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IN THE ATMOSPHERE OF MARS?

By George P. Wood
Langley Research Center

August 1974

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SUMMARY

In view of the possible finding of several tens percent of inert gas in the atmosphere of Mars by an instrument on the descent module of the USSR's Mars 6 spacecraft, the likelihood of the correctness of this result is examined. The basis for the well-known fact that the most likely candidate is radiogenic argon is described. It is shown that, for the two important methods of investigating the atmosphere, earth-based CO_2 infrared absorption spectroscopy and S-band occultation, within the estimated 1σ uncertainties of these methods 20% argon can be accommodated. Within the estimated 3σ uncertainties, more than 35% is possible. It is also stated that even with 35% argon the maximum value of heat transfer rate on the Viking 75 entry vehicle does not exceed the design value.

INTRODUCTION

One of the results of the USSR's Mars 6 mission was that an inert gas, previously unobserved, might be a major constituent of the atmosphere of Mars. In fact, it was reported by Tass, quoting V. Moroz in Izvestia, March 25, 1974, that argon might comprise several tens percent of the atmosphere: "Among the instruments carried by the descent module of 'Mars-6' was one that indicated that the planet's atmosphere contains several tens percent of some inert gas which, most probably, is argon."

To try to appraise the likelihood of the presence of this much inert gas is the primary purpose of the present paper.

SYMBOLS

B	relative effectiveness for broadening
k	Boltzmann constant
$\bar{M}$	average molecular mass
n	number density
N_s	molecular (atomic) refractivity at surface
p	pressure
p_e	effective pressure for broadening
p_s	pressure at surface
T	temperature
w	abundance of CO_2
σ	standard deviation

CHOICE OF INERT GAS

We consider which one of several inert gases might constitute several tens percent of the atmosphere; namely, N_2, He, Kr, Xe, Ar, Ne.

The possibility of N_2 as a major constituent can be disregarded. Reference 1 states that as little as 1% would have been detected by the ultraviolet spectrometers on Mariners 6 and 7, although reference 2 subsequently indicated that N_2 might have constituted as much as 5% of the atmosphere without having been detected.

Helium atoms have such a small mass that they could not remain in the lower atmosphere as a major component, but could constitute a large fraction only above the base of the exosphere (ref. 3).

Kr and Xe definitely would not be expected to be present. Their cosmic abundances are less than that of H by a factor of about 10^9 and less than that of Ar by a factor of about 10^4. If either had been present in any appreciable amount, it would have been detected by the ultraviolet spectrometers on Mariners 6, 7, and 9. The resonant, fluorescent wavelengths for these elements are 123.6 and 147.0 nm, respectively, and the LiF windows on the spectrometers would have passed these wavelengths.

The fluorescent ultraviolet wavelength of neon is too short, 73.6 nm, to be observed by the spectrometers on the Mariners. Neon is a relatively very abundant element in the universe, approximately the fifth most abundant. It is, cosmically, somewhat less than 100 times as abundant as ^{36}Ar. (In the Earth's atmosphere neon is about 50% as abundant as ^{36}Ar, which in turn is only about 0.3% as abundant as ^{40}Ar.) In the Earth's atmosphere Ne constitutes only 0.002% by volume. Owen points out (ref. 4) that, if Fanale's reconstructed history of Martian volatiles (ref. 5) is correct, then the present amount of neon in the atmosphere of Mars should be comparable to the column density of neon in the Earth's atmosphere; thus, an abundance of 0.2% might be expected. Thus, one feels justified in concluding that it is extremely unlikely that neon would be a major constituent in the atmosphere of Mars.

The amount of argon in the atmosphere of Mars can be estimated in several different ways, a number of which have been reviewed by Owen. (Fluorescence of argon in sunlight was not observed by the spectrometers on Mariners 6, 7, or 9. Whether the LiF windows could transmit at that wavelength, 104.8 nm, is not known.) Under the assumption of the "early rich" atmosphere of Fanale, Owen deduces (ref. 4) that "The value of $^{40}Ar/^{36}Ar$ should be much smaller than in our atmosphere since very little radiogenic ^{40}Ar would have been available during early outgassing, owing to the relatively long half-life of ^{40}K (1.4 AE)." Owen also states that "if the late-lean model [attributed to B. C. Murray] is correct and the entire atmosphere was produced recently, we would expect the $^{40}Ar/^{36}Ar$...ratio to be more nearly equal to telluric values." For this model, then, Owen derived in reference 6 a value of about 0.04%. Another model, the episodic, was described by Owen (ref. 6) as possibly providing up to 7-1/2% ^{40}Ar. Another way of estimating the abundance of ^{40}Ar, based on the assumption of 1000 mb of CO_2 trapped at the poles, gives approximately 0.33 mb of ^{40}Ar (Owen, ref. 7). Another method described by Owen (ref. 4) is: "If an 'inner' planet has differentiated to the same extent as the Earth, so that the surface potassium content is the same and a process exists for releasing gas into the atmosphere, then the atmospheric ^{40}Ar abundance per cm^2 of surface area should be the same on that planet as on the Earth.... A terrestrial column density of argon would have a surface pressure of about 5 mb on Mars...." The present author believes, however, that this last method should be modified in the following manner. The column density of radiogenic argon may be scaled proportionally to the planetary mass and inversely as the planetary surface area. The column density on Earth is 1.93×10^{23} cm^{-2}; the ratio of radii, Mars to Earth, is 0.53; the ratio of densities is 0.72. Thus, the column density of ^{40}Ar is calculated to be 7.4×10^{22} cm^{-2}. The corresponding surface pressure is 1.8 mb, or about 1/3 of the total.

Until the degree of differentiation of the planet is better known than at present, one can hardly predict which, if any, of the above estimates of argon abundance is correct.

THE DATA ON CO_2

The two primary methods of determining the surface pressure on Mars are S-band occultation and earth-based infrared CO_2 absorption spectroscopy. From the former we have the result for the equatorial zone on Mars (which we arbitrarily define as lying between 30°N latitude and 30° S), 5.0 mb (ref. 8). (In the Mars Engineering Model, in the interest of conservatism, we used our average of the measurements in the equatorial zone, 4.8 mb, because it was lower.) From the other method we have the result for the entire disk, 5.2 mb (ref. 9). Although the small difference between the two results does not need explaining, one possible simple explanation of it is as follows. The result from spectroscopy stems principally from observations made at the time of the 1967 opposition, when the subearth point was at about 22° north latitude. The topography of Mars is such that, very likely, a thicker average atmosphere is viewed when the latitude of the center of the whole disk is 22° N than when the center is on the equator. Thus the slightly larger value could result from this fact.

The spectroscopy of strong bands results in measurements of the equivalent widths of the lines. These in turn depend on the product of air mass (which we choose to be 3.5), abundance w, and effective pressure for broadening of the lines p_e. (The effective pressure for broadening is the sum of the products of the pressure p_i of each constituent and its effectiveness B_i, relative to that of nitrogen, for broadening the lines of the strong bands of CO_2, $p_e = \sum_i p_i B_i$.) We adopt as the best value of wp_e, derived from the basic quantity (equivalent widths) measured by the spectroscopy of strong bands of CO_2, the value wp_e = 420 m-atm mb. Our review and evaluation of references 9 to 11 leads to a value of 450 for the entire disk. We have reduced this to 420 for the equatorial zone.

The basic quantity measured by the occultation experiment is refractivity. Although the average value of refractivity at the surface for the measurements made in the equatorial zone by Mariner 9 was not reported, it is easily obtained from the pressure and temperature as $N_s = 3.1$.

We assume that the value of the basic quantity measured by infrared spectroscopy is established, and we also assume that the value of the basic quantity measured by S-band occultation is established. We assume, after evaluating the pertinent reports, that the 1σ uncertainty in wp_e is 20% and in refractivity is 10%. We thus have a self-consistent set of values:

$wp_e = 420 \pm 80$ m-atm mb

$N_s = 3.1 \pm 0.3$

$p_s = 5.0 \pm 0.5$ mb

$w = 70 \pm 7$ m-atm

HOW WELL DOES ARGON FIT?

We now examine the consequences of holding constant each of these two basic observed quantities, wp_e and N_s, in turn while assuming some portion of argon in the atmosphere. (This process entails reducing the amount of CO_2 in order to keep the value of the observed quantity constant.) First we hold constant the value of wp_e at its best value and at the 1σ limits, we assume both 20% argon (by volume) and 35% argon and calculate and examine the resulting values of N_s, p_s, and w. Likewise, we hold constant the value of N_s at its best value and at the 1σ limits, we assume 20% and 35% argon and calculate and examine the resulting values of wp_e, p_s, and w. For these calculations we used a pressure-broadening effectiveness for CO_2 of 1.2 compared to 1.0 for the standard gas N_2, and for Ar an effectiveness of 0.78. For the refractivity per molecule (or per atom) at S-band frequency we used 1.84×10^{-17} for CO_2 and 1.03×10^{-17} for Ar. From the value of wp_e the other three quantities can be calculated, as there are four equations for four unknowns:

$$w = 13.9\ p_{CO_2}$$

$$p_e = 1.2\ p_{CO_2} + 0.78\ p_{Ar}$$

$$p_{Ar} = \frac{40}{44} \frac{n_{Ar}}{n'_{CO_2}} p_{CO_2}$$

$$wp_e = \text{known}$$

We use a prime on CO_2 number density to indicate the value when argon is present.

Likewise, from the value of N_s the other three quantities can be obtained, but in a different manner. First one assumes a temperature. We used 215 K. (For a pressure of 5.0 mb, the number density of CO_2 is thus 1.7×10^{17} cm^{-3}.)

Since we are holding N constant,

$$N_s = N'_s = 1.84\ n_{CO_2} = 1.84\ n'_{CO_2} + 1.03\ n_{Ar}$$

or

$$n'_{CO_2} = \frac{n_{CO_2}}{1 + \frac{1.03}{1.84} \frac{n_{Ar}}{n'_{CO_2}}}$$

Also,

$$p_s = p_{CO_2} + p_{Ar}$$

$$= \left(\frac{44}{\bar{M}} n'_{CO_2} + \frac{40}{\bar{M}} n_{Ar} \right) kT$$

where

$$\overline{M} = \frac{44\ n'_{CO_2} + 40\ n_{Ar}}{n'_{CO_2} + n_{Ar}}$$

Then w, p_e, and wp_e follow from other equations given above.

The results of these calculations are shown in Tables I and II. In each table the group of values for 0% Ar shows the best values and the 1σ limits. The second column in each table contains the quantities that are held constant and the last three columns are the resulting values for the other quantities. Values that fit within the 1σ limits are indicated by boxes. Examination of the portions of Tables I and II that apply for 20% Ar shows no line for which all values are within the 1σ limits. Examination also shows that the values of the parameters in Table I would fall better within the limits for a value of wp_e slightly less than 420 m-atm mb and the values of the parameters in Table II would also fit better within the limits for a value of wp_e slightly greater than 380. Thus, the best fit with 20% argon under both conditions of constant wp_e and constant N_s is for the following self-consistent set of values:

$$wp_e = 390 \text{ m-atm mb}$$
$$N_s = 3.2$$
$$p_s = 5.5 \text{ mb}$$
$$w = 63 \text{ m-atm}$$

All values fit within the limits shown for 0% argon. The pressure, however, is at the upper limit and the abundance is at the lower limit. Postulating more than 20% argon would result in the pressure exceeding the upper limit and the abundance being less than the lower limit.

The least disagreement with available data, if the atmosphere cont ... 35% ^{40}Ar, appears to occur with the following self-consistent set of values:

wp_e = 375 m-atm mb

N_s = 3.3

p_s = 6.1 mb

w = 57 m-atm

p_{CO_2} = 4.1

p_{Ar} = 2.0

For this set of values, both wp_e and N_s are within their 1σ limits. Neither p_s nor w is within 1σ limits of uncertainty. This way of viewing the results is not, however, completely legitimate. The best values and the 1σ limits of p_s and w were derived from the measured values of wp_e by spectroscopy and of N_s by occultation and they were derived on the assumption that the atmosphere was 100% CO_2. If they had been derived from the same data but on the assumption that the atmosphere was 65% CO_2 and 35% ^{40}Ar, then the best value for the upper limit on p_s would have been larger than 5.5 mb and for the lower limit on w would have been smaller than 63 m-atm and thus they would have been more nearly matched by the values shown in the above group. It would thus be even easier to fit 35% Ar into the experimental results. It is, therefore, desirable to consider additional information on p_{CO_2} and w. This information is available from the spectroscopy of weak infrared bands. The lines in these bands are not appreciably broadened by pressure, so measurements of equivalent widths lead directly to abundance w and to pressure of CO_2. What are probably the four best sets of measurements on weak bands are reported in references 12 to 15. These all agree within reasonable limits; the average value for w is 68 ± 20 m-atm and for p_{CO_2} is 4.9 ± 1.4 mb. (These uncertainties can probably be considered to be approximately 3σ.) The values for w and p_{CO_2} shown in the preceding set of values for 35% Ar easily fit within these limits. Thus, one seems to be forced to the conclusion that the best data on the atmosphere derived from strong bands, from weak bands, and from occultations can accommodate at least as much as 35% argon in the atmosphere of Mars.

POSSIBLE EFFECT OF SEASONAL VARIATIONS IN PRESSURE

Another indication of whether argon is likely to be present in a major proportion is to compare the atmospheric pressure at the surface as reported from the Mars 6 mission and as given in reference 16. At the nominal landing site of the descent module of Mars 6, the expected pressure was 5.2 mb. Pravda, 17 March 1974, quotes Academician R. Z. Sagdeyev as stating that "According to preliminary estimates, the pressure at the landing area surface was approximately 6 millibars." It is natural to wonder whether the higher pressure might be due to the presence of Ar. There is, however, another possible explanation for the excess pressure. Reference 16 addresses the question of seasonal fluctuations in atmospheric pressure on Mars as determined from the occultation data of Mariner 9. It shows that at the season of the landing of Mars 6, southern autumn, the atmospheric pressure at the expected landing site might be expected to be higher by about 0.6 mb than at the season, southern summer, at which the pressure in the equatorial zone was measured by the occultation method by Mariner 9. If reference 16 is correct, then there is no need to invoke any large amount of argon in order to reconcile the two measurements of pressure.

ARGON IN THE MARS ENGINEERING MODEL

In editions of the Mars Engineering Model previous to the current one, which is M75-125-3, dated January 4, 1974, various amounts of argon were included in several of the model atmospheres. For some of the editions the inclusion of argon was done primarily to take into account the rather short-lived but not-to-be-ignored erroneous evaluation, current at that time, of some spectroscopic observations of the Martian atmosphere. For a subsequent edition, a considerable amount of additional data and also more accurate data were available. Since the accuracy of the measurements of CO_2 had been increased but they still could not account for all of the measured pressure as being due to CO_2, it remained necessary to assume the presence of some other constituent, and for this argon was chosen. (References 12 to 15, from comparisons of their results from weak bands with the then-existing results from strong bands, made various estimates of the percentage of CO_2. These generally lie somewhere in the range 50% to 100%.) For the current edition of the MEM, there were available further Earth-based observations and refined interpretations plus the voluminous results of the experiments on Mariner 9. The pressure at the mean surface level in the equatorial zone (30° N latitude to 30° S) was rather well established (thought to be within ±10%) at 4.8 mb if the atmosphere is 100% CO_2. This value was used for the Mean Model Atmosphere in the current edition. For the Maximum ρ_s Model Atmosphere, 25% additional pressure of CO_2, with no other constituent added, was used, making the surface pressure 6 mb in what was hoped and considered to be adequate coverage of all uncertainties with at least 2σ probability. Even if the atmosphere should contain as much as 35% argon, the pressure at the mean surface level very likely would not exceed 6 mb by more than a fraction of a millibar.

In order to determine whether the heating rate during entry of the Viking 75 lander would exceed the maximum design value if the atmosphere contained 20% or 35% argon, calculations of the rate were performed by John E. Nealy, Paul M. Siemers III, and Jim J. Jones, of the Langley Research Center. The calculations were made for the stagnation region on the heat shield, where the heating rate is greatest, and for the angle of entry, the lift-drag ratio, and the altitude for which the rate is greatest. The atmospheres containing argon resulted in only small increases in heating rate over the value for an all-CO_2 atmosphere. The rate did not exceed the design value.

RESUMÉ OF RESULTS

We have shown that if there is a major constituent in the atmosphere of Mars other than CO_2, it is very unlikely to be anything other than radiogenic Ar. Indeed, at the present stage of our ignorance about the evolutionary history of Mars, it does not strain credibility to postulate a history of differentiation similar to that of Earth and thus to arrive at an abundance of argon that would constitute about one third of the atmosphere.

We have also shown that the probable (1σ) uncertainties in the results of the CO_2 infrared absorption method for strong and for weak bands and of the occultation method can accommodate up to 20% argon. It seems to be fortunate that as more and more argon (up to 20%) is assumed to be present, one method approaches a limit, set by the uncertainties, from below and the other approaches a limit from above. Thus, the range of probable values is narrowed.

We have also shown that the data can accommodate argon of 35% or more within the 3σ uncertainties.

We have shown that 35% argon will not cause the maximum rate of heating to the Viking spacecraft during entry to exceed the design value.

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TABLE I.- Atmospheric parameters as function of wp_e*

% Ar	wp_e m-atm mb	N_s	p_s mb	w m-atm
0	340	2.8	4.5	63
0	420	3.1	5.0	70
0	500	3.4	5.5	77
20	340	3.0	5.2	58
20	420	3.3	5.8	65
20	500	3.6	6.3	71
35	340	3.1	5.8	54
35	420	3.5	6.6	61
35	500	3.9	7.1	67

TABLE II.- Atmospheric parameters as function of N_s*

	N_s	wp_e m-atm mb	p_s mb	w m-atm
0	2.8	340	4.5	63
0	3.1	420	5.0	70
0	3.4	500	5.5	77
20	2.8	310	5.0	55
20	3.1	380	5.5	61
20	3.4	460	6.0	67
35	2.8	280	5.4	50
35	3.1	350	5.9	55
35	3.4	400	6.4	59

*Boxes enclose values that are within 1σ limits of uncertainty.