# NO. 32 A DETERMINATION OF THE COMPOSITION AND SURFACE PRESSURE OF THE MARTIAN ATMOSPHERE

by T. C. OWEN AND G. P. KUIPER

August 24, 1964

#### ABSTRACT

The spectra of Mars obtained in the 1-2.5  $\mu$  region (*Communications* No. 31) are calibrated with the aid of laboratory spectra of pure CO<sub>2</sub> as well as mixtures of CO<sub>2</sub> with N<sub>2</sub> and Ar. Pathlengths up to 3.6 km are used and pressures down to 4 mm. With the aid of the total CO<sub>2</sub> content reviewed in *Comm.* No. 33, based on the Mt. Wilson spectrum, preliminary values are derived for the pressure in the Martian atmosphere and the total amount of gases other than CO<sub>2</sub>. The values obtained are  $17 \pm 3$  mb (13 mm Hg) and (N<sub>2</sub> + Ar)/CO<sub>2</sub> = 6. Arguments are given indicating that the Ar/N<sub>2</sub> ratio is probably similar to that for the Earth atmosphere ( $\approx 10^{-2}$ ) and that the O<sub>2</sub> content is probably <7 cm atm.

## 1. Introduction

 $\mathbf{T}$  his paper contains the laboratory calibrations that have been made for the Mars spectra published in Communications No. 31, using the maximum range of available pathlengths and an appropriate range of pressures. The program assumed its present form during the NASA conference on the Mars atmosphere, October 1-2, 1963, when the authors noted that with the total CO<sub>2</sub> content found from weak bands, both the atmospheric pressure and the abundance of any other major constituent, such as N2, could be determined empirically from measurements on the 1.6  $\mu$  CO<sub>2</sub> bands. As one of us (GPK) stated at this Conference, this is so because the band strength is a function of (1)  $CO_2$  abundance, (2) admixture of  $N_2$  or Ar or both, and (3) pressure; and, further, because there are three equations relating these three unknowns: (1) the CO<sub>2</sub> abundance found from weak bands, (2) the observed strength of the 1.6  $\mu$  bands, and (3) the computed weight or pressure of the atmospheric column, the surface gravity on Mars being known.

A completely empirical determination of the pressure effects in the gas mixtures is still not quite possible, however, because it would require a pathlength twice the scale height of the Martian atmosphere, or some 40 km. The pathlengths reached here are only about 0.1 of this. While they suffice to give a reasonably precise answer, improvements are desirable and being executed by increasing the available laboratory pathlength to at least 8 km.

## 2. The Laboratory Program

The spectra were obtained with the same spectrometer (described in *Comm.* No. 16) used for obtaining the telescopic observations of Mars. The absorption tube used has a 72-foot multiple-reflection path and was designed by Mr. Owen to fit the available laboratory space. Part of the records were obtained by the two authors jointly, but the bulk were obtained by Mr. Owen aided by a graduate-student assistant. Four traversals of the tube measure very nearly 90 meters and the program was designed to increase the pathlengths in steps of a factor of two: 90, 180, 360, 720, 1440, 2880 meters, though some intermediate steps were covered and a maximum effort was made: 540, 1080, 2160 and 3600 meters. Matching the steps of two in pathlength are steps of two in pressure: 24, 12, 6, 3, 1.5, 0.75, and 0.4 cm Hg, which correspond very nearly to the following values in millibars: 320, 160, 80, 40, 20, 10 and 5.3. In this manner products of pathlength and pressure (i.e., abundance) resulted, falling into discrete groups progressing in the ratios 1, 2, 4, 8, etc., in abundance. Within each group of constant abundance the band intensity then shows the effects of pressure.

After it was found that the strength of the Martian  $CO_2$  bands cannot be interpreted on the basis of a pure  $CO_2$  atmosphere (the empiricallydeduced pressure being inconsistent with the pressure computed from the weight of the column), it was decided to add N<sub>2</sub> to the gas, the most likely constituent of the Mars atmosphere other than small amounts of Ar<sup>40</sup>. The pressure effect of N<sub>2</sub> on CO<sub>2</sub> is less than the effect of CO<sub>2</sub> on CO<sub>2</sub>, so that these additional runs were needed. Since it was further found that Ar<sup>40</sup> affects CO<sub>2</sub> very similarly to an equal amount of N<sub>2</sub>, the work on CO<sub>2</sub> + N<sub>2</sub> seemed particularly appropriate. A 10%/90% mixing ratio for

TABLE 1 Pure CO.,

		-				
p = 0.4	0.75	1.5	3	6	12	24 cm
			1*	2*	3*	2*
	••••		1*	3*	6*	2*
		4*	4*	8*	4*	2*
	••••	5*	5	3*	••••	••••
9	8	2	4	4		••••
2	7	4	4	••••	••••	••••
		···· ···	···· ··· ··· ··· ··· ··· ··· ··· ··· ·	···· ··· ··· ··· ··· ··· ··· ··· ··· ·	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

\* 1.2  $\mu$  observed also.

TABLE 2 90% N<sub>2</sub>, 10% CO<sub>2</sub>

PATHLENGTH	p = 1.5	3	6	12	24 сп
90 m				2	2
180			3	2	2
270				••••	2
360	3*	4*	3	2	3
540				2	2
720		4	2	2	5
1080	••••	2		3	2
1440 2160		3	4	7	
2880		2		3	
2950			3		
3600			4	2	

\*1.2  $\mu$  observed also.

TABLE 3 25% CO<sub>2</sub>, 75% N<sub>2</sub>

Pathlength	p = 0.75	1.5	3	6	12	24 cm
90 m			2	3	4	3*
180		4	3	3	3*	3*
360		4	3	3	3	2*
450						2*
720		3	3	3*	3*	2*
900		••••			4*	
990			3 4 #	3* 2*	2*	••••
1440 1800	••••	4	4*	3*	3.	
1080		3	<u></u>	<b>J</b> .	••••	
2880	3	3	3	3	4	

\*1.2  $\mu$  observed also.

 $CO_2/N_2$  was adopted. When measurements on it showed that the pressure discrepancy was now reversed, a third set of spectra was obtained on an intermediate mixture,  $CO_2/N_2 = 0.25/0.75$ . Tables 1 to 3 list the combinations of pathlength and pressure actually run.

The CO<sub>2</sub> bands chosen for analysis are those at 1.575 and 1.606  $\mu$ , although the spectrometer tracings normally included the weaker bands at 1.538  $\mu$  and 1.646  $\mu$ . Occasional records were taken of the 1.206  $\mu$  and 1.221  $\mu$  bands as well. The inventory in Tables 1-3 lists available data.

A representative set of laboratory records is reproduced in Figures 1-10. At the resolution of the Mars observations and the corresponding laboratory runs, the rotational structure of the  $CO_2$ bands is not resolved. The P and R branches are distinct, however, and cause W-shaped absorptions which are well adapted to intensity measurements with a planimeter.

The Mars spectra obtained on December 8, 1962 are the most suitable for study of the 1.6  $\mu$  bands. As was reviewed in conjunction with Fig. 16a of *Comm.* No. 31, the telluric components of the 1.6  $\mu$ bands can be separated from the Martian components. The average equivalent width of the two strong Martian bands is 15.8Å.

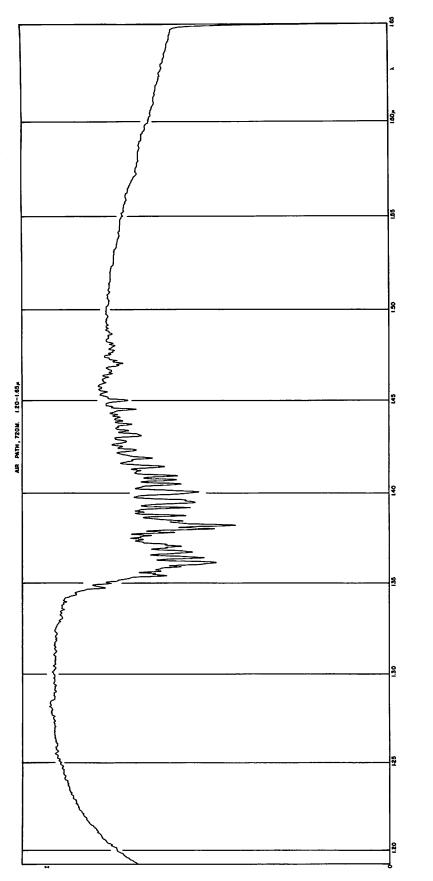
The averaged equivalent widths of the two 1.6  $\mu$  bands measured on the laboratory spectra are plotted logarithmically against pressure in Figs. 11-13. In most cases two or three spectra were measured, as available (Tables 1-3). The measures were made in duplicate by one of the authors (GPK) and by a graduate-assistant, Miss Thelma McKinney. The curves connect points representing equal abundance with the amounts indicated in the figures. The pressure effects are quite marked and the determination of the Martian atmospheric pressure requires careful consideration.

# 3. Derivation of the Pressure and Composition of the Martian Atmosphere

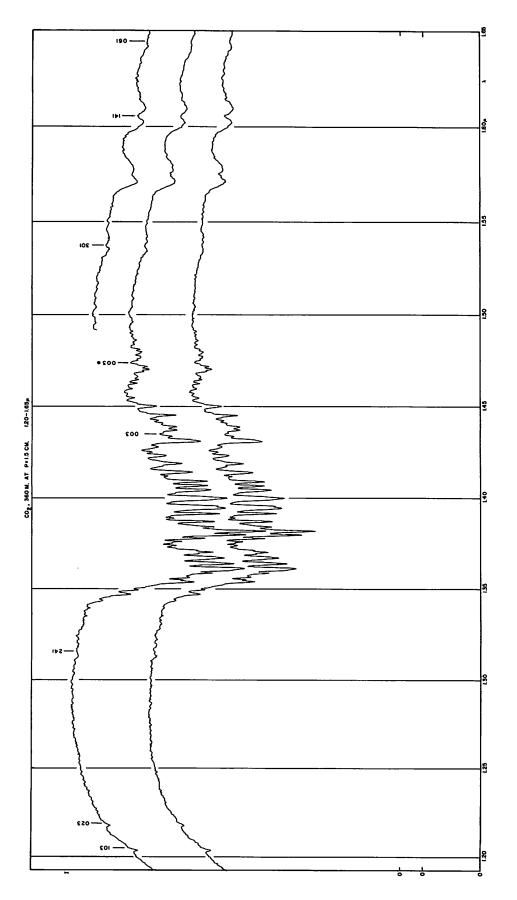
As stated in Section 1, the first requirement is information on the total CO<sub>2</sub> content from weak bands, unaffected by pressure broadening. This is provided by a calibration of the intensity of the  $5\nu_3$ band of CO<sub>2</sub> observed by Kaplan, Münch, and Spinrad (1964). These authors derived a value of  $50 \pm 20$  m atm, corresponding to an atmospheric temperature of 200° K. An independent calibration of this spectrogram is made in *Comm*. No. 33 which results in a value of  $46 \pm 20$  m atm for the same

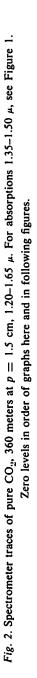
temperature. The difference between these two values is not regarded as significant; for the sake of consistency we will use the second figure. The specification of temperature is necessary for the  $5\nu_3$ abundance determination because the relative intensites of the rotational lines are strongly temperature-dependent and in this case the individual lines are resolved. The number of molecules defined by the m atm is referred to NTP. In the PbS region the lines are not resolved and thus the amount of the gas in m atm which will be required in the laboratory optical path to match the Martian equivalent width will simply be  $46 \times \frac{T_L}{273} \times \eta$  where  $T_L$  is the laboratory temperature and  $\eta$  is the effective Martian air mass through which the observations were made. In the present case the slit of the spectrometer ran equatorially across the planet and thus  $\eta = \pi$  for weak bands on the linear part of the curve of growth. For bands on the square-root part,  $\eta = 2.87$ ; in the transition region  $\eta$  will be somewhat less (see Appendix). Since the spectrometer slit accepted roughly one-third of the planet's disc, these figures must all be slightly increased. Taken together, such considerations suggest a value for  $\eta$  of about 3 (a discussion of the curve of growth effects displayed by the  $CO_2$  bands is given below). With an average laboratory temperature of 297°K, we find that 150 m atm of  $CO_2$  are required in the laboratory optical path.

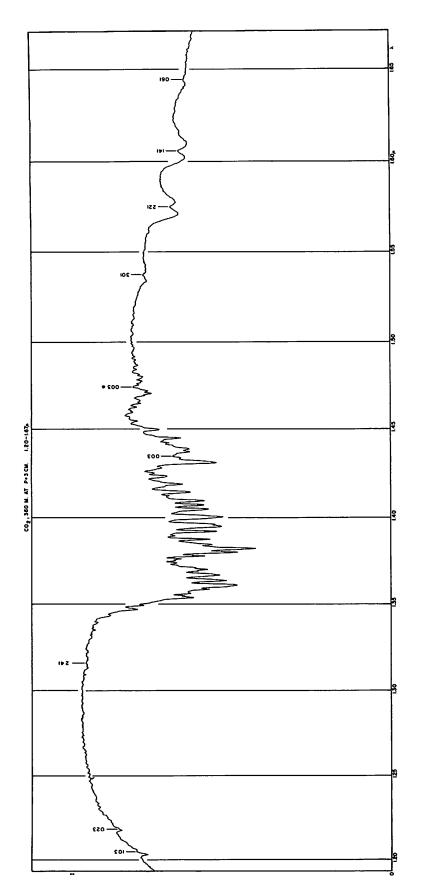
One may examine whether a verification of the total Martian CO<sub>2</sub> content could be obtained from the weaker bands of the 1.6  $\mu$  tetrad, at  $\lambda$  1.538 and 1.646  $\mu$ . Equivalent widths for the  $\lambda$  1.538 band were derived for a set of pathlengths and pressures in Comm. No. 31 (Table 6 and Fig. 23b). These are replotted against  $\log p$  (rather than  $\log wp$ ) in Figure 14, which is therefore directly comparable with Figure 11. The Martian band strength was obtained from the two upper curves of Figure 12, Comm. No. 31, and found to be 6.6  $\pm$  1Å (log EW = 0.82  $\pm$ 0.06). This value, with its present margin of uncertainty, is entered in Fig. 14. It is seen that for w < d14 m atm the bandstrength is little dependent on pressure but that already at the strength of the Martian band it is roughly proportional to  $p^{1/4}$ ; whereas at a given pressure EW increases approximately as  $w^{1/2}$ . Comparison of Figs. 14 and 11 indicates a CO<sub>2</sub> content consistent with that derived from the  $\lambda$  0.87  $\mu$  band though the accuracy of this determination is not good. The reasons are that the pressure effects  $(p^{1/4} \text{ and } p^{1/2})$  are not grossly different and that the EW values for weak bands measured as blends are



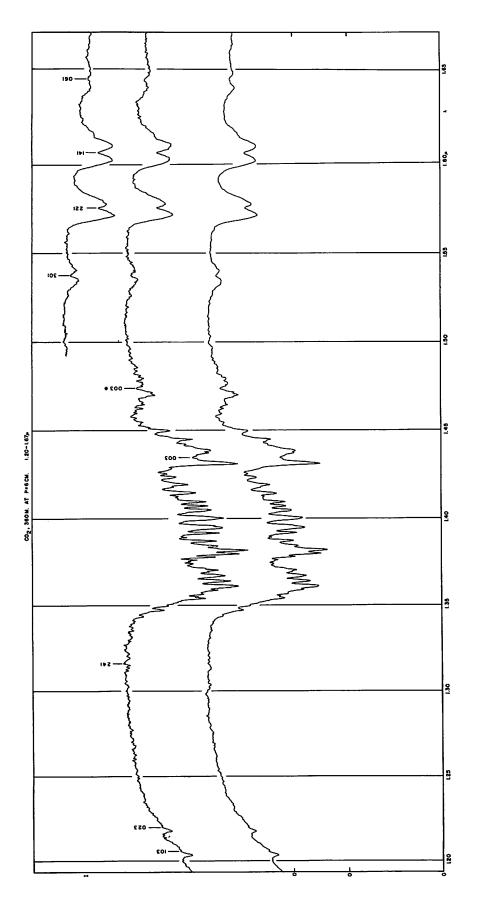




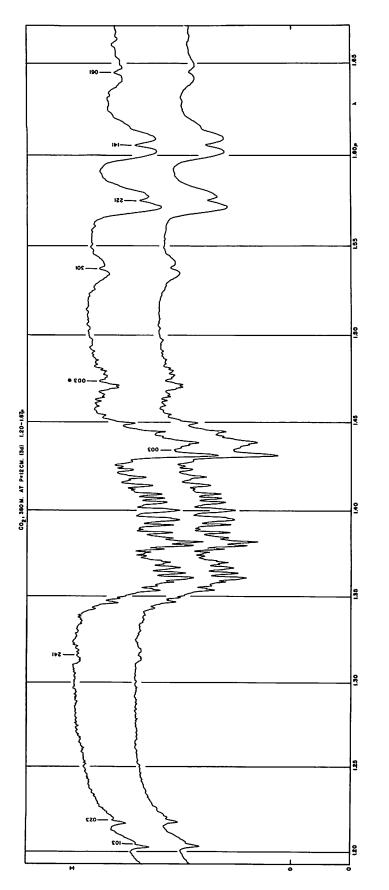


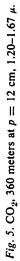












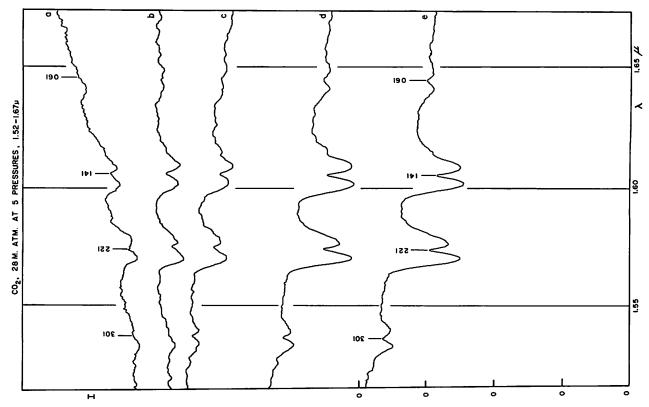


Fig. 6. Pure CO<sub>2</sub>, 1.6  $\mu$  bands for five combinations of pathlength and pressure having same total abundance; (a) 2880 m at 0.75 cm; (b) 1440 m at 1.5 cm; (c) 720 m at 3 cm; (d) 180 m at 12 cm; (e) 90 m at 24 cm. The 360 m at p = 6 cm trace is found in Fig. 4.

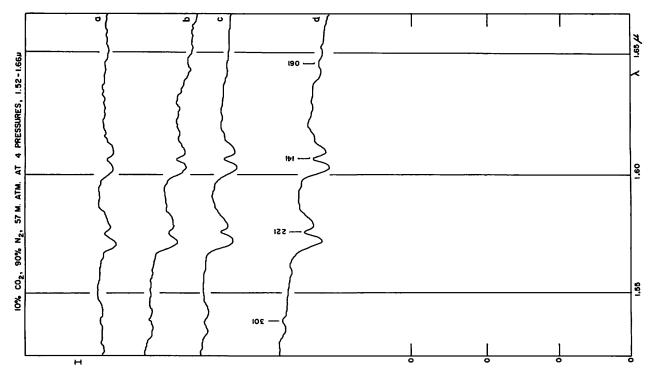


Fig. 7. Mixture of 10% CO<sub>2</sub>, 90% N<sub>2</sub>; (a) 1440 m at 3 cm; (b) 720 m at 6 cm; (c) 360 m at 12 cm; (d) 180 m at 24 cm.

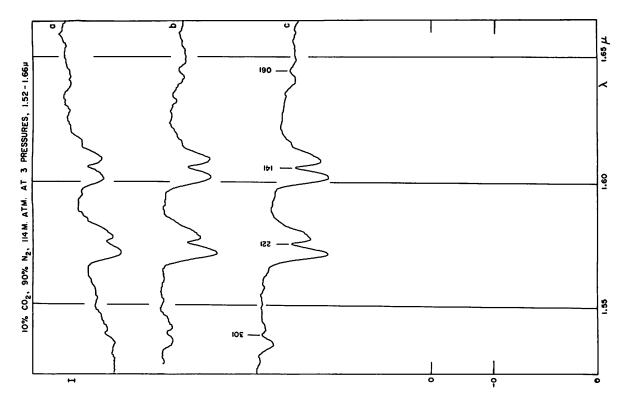


Fig. 8. Mixture as Fig. 7; (a) 1440 m at 6 cm; (b) 720 m at 12 cm; (c) 360 m at 24 cm.

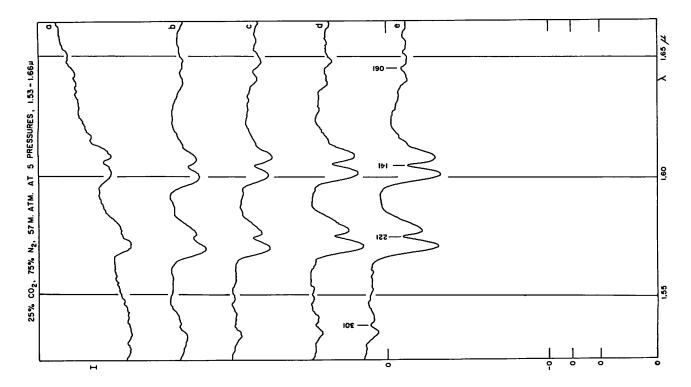


Fig. 9. Mixture 25% CO<sub>2</sub>, 75% N<sub>2</sub>; (a) 2880 m at 1.5 cm; (b) 1440 m at 3 cm; (c) 720 m at 6 cm; (d) 360 m at 12 cm; (e) 180 m at 24 cm.

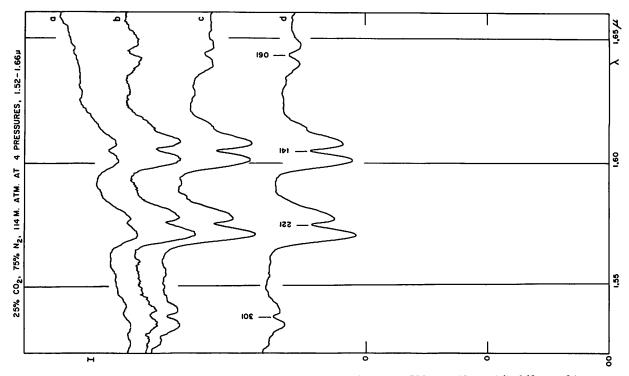


Fig. 10. Mixture as Fig. 9; (a), 2880 m at 3 cm; (b), 1440 m at 6 cm; (c), 720 m at 12 cm; (d), 360 m at 24 cm.

not precise. Weak bands for which the individual rotational lines can be observed must be used for a really good determination. This requires high-resolution spectra.

We have already noted the requirement that the pressure used in the laboratory must be consistent with the pressure exerted by a unit column of the laboratory gas mixture transferred to the surface of the planet. The appropriate relation is furnished by the Curtis-Godson approximation (Goody, 1964), which states that the mean pressure along the absorbing path in a planetary atmosphere is equal to one-half the surface pressure.

With these relationships established, the calibration is essentially defined. Using the amount of  $CO_2$ derived from the abundance analysis, one wishes to vary the pressure and the amount of the carrier gas (N<sub>2</sub>) until the equivalent width obtained is equal to that of the Martian absorptions. For a given  $CO_2/N_2$ mixture, and with the amount of  $CO_2$  fixed, only one pressure will provide a match. This pressure must then be one-half the pressure which a column of gas composed of the  $CO_2/N_2$  mixture would exert on the surface of the planet. If the pressures do not agree, then a different mixture must be used, etc. The principle of this method is straightforward but because of the very long pathlengths required, some extrapolation must still be made based on data obtained with smaller amounts of gas at higher pressures.

We have referred to Figs. 11-13, giving plots of log EW vs. pressure for three gas mixtures. The horizontal lines show the value of the Martian absorption, with the total absorption (Mars and Earth) added for reference in Fig. 11. The curves indicate the dependence of the equivalent width on the pressure for a given amount of gas. As one would expect, the equivalent width decreases with decreasing pressure, with the decrease becoming less pronounced as lower pressures are approached or smaller amounts of gas are used. For a given pressure, doubling the amount of gas results in an increase of about 0.15 in log EW, as shown in the upper part of Fig. 11; i.e., the bands are on the square-root part of the curve of growth. In the lower left of this plot the increase is less than 0.15, indicating that the bands fall in the transition region. In the lower right corner we see that the effect of increased pressure on small amounts of gas results in a removal of saturation, with a consequently slower increase in equivalent width with increasing pressure. This same general behavior is exhibited by the other graphs.

Knowing these relations it is then possible to extrapolate on the plots to the pathlength corresponding to the Martian  $CO_2$  abundance. This line is indicated on each figure by dots and labeled with the appropriate amount of gas. The intercepts of these lines with the horizontal line indicating the (in mb), effective air mass on Mars and amount of gas (in m atm). The ordinate is the same as that of the previous plots and the equivalent width of the Martian absorptions is again indicated by a horizontal line. Inspection of Fig. 15, which displays the data for pure  $CO_2$ , indicates that the relation

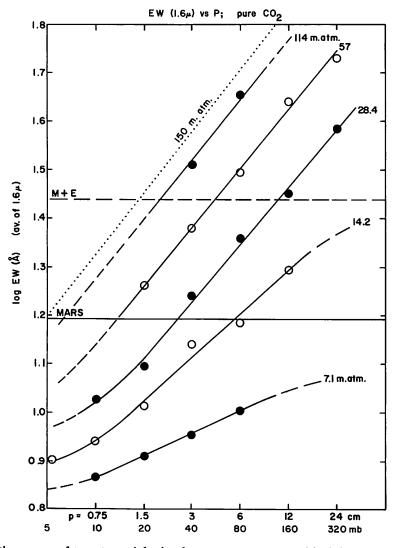


Fig. 11. Equivalent width, average of two strong 1.6  $\mu$  bands, vs. pressure, expressed both in cm Hg and mb, for pure CO<sub>2</sub>. Points representing same total abundance are connected by solid lines, with total abundance in meter-atmospheres indicated. Dotted line represents amount seen by spectrometer in Martian spectrum. Mars absorption indicated by horizontal line near log EW = 1.2. Higher dashed line Mars + telluric bands. Empirical pressure determined from diagram is approximately 5 mb (being half of surface pressure; see Fig. 18).

equivalent width of the Martian  $CO_2$  absorptions, correspond to the pressures necessary for these amounts of gas to produce absorptions of the required strength.

The second method of presenting the laboratory data is shown in Figs. 15, 16, and 17. Here the abscissa is the logarithm of the product of pressure between log EW and log  $\eta pw$  can be represented by the following equation:

$$\log EW = \frac{1}{2.32} \log \eta pw - 0.65$$
 (1)

This relation holds very well for pressures from 20-40 mb over a range of log EW from 1.0 to 1.5.

At lower pressures, there is a tendency for the line defined by Equation 1 to be approached asymptotically from the left as the amount of  $CO_2$  increases.

Fig. 11 shows that the effective pressure associated with the Martian equivalent width must be less than 10 mb. Thus the intercept with the line repre-

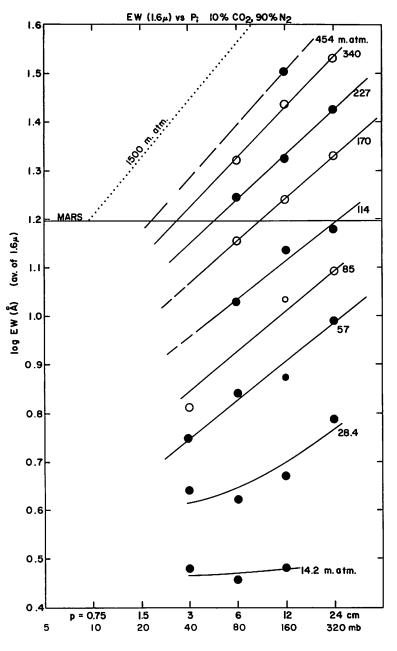


Fig. 12. As Fig. 11, for 10% CO<sub>2</sub>, 90% N<sub>2</sub>.

At higher pressures it is approached from the right. The factor multiplying log  $\eta pw$  is slightly smaller than  $\frac{1}{2}$ , suggesting that in this range of p and wthe bands fall in the transition region of the curve of growth. This is in agreement with the conclusions derived from Fig. 11. senting the Martian absorptions on Fig. 15 defines an upper limit to the effective pressure since it is essentially defined by the observations at 20 and 40 mb. With w = 150 m atm we find p (emp) = 5.8 mb. A lower limit may be set by estimating where the intercept would fall at very low pressures. Fig. 15 indicates that the 10 mb curve will become asymptotic well before the intercept is reached. At much lower pressures it is probable that the intercept will be further to the left on the diagram, but a limit will be approached beyond which decreasing the pressure has no effect on the equivalent width since the it shows the other extreme case considered, the 10% CO<sub>2</sub> mixture. The curves drawn in the lower left corner of this plot are tentatively based on the appearance of Fig. 15, since there are insufficient data to allow a precise representation. The region of the intercept with the equivalent width of the Martian

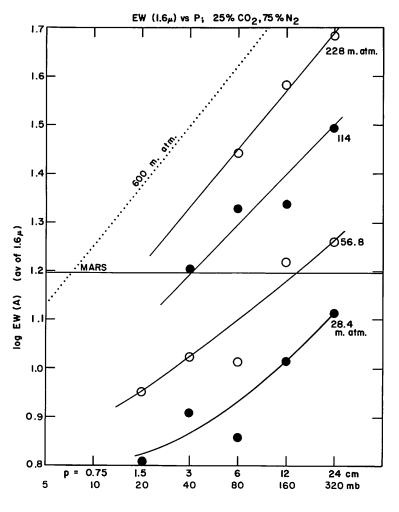


Fig. 13. As Fig. 11, for 25% CO<sub>2</sub>, 75% N<sub>2</sub>.

latter will be determined solely by Doppler broadening. This limit is difficult to define empirically since our data do not extend to low enough pressures. However, the lower left-hand corner of Fig. 15 shows that the curves, corresponding to the lowest pressures we were able to use, are beginning to crowd together indicating that the limit referred to above is being approached. This suggests an intercept no further to the left than about log  $\eta pw =$ 2.78 which corresponds to p (emp) = 4 mb.

Similar arguments may be applied to the other two figures. Fig. 16 is of particular interest since absorption is better defined and again indicates the crowding together of the lines as lower pressures are approached. The slopes of these lines are slightly *greater* than  $\frac{1}{2}$ , indicating that the bands are again in the transition region of the curve of growth, but closer to the linear part. Fig. 17 presents the intermediate case of the 25% CO<sub>2</sub> mixture.

As stated above, the pressures derived empirically from the equivalent widths (p emp) are equal to  $\frac{1}{2}$  the surface pressure. The upper and lower limits on the surface pressure, as deduced from Figs. 15-17, are given in Table 4. The calculated surface pressures for the three cases are also given in the table as p (cal). These values are presented graphically in Fig. 18.

The diagonal line in this illustration represents the locus of points for which the calculated and satisfy both the laboratory observations and the constraint imposed by the Martian gravitational field. Since the lower limits are deliberately somewhat conservative, a value of  $17 \pm 3$  (p.e.) is regarded representative of this determination. The medial

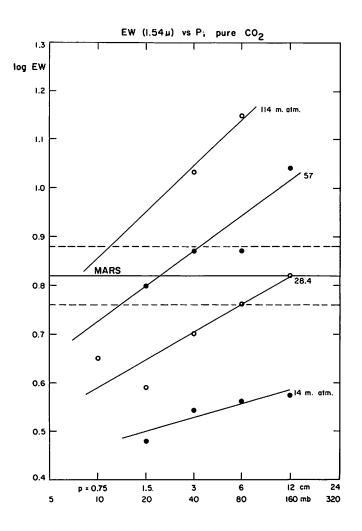


Fig. 14. As Fig. 11, pure CO<sub>2</sub>, but for 1.54 µ CO<sub>2</sub> band. Dashed horizontal lines delimit area of uncertainty of Mars absorption.

empirically determined pressures are equal. Thus the intersection of the diagonal with the region de-

TABLE 4 Calculated and Empirical Pressures of Mixtures of CO $_2$  at the Surface of Mars

		p (emp)		
% CO,	p (cal)	LOWER LIMIT	UPPER LIMIT	
100	3.5	8.0	17.6	
25	10.1	10.5	17.6	
10	23.4	13.2	22.2	

fined by the upper and lower limits derived for each gas mixture yields the range of pressures which

dashed line in Fig. 18 corresponds to the solutions defined by the dotted lines in Figs. 11-13.

The interpretation of this result may be expressed in the following way: A pure CO<sub>2</sub> atmosphere consisting of the known amount of gas would not exert a high-enough surface pressure to produce the amount of broadening required to match the observed Martian equivalent width. On the other hand, a 10% CO<sub>2</sub> atmosphere would be too massive. For a surface pressure of 17 mb the fraction of CO<sub>2</sub> in a predominantly nitrogen atmosphere is 0.14, or the mixing ratio N<sub>2</sub>/CO<sub>2</sub> = 6/1. Up to this point, we have assumed that the broadening of the  $CO_2$  bands is due primarily to  $N_2$ . Another gas likely to be present in the Martian atmosphere is radiogenic argon (see discussion below). It is thus of interest to investigate the effects

+ Ar, p = 6 cm. Reference to Fig. 11 indicates that for pure CO<sub>2</sub> at p = 3 cm, log EW = 1.38, indicating good reproducibility of the data. Fig. 13 shows that for 228 m atm of a 25% CO<sub>2</sub>/N<sub>2</sub> mixture (i.e., 57 m atm of CO<sub>2</sub>) at p = 6 cm, log EW =

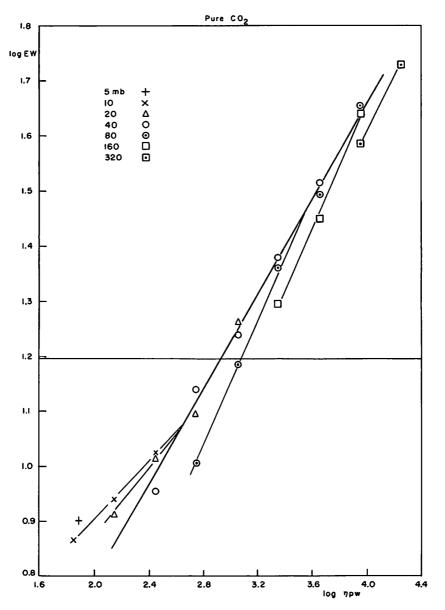


Fig. 15. Data of Fig. 11 presented with log  $\eta pw$  as abscissa instead of log p.

of broadening induced by this gas. With this in mind, laboratory tracings were obtained of 57 m atm of CO<sub>2</sub> at a pressure of 3 cm. Argon was then added to produce a total pressure of 6 cm. The two values of log EW obtained from the 1.6  $\mu$  bands were 1.38 for pure CO<sub>2</sub>, p = 3 cm and 1.44 for CO<sub>2</sub>

1.45. In other words, the effect of broadening by Ar appears to be essentially the same as that produced by N<sub>2</sub>, at least in this range of pressure. Therefore, the N<sub>2</sub>/CO<sub>2</sub> ratio derived above may be regarded as actually representing the  $(N_2 + Ar)/CO_2$  ratio, with the ratio Ar/N<sub>2</sub> left undetermined.

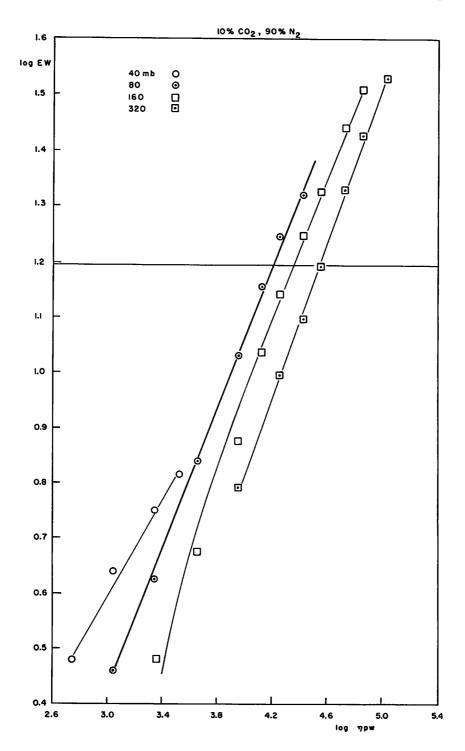


Fig. 16. Data of Fig. 12 presented with  $\log \eta pw$  as abscissa instead of  $\log p$ .

The surface pressure can also be determined directly from the equivalent widths of the Martian and telluric 1.6  $\mu$  bands. This method was applied by Kaplan, Münch, and Spinrad (1964) to the stronger band at 2.06  $\mu$ . As we have seen from the discussion of the laboratory data,

$$W \sim (\eta p w)^n, \tag{2}$$

where the exponent can in principle be determined empirically. One can thus write:

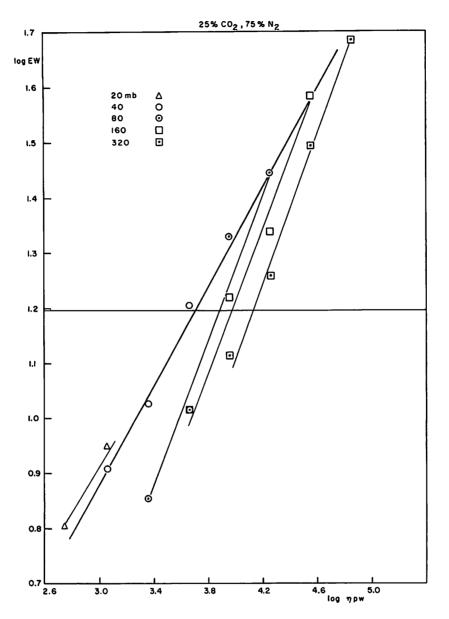


Fig. 17. Data of Fig. 13 presented with  $\log \eta pw$  as abscissa instead of  $\log p$ .

$$P_{M} = \frac{\eta_{E} P_{E} w_{E} W_{E}}{\eta_{M} w_{M} W_{M}}$$
(3)

where  $n_M$  and  $n_E$  represent the appropriate exponents for the Martian and telluric bands, respectively. The laboratory data indicate a value for  $1/n_M$  of ~ 1.5; we shall assume  $n_M = n_E$  for this discussion. The equivalent widths of the Martian and telluric 1.6  $\mu$  bands are given in *Comm.* 31.

With  $p_E \approx 800$  mb,  $\eta_E = 1.05$ , and  $w_E \approx 2.1$  m atm, we find  $p_M = 18$  mb. This pressure must be corrected for the difference in pressure broadening induced in a N<sub>2</sub>/CO<sub>2</sub> mixture where dilution by N<sub>2</sub> is not infinite. This leads to the lower value of p = 15 mb, in good agreement with the laboratory determination. If  $1/n_M = 1/n_E = 2$ , this figure is increased to 16 mb.

The most important source of error associated with these determinations is the uncertainty in the Martian CO<sub>2</sub> abundance. If w = 60 m atm, the

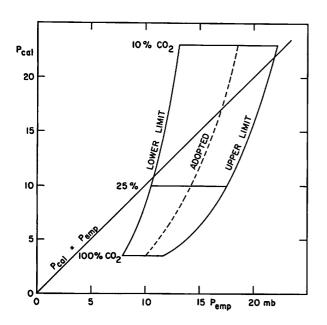


Fig. 18. Calculated pressures at Martian surface (based on weight of gas column) vs. pressures determined empirically from 1.6  $\mu$  bands, for 3 gas mixtures. Dashed median line represents adopted solution; intersect with diagonal gives derived pressure of Martian atmosphere,  $17 \pm 3$  mb.

pressure determined from the laboratory measures is reduced to 15 mb with a concomitant decrease in the amount of N<sub>2</sub>. Conversely, a reduction of the amount of CO<sub>2</sub> leads to an increase in the surface pressure and N<sub>2</sub> content. Including the uncertainty in the air mass, we find the results of the two approaches to the determination of the surface pressure can be summarized as:

$$p_{\rm emp} = 17 \pm 3 \text{ mb} (p.e.).$$

The difference between 17 and  $25 \pm 15$  mb, obtained by Kaplan, Münch and Spinrad (1964), probably results from the fact that the 25 mb determination was made from observations of the strong bands near 2  $\mu$  where both the Martian and telluric components are saturated. The two components were not well separated by the Doppler shift and there is the additional possibility of contamination due to telluric water vapor, problems which were not encountered at 1.6  $\mu$ .

### 4. The Argon and Oxygen Contents

The Martian argon content will have an origin similar to that of the terrestrial atmosphere: be overwhelmingly composed of radiogenic  $Ar^{40}$  exhaled from the crust. The amount per cm<sup>2</sup> of surface present might therefore be as great as on the Earth *if*  the enrichment of the surface layer in potassium had been the same and *if* the degassing of radiogenic argon had been equally efficient. Both assumptions are likely to be very extreme for a planet having a mass of only 10% of the Earth. The gross upper limit so obtained would cause a weight of the column of Ar on Mars of  $9.3 \times (40/29) \times 0.38$  mb = 4.8 mb, 0.93 being the volume percentage of argon in the terrestrial atmosphere.

A fairly realistic value might be found by the assumption that the crustal exhalation process leading eventually to the formation of atmospheric N<sub>2</sub> would have had similar efficiency relative to the Earth as that of argon, although, admittedly, this involves an assumption about the time sequences of these events. Then one finds that the  $Ar/N_2$  ratios on the two planets will not be grossly different, or both roughly 1.2% by volume. The fractional volume of Ar in the Mars atmosphere will then be about  $0.012 \times 0.86 = 0.010$  (one per cent); and the weight of the column 0.23 mb,  $20 \times \text{less than}$ the gross upper limit mentioned above. (The ratio 20 represents, of course, essentially the abundance ratio of the two atmospheres, N<sub>2</sub> being the chief constituent of both).

On the basis of a diagram by Paetzold (1963), relating the computed Martian  $O_3$  content to the assumed fractional  $O_2$  content, and the limit of  $O_3$ established by Kuiper (1952), the upper limit to the fractional  $O_2$  content is found to be 0.0002.

Including the upper limits for several gases derived before (Kuiper, 1952 and *Comm.* No. 31), and Mr. Marshall's result in *Comm.* No. 35, we find the preliminary composition model of the Mars atmosphere listed in Table 5.

Acknowledgments. We are indebted to Government agencies which have made this research possible. The program in planetary spectroscopy at this Laboratory has been supported by NASA through Grants NsG 61-161 and NsG 223-61. Mr. Owen's contributions have been assisted by ONR Grants Nonr (G)-00050-62 and ONR G-00014-64.

### APPENDIX

#### Air Mass

The equivalent width of a band will be proportional to  $(\eta pw)^n$  where  $\eta$  is the air mass, p is the effective pressure, w is the amount of absorbing gas in a unit column, and n has a value between 0 and 1. The effective air mass  $\eta$ , which gives a measure of the amount of gas contributing to the absorption, is

Gas	ABUNDANCE (cm, NPT)	VOLUME Fraction	Gas	ABUNDANCE (cm, NPT)
N <sub>2</sub>	30000	0.85	COS	< 0.2
CÔ <sub>3</sub>	5000	0.14	CH"O	< 0.3
Ar	400	0.01	N₀Õ	< 0.08
Н <sub>2</sub> О	1.		NÕ	<20.
0 <sub>2</sub>	< 0.05		NO,,	< 0.0008
O	< 7.		H <sub>2</sub> S	< 7.5
SÕ,	< 0.003		СЙ,	< 0.4
co <sup>2</sup>	< 1.		NH,	< 0.1

 TABLE 5

 Preliminary Composition Model of Martian Atmosphere

obtained by averaging sec<sup>n</sup>  $\theta$  over the equatorial strip of the planet which was accepted by the slit of the spectrometer.

$$\eta^{n} = \frac{\int_{0}^{\pi/2} \sec^{n} \theta \cos \theta \, d\theta}{\int_{0}^{\pi/2} \cos \theta \, d\theta} = \int_{0}^{\pi/2} \cos^{1-n} \theta \, d\theta.$$

This integral may be expressed in gamma functions:

$$\eta^{n} = \frac{\sqrt{\pi}}{2} \frac{\Gamma\left(1 - \frac{n}{2}\right)}{\Gamma\left(\frac{3 - n}{2}\right)} = \frac{\sqrt{\pi}}{2} \frac{1}{\left(1 - \frac{n}{2}\right)} \frac{\Gamma\left(2 - \frac{n}{2}\right)}{\Gamma\left(\frac{3 - n}{2}\right)}$$
$$\eta = 2 \left[\frac{\sqrt{\pi}}{2 - n} \frac{\Gamma\left(\frac{4 - n}{2}\right)}{\Gamma\left(\frac{3 - n}{2}\right)}\right]^{\frac{1}{n}}$$

Values for  $\eta$  for several values of *n* are given in the accompanying table:

n	1/n	η
1.00	1.00	3.14
.80	1.25	3.00
.75	1.33	2.99
.67	1.50	2.96
.50	2.00	2.87
.40	2.50	2.84
.33	3.00	2.82
.25	4.00	2.81
.20	5.00	2.78
.10	10.00	2.74
0.02	50.00	2.21

The exponent depends on the position of the band on the curve of growth. In the case of an isolated line, the curve of growth has three principal regions: the linear part (n = 1, weak lines); the transition region  $(n \sim 0, \text{ saturation just beginning})$ and the square-root part  $(n = \frac{1}{2}, \text{ strong lines})$ . For an unresolved band, an average is taken over weak and strong lines and one must also contend with effects due to overlapping. Summing over weak and strong lines will simulate adding curves of growth for different amounts of gas: the linear part merges into a region where the slope n is between 1 and 0 but closer to 1, while the lower section of the square-root part will approach a slope between  $\frac{1}{2}$  and 0. The transition zone will thus be extended into a region of gradually-changing slope. The effect of overlapping will be most noticeable for the strongest lines where it will lead to a "rounding off" of the square-root region with increases in the amount of gas having less effect on the equivalent width.

## REFERENCES

- Goody, R. M. 1964, Atmospheric Radiation I, Theoretical Basis (Oxford: Clarendon).
- Kaplan, L. D., Münch, G., and Spinrad, H., 1964, *Ap. J.*, 139, 1.
- Kuiper, G. P. 1952, *The Atmospheres of the Earth* and Planets, ed. G. P. Kuiper (Chicago: University of Chicago Press), p. 374, Table 9.
- Paetzold, H. K. 1963, La Physique des Planètes, (Liège) Chap. 44, p. 452.