 2
SUBLIMATES NOT PRESENT ON VENUS IN VISIBLE
YELLOW HAZE LAYER

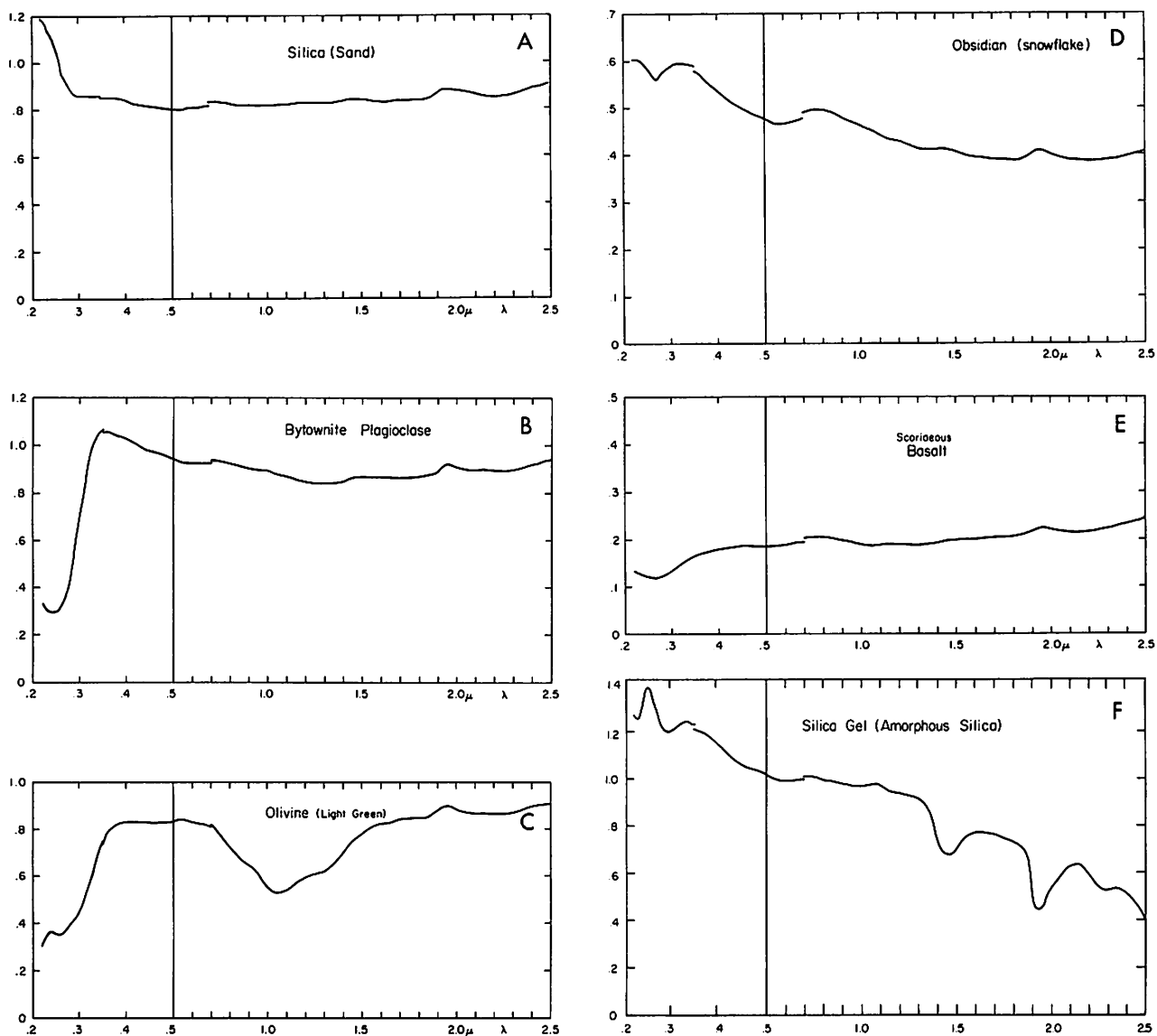|					
C_2N_2	HCN	H_2S	NOCl	CO_2	H_2Se
HI	H_2S_2	NO	SiH_4	CO	NH_3
HCl	SO_2	N_2O	$SiCl_4$	H_2O	UF_6
HF	SO_3	N_2O_4	Cl_2	SiF_4	WF_6
HBr	PCl_3	N_2O_5	COS	SiF_3Cl	$TiCl_4$
$Ni(CO)_4$			CS_2	SiF_2Cl_2	$SOCl_2$
$Fe(CO)_5$				$SiFCl_3$	SO_2Cl_2

Fig. 6 Reflectance measurements of possible solid constituents in Venus atmosphere made by G. Sill (O. Carm.) with a Zeiss Reflectance Spectrophotometer, using a Li F (white) standard.

that these substances are entirely absent from Venus. They could be present in amounts insufficient to obliterate the absorptions referred to. Therefore, we have retained in Table 3 (and in the graphs in Fig. 6), some compounds of non-transition metals. In addition, we have added some well-known com-

pounds of the transition metals: Fe, Ni, Mn, Cu, Co, Ti, V, Cr, Hg, Zn[1]. Table 3 is far from complete and is based in part on geochemical considerations. Thus, we have included the principal halides,[2] particularly metallic chlorides, because of their expected presence in a planetary atmosphere almost devoid of water; as well as other gases or sublimates found in terrestrial volcanic exhalations (other than water). The elements present in fumarole deposits of the volcano Stromboli (Rankama and Sahama, *Geochemistry*, 1950, p. 188) are: Fe (abundant hematite, α-Fe_2O_3; magnoferrite, $MgFe_2O_4$; soluble com-

[1] The cosmic abundances of these metals are, in terms of Si = 1000: 600, 27, 7, 0.2, 1.8, 2.4, 0.2, 7.8, .0003, and 0.5, respectively.

[2] The cosmic abundances of the halogens are, in terms of Si = 1000: Cl = 8.8, F = 1.6, I = .001, Br = .013 (Suess and Urey, 1956).

TABLE 3
WORKING LIST OF SUBLIMATES POSSIBLY PRESENT IN VENUS YELLOW HAZE LAYER

SUBSTANCE	n	M.P. °C	log p (mm) 250°K	500°K	700°K	COMMENTS
* $AlCl_3$	—	192	— 8.3	E	E	$AlCl_3. 6H_2O$, n = 1.56; (Fig. 6, i)
$AsCl_3$	1.62	— 8.5	— 0.5	E	E	boiling pt. 130° C; *d*ecomp. in pres. of H_2O
* $CaSO_4$	1.57-1.6	1450	—	—	—	SO_3 vapor
* $CaCl_2$	1.52	772	—29.8	—10.6	— 5.1	white at least up to 2.5 μ
$CoCl_2$	—	735	—18.	— 5.1	— 1.4	
$CrCl_2$	—	824	—	—	—	
Cu_2Cl_2	1.93	422	—14.1	— 4.0	— 1.2	(6,j)
$FeCl_2$	1.57	670	—20	— 4.8	— 1.5	(6,l); stable as gas
$FeCl_3$	—	308	—11	+ 0.8	E	*d*, 315°C, to $FeCl_2+Cl_2$; (6,o) M.P. on $FeCl_3. 6H_2O$ 37°C
FeF_2	—	>1000	—	—	—	
$FeCO_3$	1.64-1.88	—	—	—	—	CO_2 in vapor; (6,b)
$FeSO_4$	—	—	—	—	—	(6,s)
Hg	0.99-2.25	—39	— 4.9	+ 1.6	+ 3.4	(6,h)
$HgCl_2$	1.86	276	— 6.9	+ 1.9	+ 3.9	(6,h)
Hg_2Cl_2	1.97,2.65	—	—	—	—	(6,g); sublimes at 400°C
* KCl	1.49	776	(—28)	— 9.9	— 4.5	white into IR
* K_2SO_4	1.49	1074	—43	—16.1	— 8.4	white into near IR; SO_3 vapor
* $MgCl_2$	1.59,1.67	708	—20	— 7.0	— 3.2	white in IR; hexahydrate, (6,f)
* $MgSO_4$	1.56	1185	—	—	—	SO_3 vapor
$MnCl_2$	—	650	—20	— 6.0	— 2.3	n (tetrahydrate) = 1.55-1.57
* Na	4.22	98	—14	— 3.2	— 0.2	
* NaCl	1.54	801	—29	—10.5	— 5.1	(6,e)
* Na_2SO_4	1.47	884	—32.8	—11.2	— 5.0	SO_3 vapor
NH_4Cl	1.64	(335)	— 7.4	+ 1.3	+ 3.7	*d*,350°C, into NH_3, HCl vapor; (6,k)
NH_4CN	—	—	— 1.3*	E	E	NH_3, HCN vapors; *d*, 36° K
NH_4HS	1.74	—	— 1.1*	+ 5.9	+ 7.3	NH_3, H_2S vapors
$(NH_4)_2SO_4$	1.52-1.53	—	—	—	—	NH_3, H_2SO_4 vapors
$NiCl_2$	—	1001	—32	—10.4	— 4.1	(6,r)
* $PbCl_2$	2.2	501	—21	— 7.3	— 2.3	white into IR
S_8	1.96	113	— 7.1	(0.8)	(2.8)	$S + CO \rightarrow COS$; (6,a)
S_2Cl_2	1.67	—80	— 0.4	E	E	yellow liquid; *d* in pres. of H_2O
$TiCl_4$	1.61	—30	— 0.7	E	E	light yellow liquid; *d* in pres. of H_2O
$ZnCl_2$	1.68-1.71	365	—15	— 3.3	0.0	white

Asterisk in first column: compound of non-transition metal (white); in 250° K column, excluded from Venus atmosphere by gas spectroscopy. E, pressure in excess of 1 atm.

pounds); S, Se, Te; Li, Tl (sulfates); I; P; Zn, Sn, Pb, Bi, Cu (soluble compounds); B (boric acid); N (sal ammoniac); As (realgar; soluble compounds); K, Rb, Cs (alums); Na (mirabilite, $Na_2[SO_4].10H_2O$; glauberite, $Na_2Ca[SO_4]_2$); Ca (glauberite). The gases emitted in the Katmai are CO_2, CO, CH_4, H_2S, N_2, HCl, and HF (*Ibid*, p. 186). The Kilauea gas samples discussed by Heald, Naughton, and Barnes (1963) contained H_2O, N_2, O_2, CO_2, CO, SO_2, and traces of CH_4, H_2S, H_2, Ar.

Venus may conceivably have substances similar to terrestrial *evaporates* also (though the planet probably never had seas or lakes). Among those are chlorides of Na, Ca, Mg; sulfates of Na, K, Ca, Mg; carbonates, nitrates, ammonium salts, and oxides *(Geochemistry*, p. 220). Some of these categories, such as the nitrates, are likely to be absent from Venus and have been omitted from Table 3. The physical parameters entered in Table 3, taken from standard reference tables or computed from data provided, are often order-of-magnitude only, sufficient for general orientation.

Table 3 only lists some of the simpler com-

pounds, especially chlorides. Not included explicitly, but important to consider throughout, are their *hydrates* (some halides are extremely hygroscopic), their ammines, and their carbonyls. The likelihood of their presence may often be judged from the thermodynamic data in *International Critical Tables*, Vol. VII, based on discussions such as accompany Fig. 7, below.

Many of the compounds in Table 3 can be eliminated either by gas spectroscopy, available or potential; or else by broad-band spectral observation of the sublimate and direct comparisons with Venus (Fig. 2). This is a large program and only preliminary results are included here.

The combined results of the spectroscopy of the gases and the solids must finally be tested and explained in terms of volcanic exhalations, the presumed ultimate source of the planetary atmosphere. The study of terrestrial volcanic exhalations is suggestive. Heald, Naughton, and Barnes (1963, p. 556) concluded: "Volcanic gases approach a state of chemical equilibrium in the gas phase. Equilibrium is usually not attained between the volcanic gas and
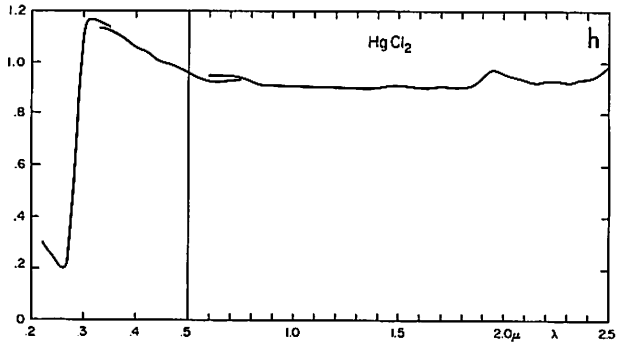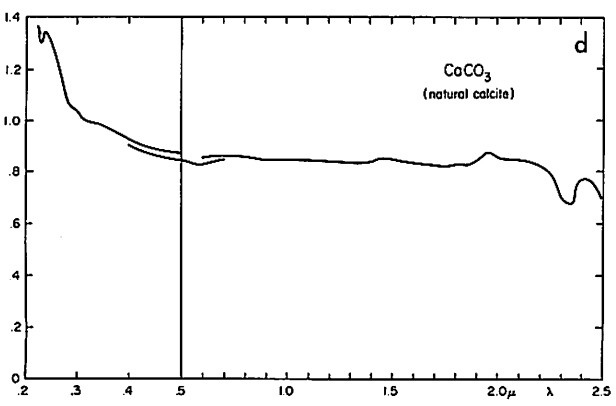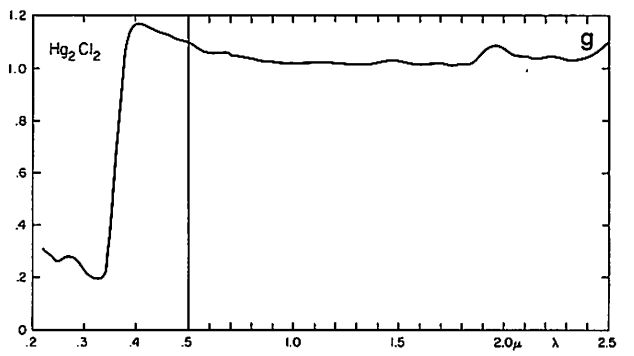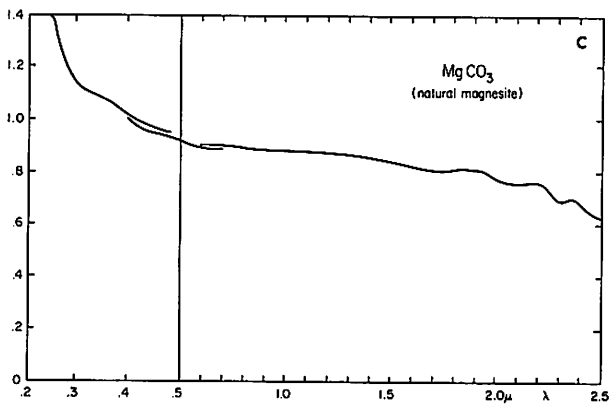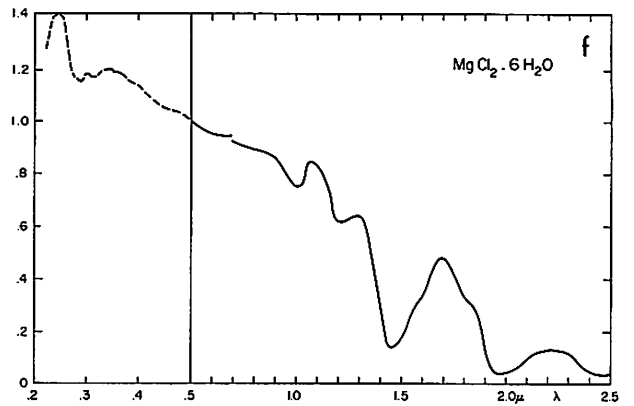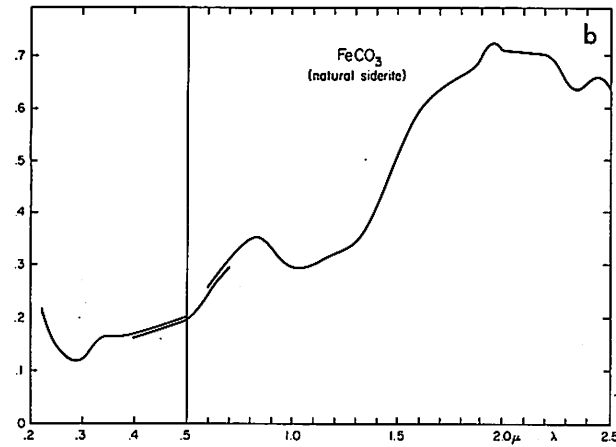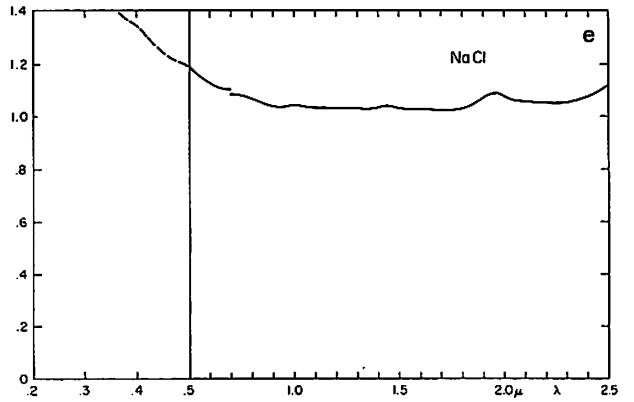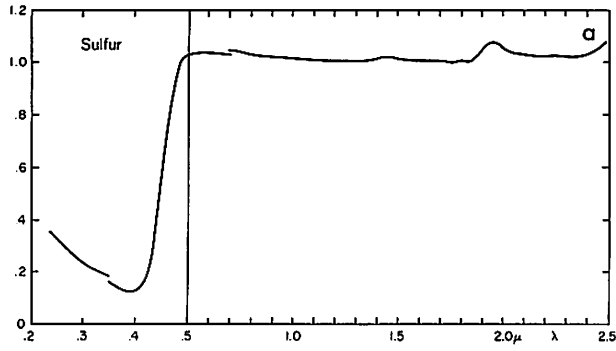
Fig. 6 continued.

surrounding rocks . . ." This work followed an earlier study by Ellis (1957) "indicating that volcanic gases may be regarded as an equilibrium system." On the other hand, the comparatively high surface temperature of Venus and the long interaction time available may shift the balance on that planet in favor of *gas reactions with the surface rocks,* an assumption underlying the analysis by Lewis (1968).

The spectral reflectance curves for the selected sublimates, recorded by Rev. G. Sill, are reproduced in Figs. 6a-q. Three source-detector combinations were used at different wavelengths, which explains the breaks in the curves (it is seen that the internal agreement is generally excellent).

Fig. 6 shows vast differences among the substances selected for measurement. The carbonates and sulfur do not match Venus at all, nor do any of the anhydrous chlorides: NaCl, $MgCl_2$, NH_4Cl, $FeCl_2$, $FeCl_3$, $NiCl_2$. Of the hydrated chlorides neither ferrous-chloride tetrahydrate ($FeCl_2.4H_2O$) nor $FeCl_3.6H_2O$ matches the planet, but ferrous chloride dihydrate ($FeCl_2.2H_2O$) shows a remarkable resemblance: in the UV, with the shoulder at 4500 Å, with the maximum around 7000 Å, the dip near 1.0 μ, and the general shape at longer wavelengths. In making comparisons with Fig. 2, it should be borne in mind that the Venus haze particles

may be smaller than the grains in the powdered laboratory samples used for Fig. 6; so that an absorption feature might be shallower in Fig. 2 than in Fig. 6 Also, there is some uncertainty at $\lambda < 0.3 \mu$ (Sec. 2).

The drop beyond $\lambda = 2.5 \mu$ is explained by the H-O bond of the hydrate. Dr. U. Fink kindly obtained the reflectivity of $FeCl_2.2H_2O$ beyond 2.5 μ, using the Perkin-Elmer spectrometer of the Optical Sciences Department. His data for 2.5-3.6 μ are added in Fig. 6. Other hydrates, such as of cuprous chloride, showed an almost identical dip centered at about 3.05 μ. The extended Venus "absorption," 3.2-4.0 μ, according to Fig. 2 and Fig. 2a, needs further explanation. It could be due in part to a larger hydrate ($4H_2O$ or $6H_2O$), or an additional sulfate, as shown by Dr. Fink in laboratory tests; or, in part, to small backscattering for particles of $\simeq 0.7 d$. The very deep absorption centered on 4.3 μ is due to ν_3 of CO_2. Some supplementary results are contained in Appendix 2.

In order to assess the uniqueness of the identification of the Venus reflection curve of Fig. 2 with that of partially-hydrated ferrous chloride, one wishes to identify, if possible, each major absorption feature in Fig. 2 with a specific molecular transition. The writer is indebted to Dr. Feltham for a discussion on this subject (cf. Ballhausen 1962, p. 252; Miller and
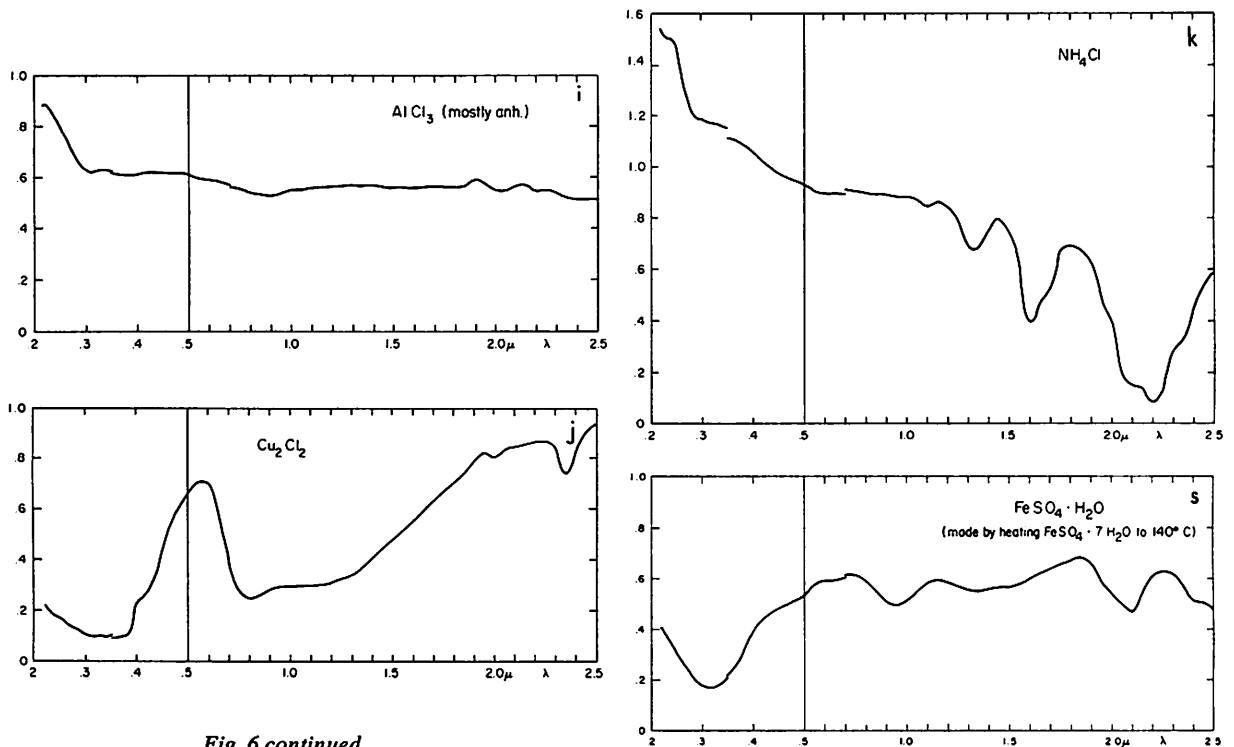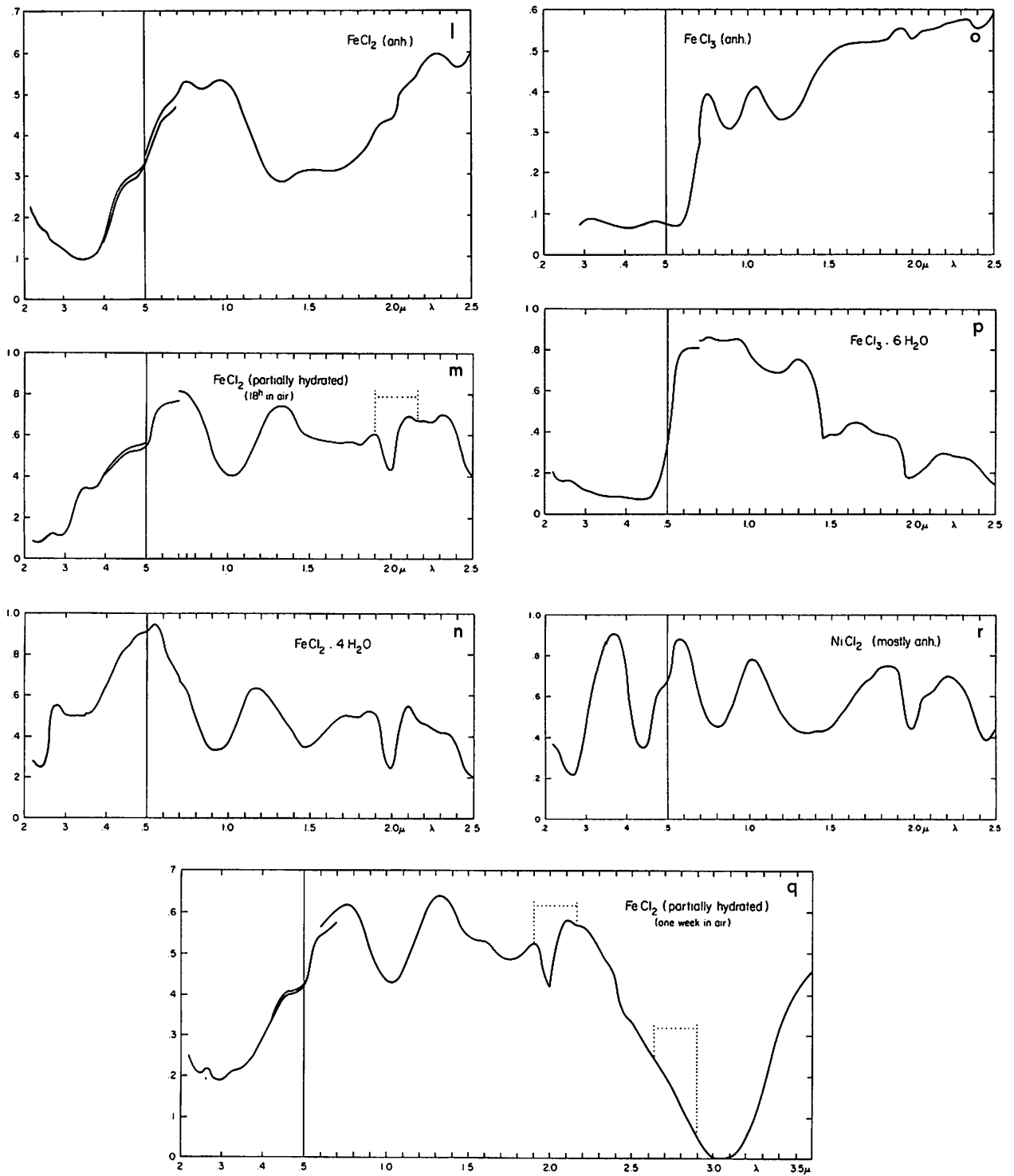

Fig. 6 continued.

Fig. 6 continued. (Rev. Sill produced the anhydrous $FeCl_2$ from $FeCl_3$ by H reduction.)

Wilkins 1952). Comparison of the laboratory curves of Fe Cl$_2$ (anh.), Fe Cl$_2$.2H$_2$O, and Fe Cl$_2$.4H$_2$O shows that the minimum at 0.24 μ is due to the presence of H$_2$O; it involves a charge transfer between Fe and H$_2$O. This minimum is present in Venus. At 0.29-0.30 μ an absorption exists, well shown in Figs. 6m and 6q and less well in 6n and 6l, and present in Fig. 2 (Venus) at about 0.29 μ, which is explained as due to a charge transfer between Fe and Cl. The next absorption in Fe Cl$_2$ (anh.) is at 0.35 μ, also well shown in Fe Cl$_2$.4H$_2$O and shown as a shoulder in Fe Cl$_2$.2H$_2$O. It is similarly shown as a shoulder in Venus. It is due to a d to d transition of Fe^{2+}. The same is true for the more prominent shoulder at 0.46-.50 μ, so well shown in Venus and in both the anhydrous and partially hydrated Fe Cl$_2$. A third d to d transition of Fe^{2+} is shown at about 1.0 μ. It is possible that in the hydrous minerals this minimum is somewhat deepened by an O-H absorption of the hydrate. The very prominent absorption in Venus between 2.5 and 3.4 μ is due to the hydrate (O-H bond), as remarked before. The moderately-strong and rather-narrow hydrate absorption at 2.0 μ cannot be readily observed in Venus because of the overlying very strong CO$_2$ absorptions:

It appears then, that the identification of partially hydrated FeCl$_2$ is definite, and that the state of hydration is close to or slightly below the *dihydrate*.

The next question must be whether the observed H$_2$O content of the Venus atmosphere is compatible with Fe Cl$_2$.2H$_2$O in the observed layer at about 220°-250° K. In Fig. 5 the total pressure at the 250° K level is log p (atm.) $= -0.8 \pm 0.3$. The water-vapor pressure is therefore about log p (atm.) $= -6.8 \pm 0.5$. The dissociation pressure in the reaction FeCl$_2$.2H$_2$O(s) $=$ FeCl$_2$.H$_2$O(s) $+$ H$_2$O(g) is found by extrapolation to be log p (atm.) $= -5.3$ at 250° K or -6.7 at 220° K (International Critical Tables, Vol. VII, p. 277) (cf. Fig. 7). We conclude that the *existing water-vapor pressure on Venus is roughly in the amount expected from the presence of the dihydrate of Fe Cl$_2$*. For the mono-hydrate, the dissociation pressure, according to a single measurement at T $= 428°$ K, is some 10× lower (*op. cit.* and Fig. 7); for the tetrahydrate measures appear lacking but the H$_2$O pressure would presumably be much higher. The study of the dissociation vapor pressures is being pursued by Dr. U. Fink.

An intriguing problem is the nature of the haze layer *below* the visible parts. In Fig. 7 two graphs give the p.T relationships for two constant mixing ratios of H$_2$O/CO$_2$, 10^{-3} and 10^{-6}. It follows that either the mixing ratio must increase with depth, to about 10^{-3} at the level where Venera 5 made its H$_2$O measurement, if Fe Cl$_2$.2H$_2$O is to persist to that level; or else the *anhydrous form,* Fe Cl$_2$ (anh.) *is to take over beneath the 250° K level.* In the second case, the Venera 4-6 H$_2$O measures would have to be in error. If they are correct, the true H$_2$O mixing ratio would at the 0.6 atm. level probably be around 10^{-3} (cf. Fig. 7), with the remainder
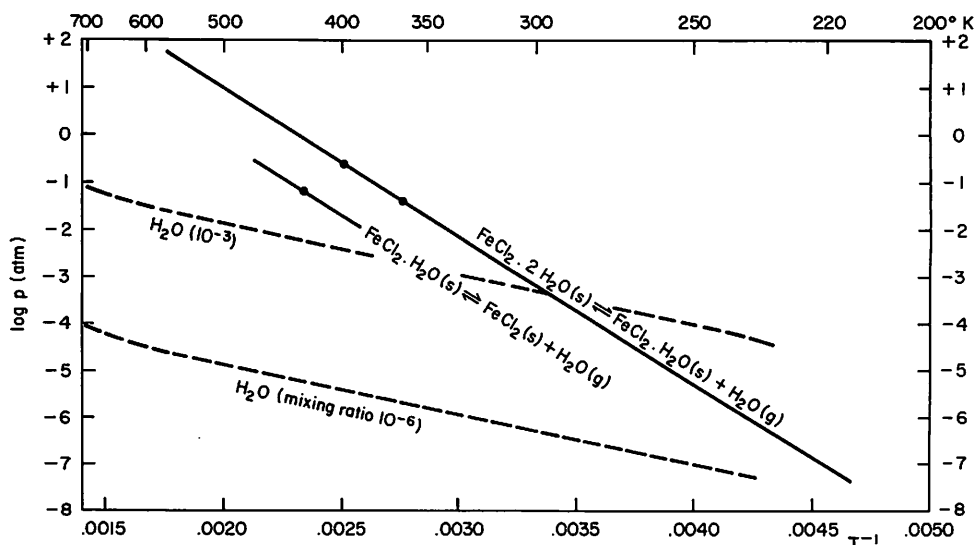

Fig. 7 Dissociation pressures for hydrated ferrous chloride in p, T diagram, also showing two H$_2$O mixing ratios for Venus atmosphere.

of the P_2O_5 reaction to be explained by water drawn from Fe $Cl_2.2H_2O$ (I am indebted to Rev. G. Sill for pointing out this interesting possibility, the H_2O bond with P_2O_5 being much the stronger). In this case the mixing ratio H_2O/CO_2 would reach 10^{-2} at the planetary surface, where the anhydrous form or the monohydrate would dominate. However, such a high mixing ratio of H_2O is entirely *excluded by the microwave intensity* of the planet at 1.35 cm, which has given no indication of the presence of water-vapor absorption. This places an upper limit to its abundance of 1 to 3 mm precip. H_2O for the vertical column or a mixing ratio 1 to 3 $\times$ 10^{-6} for the entire atmosphere, the same as the spectroscopic amount actually found. It is concluded that the high H_2O contents quoted can *not* be correct. In the deeper layers $FeCl_2$ must be anhydrous. (After the above was written it was learned that Venera 5–6 obtained a second H_2O mixing ratio at greater depth, very much lower; indicating that degassing of the spacecraft may have been a factor.)

For the visible layers Moroz (1965) has estimated from the scattering properties of the atmosphere a particle density of $100/cm^3$ and a particle radius of 1 μ, not substantially different from Coffeen's diameter of 2.5 μ derived from polarization measures. If these figures be adopted* and the bulk density of the particles be assumed 1.0, the space density of the solid is found 10^{-9}. The ferrous chloride particles could be produced from $FeCl_3$ exhalations (because of its much higher vapor pressure), as suggested by Rev. Sill, as follows:

$$2\,FeCl_3 + CO + H_2O = 2\,FeCl_2 + 2HCl + CO_2,$$
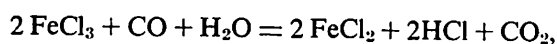
with $FeCl_3$ decomposed above 315°C or 588° K (cf. Table 3). The resulting numbers of $FeCl_2$ and HCl molecules *would be equal.* Curiously, *this equality is found to exist* with the Moroz estimate of the particle frequency and the Connes et al. abundance of HCl: with p = $10^{-0.8}$ atm., T = $250°$ K, m = 44, the CO_2 gas density is $10^{-3.5}$, and the HCl density $10^{-9.8}$. Allowing for the molecular weight ratio $(FeCl_2.2H_2O)/HCl = 163/36.5 = 4.5$, the computed volume density of the solid particles would indeed be 10^{-9}. It remains to be shown whether this equality is in fact due to the suggested process and thereby *explains the amount of HCl* in the Venus atmosphere in terms of the existing cloud particles. In any case, the near-equality of the mole fractions

*With opaque particles $d = 2$ μ, it takes $10^8/\pi$ particles/ cm^2 column to make $\tau = 1$. For a constant mixing ratio, particles/gas, the scale height is 6.10^5 cm, and the space density at $\tau = 1$ about 50/cc.

of $FeCl_2$, H_2O, and HCl, is noteworthy, and, as remarked by Rev. Sill, they are also close to the saturation fraction of $FeCl_2$ at T = $700°$ K (Table 3).

For compounds whose dissociation pressures have been measured, predictions are possible regarding the state of hydration, which saves laboratory examination of substances that cannot occur. As an example, the hexa-, tetra- and dihydrates of $NiCl_2$, will not be present with the known atmospheric $H_2O(g)$ concentration, but the anhydrous form can exist (Fig. 6r); by Fig. 2 its abundance is clearly much less than that of $FeCl_2.2H_2O$, as expected from the abundance ratio Fe/Ni $\simeq$ 22 and the ratio of the vapor pressures at the surface ($\simeq 400$; cf. Table 3). Similarly, $FeSO_4$ can occur in the Venus atmosphere only in the anhydrous form. Its reflectance curve (Fig. 6s) has some distinct similarities with that of Venus and its reflectance beyond 2.5 μ is interesting (see Appendix 2).

The reflection spectrum of $(NH_4)_2SO_4$, an entry in Table 3 and a minor constituent of the terrestrial stratosphere, was investigated by Rev. G. Sill for the interval 0.2–2.5 μ; and by Mr. S. Burk for 2.5–7 μ. For both spectral intervals the reflectance curve is almost *undistinguishable* from that of NH_4Cl (Figs. 6,k and 8b). The only difference is the absence of the minor absorption at 5.4 μ of NH_4Cl. The conclusion is that $(NH_4)_2SO_4$ is excluded as the chief component of the visible Venus haze layer.

Reference is made to the most interesting observations of "Volcanic Smoke Clouds" by McClaine et al. (*J. Geophys. Res. 73,* 5235–46, 1968), in which, by X-ray spectroscopy, the elemental composition is determined of the micron-sized particles of the smoke column, collected from aircraft. No close correspondence to the *composition* of the Venus haze particles exists, apparently because of the high ratio of H_2O/Cl in the volcanic gases; but the *atmospheric injection mechanism* is of interest here.

6. Interpretation of the UV Cloud Layer

The phase curve of $FeCl_2$ in Fig. 5 suggests that $FeCl_2(s)$ exists in the upper troposphere only as a result of tropospheric convection. The mole ratio $FeCl_2/CO_2$ is about 10^{-6} throughout, with the vapor dominant near the surface and the solid higher up. At $250°$ K the vapor pressure is only 10^{-23} atm. (Table 3) so that in a tranquil stratified atmosphere at that temperature no applicable amount of the sublimate would exist. At the tropopause the vertical transport ceases and $FeCl_2(s)$ is not expected

in the stratosphere. (The problem of the atmospheric $FeCl_2$ distribution is probably more complex, owing to the presence of other gases. A detailed investigation, involving reaction rates vs. transport rates, is needed; but the simple picture used appears to account approximately for the observable layers.)

The UV clouds behave as a condensation product (Sec. 1). In Fig. 5 we have drawn heuristically a line separating the gas and the solid phases of a hypothetical substance that would condense around the 6145 km level (Sec. 4), but not in the troposphere. One might identify this substance with NH_4Cl on the following grounds: (a) $NH_3(g)$ + $HCl(g)$ in low concentrations produce a blue haze of $NH_4Cl(s)$, evidently composed of crystals ~ 0.1 μ in diameter, much like the Venus UV clouds; (b) the phase boundary in Fig. 5 will actually represent NH_4Cl (cf. Table 3) if its mole fraction is 10^{-10} [in reality $NH_4Cl(g)$ occurs as $NH_3(g)$ and $HCl(g)$; the required mole fraction is to be interpreted as the geometric mean of the mole fractions of $NH_3(g)$ and $HCl(g)$]. Since the mole fraction of $HCl(g)$ is $10^{-6.2}$, the $NH_3(g)$ mole fraction would, in the observable zone, need to be 10^{-14}, too small to be discovered spectroscopically (Table 1) but not unreasonable in view of the large equilibrium mole fraction of NH_3 at the planetary surface (Lewis, 1968, p. 445). One may alternatively examine whether $(NH_4)_2SO_4$ might explain the UV haze on Venus, especially since it occurs as an aerosol in the terrestrial stratosphere. An estimate may be made of its abundance in terms of NH_4Cl since both compounds require the presence of NH_3 for their production and one requires SO_2 (whose upper limit is found in Table 1), and the other HCl, of known abundance. I am indebted to Rev. G. Sill for a discussion on this question; using the upper limit of the SO_2 abundance (Table 1) he has computed the abundance ratio to be at least ten orders of magnitude in favor of the chloride.

It would appear that considerable additional information would be derivable from spectral polarimetry of the thin crescent or complete ring observed near the planet's inferior conjunction, from a high-altitude station or preferably from outside our atmosphere. Reference is made to a study of "The Twilight Atmosphere of Venus," by G. F. Schilling and R. C. Moore (1967).

Additional laboratory work will be required to (a) extend the studies of Table 3 and Figs. 2 and 6, and possibly note additional constituents; (b) examine the *shapes* and dimensions of the sublimate particles and their effects on the polarization curves for different wavelengths; and on the absolute ordinates of Fig. 2 as well as the photometric phase curves; (c) to extend the study to greater depths in the Venus atmosphere with reference to the spectrum and phase effects from 10 μ < λ < 1 cm; (d) initiate laboratory simulation studies suggested by the Venus atmosphere. Rev. Sill is currently organizing program (d) as part of his doctoral requirements; (e) refine Fig. 2, 1–4 μ based on new precise observations, with $\Delta \lambda / \lambda \simeq 0.01$, a program now underway at LPL; and attempt to obtain the planetary emission spectrum 10 μ–1000 μ from high altitudes or, better, from outside the atmosphere. The Venus CO_2 band at 15 μ, whose intensity will be produced near p = 10^{-6} atm., will reflect *the temperature minimum at the mesopause* (cf. Fig. 5). Other bands will define temperatures at deeper layers, and gaps between them will show the surface, allowing an estimate to be made of the *upper limit to the particle sizes at greater depths*. Some information may thus be gained also on the emissivities of the Venus surface layers (which may be much below unity), and, if so, on their composition, depending on depth. Specifically, it may be possible to determine whether *a deposit of sublimates* covers the silicate crust. Laboratory work on both the atmospheric gases and prospective surface materials at prevailing temperatures, pressures, and abundances, will be needed for the interpretation of the far-IR spectrum.

APPENDIX I
ATMOSPHERIC DISCOLORATION
OF CLOUDS

Since the other planets are observed from outside their atmospheres, it is of interest to examine

under what conditions observed clouds are discolored. Specifically, are the yellow Venus clouds in reality white and their coloration merely caused by the overlying gases? This question is examined theoretically and empirically.

The theoretical argument is as follows: The overlying Venus atmosphere has a mass of 0.1-0.2 terrestrial atm. and at $\lambda = 5500$ Å, the optical depth τ due to Rayleigh scattering in a CO_2 atmosphere is therefore about 0.05. The visual A of the planet is 0.7. For the subsolar point on the planet the fraction of the solar flux reaching the clouds is $(1-\tau)$; of the light scattered by the atmosphere, $\tau/2$ is cast upward and added to the observed albedo; $\tau/2$ downward and added to the solar flux reaching the clouds. Together the clouds reflect therefore $A\left(1 - \dfrac{\tau}{2}\right)$ of which $\left(1 - \dfrac{\tau}{2}\right)^2 A$ emerges upward from the atmosphere (including the cloud radiation scattered upward by the atmosphere). The amount $\dfrac{\tau}{2}\left(1 - \dfrac{\tau}{2}\right)A$ is scattered back down and illuminates the clouds. Of this contribution $\left(1 - \dfrac{\tau}{2}\right)\dfrac{\tau}{2}\left(1 - \dfrac{\tau}{2}\right)A^2$ goes back out. Neglecting higher-order terms we find for the total emergent flux

$$\frac{\tau}{2} + \left(1 - \frac{\tau}{2}\right)^2 A + \frac{\tau}{2}\left(1 - \frac{\tau}{2}\right)^2 A^2,$$

or, neglecting terms in τ^2,

$$A + \frac{\tau}{2}\left(1 - A\right)^2.$$

For $\tau = 0$ the emergent flux is A; for small τ and $A = 0.7$, the flux is $A + 0.05\,\tau$; for $A = 1$, the flux is 1 for any small value of τ. Since $\tau \sim \lambda^{-4}$, the overlying atmosphere makes the planet Venus slightly *bluer*, not yellower, than the Venus cloud layer observed by itself.

The theoretical conclusions are confirmed by high-altitude observations of terrestrial clouds, as may be made by any traveler using modern high-altitude jets. Cumulus clouds over industrial areas show little color distortion for the cloud tops, but the cloud base is often embedded in industrial smog, causing them to have a deep yellow color. By contrast, in a high-altitude view of similar cloud formations over the Pacific, where no such air pollution is present, the cloud structures appear white throughout. It is noted that the air mass between the observer and the

cloud tops is normally well in excess of the amount present above the yellow haze layer of Venus, reenforcing the conclusion of the preceding paragraph, that discoloration is not due to Rayleigh scattering, but to true absorption.

APPENDIX 2
REFLECTANCES BEYOND 2.5 μ

Through the cooperation of Dr. U. Fink and Mr. S. Burk, I am able to reproduce in Fig. 8 reflection spectra of some compounds whose reflectance beyond 2.5 μ are of special interest in connection with the interpretation of the Venus curve in Fig. 2.

Fig. 8a, $MgCl_2 \cdot 6H_2O$ is an example of a large hydrate whose OH absorptions are already very prominent at 1.95, 1.45, 1.2, and 1.0 μ. The $\lambda > 3.0$ μ absorption is seen to be enormous.

Fig. 8b, $NH_4Cl(s)$, identified to exist in Venus stratosphere, is not expected in the troposphere (Fig. 5), but its behavior is obviously important. The curve shortward of 2.5 μ does not fit the Venus curve but the absorption at 3.5 μ partly resembles the depression in Fig. 2. However, many other substances absorb from 3-4 μ. A positive spectral identification of NH_4Cl in the 0.2-0.4 μ region of Venus appears feasible, and will be attempted with ultra-
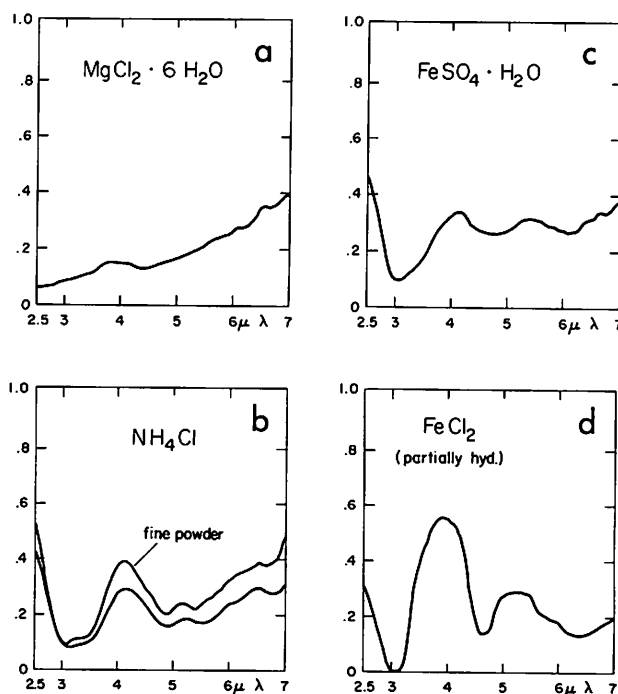

Fig. 8 Reflectance curves, 2.5-7 μ, for four substances (cf. Appendix 2).

fine NH_4Cl crystals. This should also allow an estimate to be made of the ratio between the NH_4Cl and $FeCl_2.2H_2O$ contributions in the UV, probably variable, with NH_4Cl dominating at the crescent phase.

Fig. 8c, $FeSO_4$, as indicated in the text, should be studied in the anhydrous form; but our best result so far is that of the monohydrate, produced from the heptahydrate, as indicated in Fig. 6s. Its reflectance beyond 2.5 μ is interesting and work on other sulfates is indicated to determine whether the haze contains such contributions.

Fig. 8d, $FeCl_2$ has been discussed in connection with Fig. 6q.

Dr. Fink intends to publish a more complete set of records for $\lambda > 2.5$ μ shortly.

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Note added in Proof. The further possibilities that Hg_2Br_2, $HgBr_2$, Hg_2I_2, or HgI_2 might explain the absorption features of Fig. 2 were examined by G. Sill. The reflection spectra somewhat resemble that of Fig. 6, *g* (Hg_2Cl_2) and are completely unlike Venus. The planet may have been depleted of volatiles.