

The Upper Atmosphere of Venus: A Review

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ABSTRACT

The implications of recent data on Venus obtained by Mariner 5, Venera 4 and ground based observations for the aeronomy of Venus is received. The theoretical thermal structure model of McElroy based on a pure CO₂ atmosphere is in good agreement with the temperature deduced from the hydrogen distribution obtained by Mariner 5. No credible mechanism has been devised to recombine CO and O to CO₂ in the upper atmosphere. It is suggested that O₂ is formed but that CO and O₂ recombine to CO₂ in the dense atmosphere far enough above the cloud tops to agree with abundance measurements. Serious difficulties exist for the H₂ model of the upper atmosphere. It is suggested that deuterium can account for the anomalous Lyman α glow observed by Mariner 5 without implying a large D/H planetary ratio. Other problems such as the maintenance of the ionosphere at night and the escape of water are discussed.

1. Introduction

The atmospheric composition experiments performed on the Soviet spacecraft Venera 4 (Vinogradov *et al.*, 1968), and the measurements of temperature, pressure and density made on Venera 4 (Avduevsky *et al.*, 1968) and Mariner 5 (Kliore *et al.*, 1967) indicate that the Cytherian atmosphere is composed of at least 90% CO₂. The implications of these results for the thermal structure of the atmosphere above the cloud tops has been examined by McElroy (1968). He has evaluated the heating by ultraviolet and infrared absorption as a function of altitude along with the cooling by thermal conduction and infrared radiation by CO₂ to determine the profiles of temperature and atmospheric density. His calculations show that the heat produced by ionization and photodissociation should be conducted down a temperature gradient to a mesosphere about 50 km above the tops of the clouds. Here the infrared radiation from vibrationally excited CO₂ molecules becomes an important source of heat loss. The thermopause temperature, according to his calculation, should lie between 620 and 700K.

McElroy's thermal model accords with the determination of the exospheric temperature determined from the distribution of exospheric hydrogen made by the Lyman α experiment (Barth *et al.*, 1967) on Mariner 5. The variation of Lyman α emission rate with distance beginning about 9000 km from the center of the planet on the dayside indicates that the density of hydrogen is about 7% as large as it is at comparable distances above the earth and follows the distribution expected for a 650K exosphere (Barth *et al.*, 1968).

2. The recombination of CO and O

On Venus as on Mars the discovery that the atmosphere consists predominantly of CO₂ creates an in-

teresting problem in aeronomy. The question arises as to why the oxygen in the atmospheres of these planets is in the form of CO₂ whereas it exists primarily as O₂ on earth. The escape of hydrogen can explain why all three planets have developed oxidizing atmospheres. Furthermore, the presence of large amounts of liquid water on earth affords a mechanism that explains the low level of CO₂ in the atmosphere of earth. (Why Venus and Mars should be relatively so poor in water is another problem, and I shall return to that question later.) Great amounts of CO₂ are locked in the oceans, in carbonates layered down as sediments or converted to O₂ through green plant photosynthesis on earth, and all of these processes depend on the presence of liquid water on the surface. But even in the absence of this sink for carbon on the surface of the other two planets, there remains a problem in explaining why the CO₂ in their atmospheres has not been converted to O₂ and CO.

CO₂ in the presence of ultraviolet below 1700Å is dissociated into CO and O in the ¹D state. According to McElroy (1968), in the optically thin regions of Venus the rate of dissociation is given by

$$P(\text{O,CO}; z) = 2.2 \times 10^{-6} n(\text{CO}_2; z). \quad (1)$$

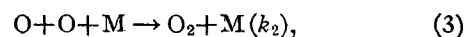
The recombination of CO and O(³P) is spin forbidden and proceeds very slowly. The most reliable value for the rate coefficient of



has been determined by Clyne and Thrush (1963) to be given by

$$k_1 < 8 \times 10^{-35} \text{ cm}^6 \text{ sec}^{-1} \text{ at } 300\text{K}.$$

In competition with this sluggish reaction is the formation of O₂ through



with

$$k_2 = 2.7 \times 10^{-33} \text{ cm}^6 \text{ sec}^{-1} \text{ at } 300\text{K}. \quad (4)$$

On Venus as on earth, even this recombination to O₂ is too slow to compete with the photoproduction *in situ*. The oxygen (and the CO) must be transported downward to recombine at levels below the production region. Times long compared to the 100-sec lifetime of O(¹D) are required and the 40-fold faster conversion of O to O₂ will surely overwhelm the recombination of O to CO₂. The equation of continuity for O is

$$\frac{d}{dz} -n(\text{O})w = 2.2 \times 10^{-6} n(\text{CO}_2) - L(z), \quad (5)$$

where *w* is the flow velocity and for the loss term *L*(*z*) I contemplate for the moment only that

$$L = k_1 n(\text{CO})n(\text{O})n(\text{CO}_2) + k_2 n(\text{O})n(\text{O})n(\text{CO}_2). \quad (6)$$

At the base of the production region *z*₀ where *n*(CO₂) is 2 × 10¹¹ cm⁻³, integration of the continuity equation requires

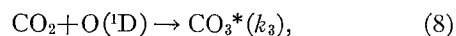
$$n(\text{O})w(z_0) \cong 2.2 \times 10^{11} \text{ cm}^{-2} \text{ sec}^{-1}, \quad (7)$$

where *w* should be of the order of 10 cm sec⁻¹ at this density level and therefore both the oxygen and CO densities should be of the order of 2 × 10¹⁰ cm⁻³. Even here the recombination rate is only about 0.25 cm⁻³ sec⁻¹ compared to an average production rate above of some 10⁵ cm⁻³ sec⁻¹, so the transport and density build-up must continue down to much lower altitudes before the oxygen will have recombined. There seems to be no simple way to prevent the accumulation of O₂ (and O₃) in the upper atmosphere. The molecular oxygen in turn should be transported downward by eddy diffusion and the atmosphere gradually converted to an O₂ rich one. Although the O₂ will shield the CO₂ from photodissociation because of the longer wavelength cut-off and much larger absorption coefficient in the Schumann-Runge continuum than in the CO₂ continuum, the CO₂ will inexorably continue to be transported upward into regions where it can dissociate and the process of conversion of CO₂ to O₂ and CO should continue.

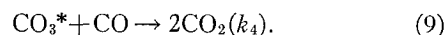
Obviously, the CO₂ atmosphere is reasonably stable. In the course of 4.5 × 10⁹ yr, half of them in sunlight, about 10²⁸ molecules cm⁻² of CO₂ would have been dissociated. The upper limit of the present CO₂ content of the atmosphere is about 5 × 10²⁷ molecules cm⁻². Thus, O₂ and CO₂ would be about equal in abundance if the atmosphere were initially pure CO₂ and recombination had yielded principally O₂. On the other hand, Belton *et al.* (1968) report that the concentration of O₂ < 2.5 parts in 10⁴ above the cloud tops. Two values, both low, have been reported for the CO concentration, one of 2.2 parts in 10⁴ (Benedict¹) and the other 5 in 10⁵

(Kuiper²). Unfortunately, the evidence is somewhat ambiguous with regard to atomic oxygen. The Venera 4 ultraviolet experiment of Kurt³ obtained a negative result on the night side of the terminator which is interpreted to set an upper limit to the atomic oxygen concentration at 10⁻⁸ times the terrestrial density at comparable altitudes. Because of the large light levels prevailing close to the bright limb, the Mariner 5 ultraviolet experiment has been analyzed for the OI resonance lines only beyond 6500 km—with negative results. There is a possibility that a weak (100 Rayleigh) 1304 Å glow was detected just beyond the terminator. On the other hand, a low resolution spectrum of Venus obtained in a sounding rocket experiment by Moos *et al.*⁴ had a bright feature near 1300 Å which might imply an average dayglow emission rate of Venus of about 5 kR in the resonance triplet. Such a large emission rate would demand an optically thick atomic oxygen atmosphere irrespective almost of the excitation mechanism. From resonance scattering of sunlight an optical depth of 10⁴ in oxygen (10¹⁷ atoms cm⁻²) would produce an average emission rate of only 2 kR. Even if it should be true that the atomic oxygen concentration in the Cytherian upper atmosphere reaches a level comparable to that on earth, the low concentration of O₂ and CO together with the overall stability of the CO₂ atmosphere would require that some mechanism exist to recombine the CO and O after the transport of these species downward. If the O₂ concentration is to be low at all altitudes, this recombination mechanism must be fast compared to that which recombines O to O₂. But if the atomic oxygen density also should be very small everywhere, a very fast recombination mechanism, presumably two-body in nature, would have to be found to recombine CO and O near the level where they are formed.

In the laboratory it has been observed repeatedly that the yield of O₂ from photolysis of CO₂ is not unity. Although it is not clear that wall effects are not involved, it has been suggested several times that a fast two-body like recombination of CO and O may occur at laboratory pressures involving the formation of a sufficiently long lasting complex CO₃ molecule from CO₂ and O(¹D). The scheme is



followed by



McElroy (1967, 1968) has proposed that these reactions provide the path for rapid recombination of CO₂ in the Martian and Cytherian upper atmospheres.

² Kuiper, G. P., 1968: Paper presented at the Second Arizona Conference on Planetary Atmospheres, Tucson, 11-13 March.

³ Reported by A. D. Kuzmin at the Second Arizona Conference on Planetary Atmospheres, Tucson, 11-13 March.

⁴ Moos, W., W. G. Fastie and M. Bottema, 1968: Paper presented at the Second Arizona Conference on Planetary Atmospheres, Tucson, 11-13 March.

¹ Benedict, W. S., 1968: Paper presented at the Second Arizona Conference on Planetary Atmospheres, Tucson, 11-13 March.

The efficient functioning of (8) and (9) would not only explain the low concentrations of CO and O₂ but would also prevent an accumulation of atomic oxygen.

Since the lifetime of O(¹D) is 100 sec, the first step must occur with a rate coefficient large enough to prevent the radiation of the red doublet in regions where the CO₂ density is of the order of 10¹¹ cm⁻³. Thus, there is a condition which sets a lower limit on k_3 , to wit,

$$\frac{1}{k_3 n(\text{CO}_2)} \leq 10^2 \text{ sec},$$

or

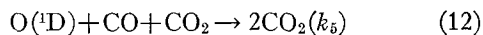
$$k_3 \geq 10^{-13} \text{ cm}^3 \text{ sec}^{-1}. \quad (10)$$

McElroy (1968) obtains the same requirement on k_3 by placing an upper limit on the abundance of O. The difficulty with this proposal is that the unstable CO₃* must endure for hundreds of seconds before it can encounter a CO molecule to complete the recombination process. Thus, even if $k_4 = 10^{-10}$ cm³ sec⁻¹,

$$\frac{1}{k_4 n(\text{CO})} = \frac{10^{10}}{n(\text{CO})}, \quad (11)$$

and even if we permit a hundred-fold increase in the relative CO abundance in the diffusion region above the overall planetary value of at most $5 \times 10^{-5} n(\text{CO}_2)$, the lifetime of CO₃* would need to be 20 sec.

Similarly, a three-body reaction

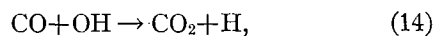


would have to occur with a rate constant large enough to prevent the decay of the ¹D term and this would demand a three-body rate coefficient satisfying

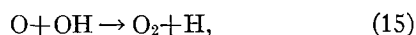
$$k_5 \geq 2 \times 10^{-22} \text{ cm}^6 \text{ sec}^{-1}. \quad (13)$$

An additional handicap for either of these schemes is that neither could tolerate competition from a large cross section for quenching of O(¹D) in collisions with CO₂. There is evidence that the interaction of O(¹D) with CO₂ is fast but that it results in quenching rather than reaction (Young *et al.*, 1968).

There have been proposals also that recombination of CO to CO₂ can proceed via the reaction



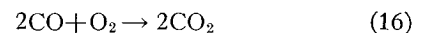
which has a measured rate constant of 2×10^{-8} cm³ sec⁻¹ at 300K (Reeves *et al.*⁵). It should be remarked, however, that unless the OH is formed from the atomic oxygen partner of CO in CO₂, the much faster reaction



with a rate constant of 5×10^{-11} cm³ sec⁻¹ which also must occur, will result in production of one O₂ molecule for each CO₂ dissociated. Thus, while this process

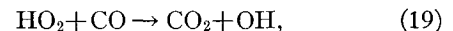
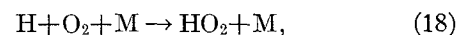
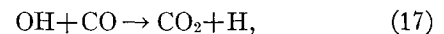
prevents the buildup of CO it does not prevent the growth of O₂. A very large concentration of OH is also required. However, a much more fundamental objection to this or any recombination scheme involving the liberation of atomic hydrogen in the upper atmosphere is that they involve a production of H at least equal to the CO₂ photodissociation rate, or 2×10^{11} atoms cm⁻² sec⁻¹. This is entirely incompatible with the hydrogen densities observed on Venus which will support a production rate of only 2×10^6 atoms cm⁻² sec⁻¹. To operate these schemes one must find channels for recombining hydrogen atoms (without liberating oxygen) at prodigious rates.

The problem of CO₂ recombination in the upper atmosphere is a difficult one whether it is supposed that the atomic oxygen density is very low or not. In the first case some very fast reactions are required that can effect the recombination in the region where the dissociation occurs. In the second case a process must be found which can recombine the O and CO after they are transported downward so rapidly that the mixing ratio of CO and O atoms in CO₂ above the cloud tops remains below 5×10^{-5} despite the fairly fast recombination of the O atoms to form O₂. Since neither of these alternatives has found the support of a reasonable mechanism, it may be necessary to examine the possibility that O₂ is formed in the region where the atmospheric density is about 10¹⁴ cm⁻³ and that the CO-O₂ mixture is carried downward by eddy mixing. In this case, somewhere above the 0.2-atm pressure level, the reaction



must take place with sufficient efficiency that the spectroscopic limits on CO and O₂ above the cloud tops are respected.

The reaction (16) is known to be slow in a pure atmosphere of CO₂, CO and O₂, but it is catalyzed readily by small concentrations of impurity. In particular, very low admixtures of water vapor lead to the chain



which amounts to (16) without the consumption of OH and H. Admittedly, it is going well beyond laboratory experience to ask that this chain be efficient enough to convert essentially all of the CO and O₂ to CO₂ in the presence of a large excess of CO₂ containing only 10⁻⁴% water vapor at a temperature of 230K. On the other hand, no alternative seems acceptable to the proposal that atomic oxygen is first converted into O₂ and that somewhere above the clouds CO and O₂ undergo some kind of catalyzed recombination to CO₂. To recombine the CO and O₂ at a rate of 2×10^{11} cm⁻² sec⁻¹ above the 10¹⁸ cm⁻³ level of CO₂, the effective three-body rate constant for (16) needs to be only 10⁻³⁷

⁵ Reeves, R. R., *et al.* 1965. Paper presented at the 150th Meeting of the American Chemical Society, Atlantic City, N. J.

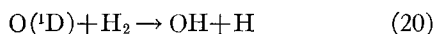
cm⁶ sec⁻¹ even if the O₂ and CO densities are only 10⁻⁵ times the CO₂ density. If the CO and O₂ densities are of the order of 10⁻² times the CO₂ density at this altitude, the effective rate constant must only be 10⁻⁴⁸ cm⁶ sec⁻¹.

3. Lyman α glow : H, H₂ and D

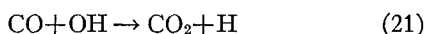
A very puzzling observation made by the ultra-violet experiment on Mariner 5 was the bright glow in the Lyman α channel between 6500 and 9000 km from the center of the planet. The fact that the scale height of this signal is about half that of the glow produced, apparently, by atomic hydrogen at 650K beyond 9000 km has given rise to two possible interpretations. One of these is that the glow is Lyman α produced by photodissociative excitation of H₂, another is that the glow is Lyman α resonantly scattered from deuterium (Barth, 1968).

Several serious aeronomic problems confront the H₂ model. To produce the observed light intensity some 10¹⁷ H₂ molecules cm⁻² are required above 6500 km and their density must be 10¹⁰ cm⁻³ at 6500 km. The photodissociative process creates 2.5×10¹⁰ H atoms cm⁻² sec⁻¹ above 6500 km. The atomic hydrogen distribution will support an escape flux of only 5×10⁵ cm⁻² sec⁻¹ in this H₂ atmosphere. There are, in fact, only about 3×10¹¹ H atoms cm⁻² above 6500 km or about 10 times the number being created from H₂ each second. Although the atoms produced by photodissociation are fast, they will travel only about 1 km before collision and will surely be thermalized before they escape or before they get far below 6500 km. Thus, they must diffuse at a velocity appropriate to a temperature of 650K. To transport the atoms downward to some unknown chemical sink below 6500 km rapidly enough for the low atomic hydrogen density to cope with the net production rate would require a velocity of at least 10 km sec⁻¹.

Furthermore, the reaction

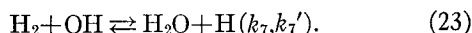
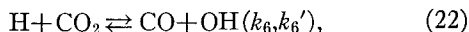


is very fast (2×10⁻¹⁰ cm³ sec⁻¹ according to Young *et al.*, 1968) and also produces hydrogen atoms. In the proposed H₂ atmosphere every O(^1D) created by CO₂ dissociation would react in about half a second with H₂. This leads to an additional production of H atoms equal to the CO₂ photodissociation rate of 2×10¹¹ cm⁻² sec⁻¹. This is an order of magnitude greater than even the overwhelming generation of H atoms from photodissociation of H₂. It is, on the other hand, a mark for this model that reaction (20) would produce copious quantities of OH and would be followed quickly by

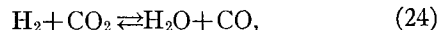


to complete the recombination of CO₂. Unfortunately, reaction (21) will also have produced another 2×10¹¹ H atoms cm⁻² sec⁻¹.

The mixture of H₂ and CO₂ is one which has received a great amount of attention from combustion chemists. In the presence of some dissociation of H₂ two reactions can occur, i.e.,



These reactions use OH and H as catalysts and amount to the reactions



which are called the water-gas reactions. The reaction rates (Schofield, 1967) are:

$$k_6 = 5 \times 10^{-10} \exp \left[\frac{-25.7}{RT} \right] \begin{cases} 10^{-28} \text{ cm}^3 \text{ sec}^{-1} \text{ at } 300\text{K} \\ 2.5 \times 10^{-17} \text{ cm}^3 \text{ sec}^{-1} \text{ at } 640\text{K} \end{cases} \quad (25)$$

$$k_6' = 1 \times 10^{-12} \exp \left[\frac{-1.0}{RT} \right] \quad (26)$$

$$k_7 = 10^{-10} \exp \left[\frac{-5.9}{RT} \right] \begin{cases} 4.5 \times 10^{-15} \text{ at } 300\text{K} \\ 10^{-12} \text{ at } 640\text{K} \end{cases} \quad (27)$$

$$k_7' = 3.0 \times 10^{-10} \exp \left[\frac{-20.6}{RT} \right] \quad (28)$$

From these rate coefficients we have the following values for the water-gas equilibrium constant:

$$K = \frac{n(H_2O)n(CO)}{n(H_2)n(CO_2)} \begin{cases} 2.7 \times 10^{-9} \text{ at } 200\text{K} \\ 10^{-5} \text{ at } 300\text{K} \\ 3.5 \times 10^{-2} \text{ at } 600\text{K} \end{cases} \quad (29)$$

Of course, the forward reaction (22) and the backward reaction (23) are both very slow at low temperature. Hence, in considering these reactions one must take care that the approach to equilibrium is not too slow. At the altitude where n(CO₂) is 10²⁰ cm⁻³ and the temperature is 300K, a time constant of about 10⁸ sec is indicated by reaction (22). Hence, since at higher altitudes both the densities and temperature are reduced, use of the equilibrium condition is safe only below the 10²⁰ cm⁻³ density level.

At that altitude if we take

$$n(CO) = 5 \times 10^{-5} n(CO_2), \quad (30)$$

and

$$n(H_2O) = 10^{-6} n(CO_2), \quad (31)$$

we find that

$$\frac{n(H_2)}{n(CO_2)} = 5 \times 10^{-6}. \quad (32)$$

Similarly, if at the Venera 4 surface

$$10^{-3} < n(H_2O) < 7 \times 10^{-3}, \quad (33)$$

we find

$$1.4 \times 10^{-6} < \left(\frac{n(\text{H}_2)}{n(\text{CO}_2)} \right) < 10^{-5}. \quad (34)$$

Hence, a mixing ratio for H_2 and CO_2 of the order of 5×10^{-6} is to be expected. Assume that this ratio prevails up to the "turbopause" where the H_2 density is of the order of 10^{10} cm^{-3} according to the H_2 model for Lyman α production. In that case the turbopause must occur where the CO_2 density is $2 \times 10^{15} \text{ cm}^{-3}$. If, as on earth, it does not occur until the $2 \times 10^{12} \text{ cm}^{-3}$ level is attained, the H_2 density could only be 10^7 cm^{-3} , some three orders less than the model needs.

Another serious problem created by this model relates to the thermal structure of the atmosphere. The solar spectrum shorter than 804 \AA will be absorbed in ionizing H_2 above 6500 km. The flux between 845 and 804 \AA will be absorbed there in dissociating H_2 . This leaves only a 50 \AA band available to ionize CO_2 at lower altitudes. In contrast with McElroy's pure CO_2 model, most of the ultraviolet heating occurs above 6500 km instead of between 6200 and 6300 km. This creates a large gap between the locus of ultraviolet heat input and the CO_2 radiation region. The temperature gradient must extend over a much larger domain and the exospheric temperature must be much greater than a pure CO_2 model would produce. Furthermore, H_2 is a significantly more effective partner of CO_2 in quenching vibrational excitation than CO_2 itself. One collision in every 400 between H_2 and CO_2 in the ν_2 vibrational mode results in a transfer of vibrational to translational energy, whereas 10^5 at 200K to 10^6 at 600K collisions between $\text{CO}_2(\nu_2)$ and CO_2 are required (Taylor and Bitterman, 1967).

A final difficulty for this atmosphere rich in H_2 will be to explain the ionospheric electron distribution observed by Mariner 5. Most of the ionization by solar ultraviolet will occur in the H_2 above 6500 km. In the region near 6195 km where the principal ionospheric peak occurs, only the ultraviolet between 850 and 900 \AA , and x rays are available to ionize CO_2 . The principal ion at high altitude, where there is a negligible amount of CO_2 , will be H_3^+ and at low altitude in the $\text{CO}_2\text{-H}_2$ mixture, it will be CO_2H^+ . It is difficult to see under these circumstances how the electron density at 6195 km could even be as large as 10^5 cm^{-3} or how a pronounced layer could develop there.

The alternative explanation for the rapidly varying Lyman α component between 6500 and 9000 km is that it is produced by deuterium whose density at 6500 km is about $6 \times 10^4 \text{ cm}^{-3}$ compared to a hydrogen density of about $5 \times 10^3 \text{ cm}^{-3}$. In this model the H and D densities are equal at about 9000 km. Although at first glance a 10:1 deuterium to hydrogen ratio about 500 km above the surface of Venus seems absurd, it is really not far from the expected ratio if the exospheric temperature is only 650K and the ratio of deuterium to hydrogen compounds in the mixing region is "normal"

(a few times 10^{-4}). It is the ratio of the escape fluxes near 500 km which is significant, for this must be the same as the photoproduction ratio below. In turn, this ratio will be equal to the ratio in density of deuterium and hydrogen compounds. The escape flux of deuterium is proportional to

$$\frac{n_2(R_c)}{\sqrt{H_2}} \left(1 + \frac{H_2}{R_c} \right) \exp \left[\frac{-R_c}{H_2} \right], \quad (35)$$

where R_c is the planetocentric distance to the base of the exosphere and H_2 is the deuterium scale height. Thus,

$$\left(\frac{n_2}{n_1} \right)_0 = \left(\frac{n_2}{n_1} \right)_{R_c} \left(\frac{H_1}{H_2} \right)^{\frac{1}{2}} \left(\frac{R_c + H_2}{R_c + H_1} \right) \exp \left[-\frac{R_c}{H_2} + \frac{R_c}{H_1} \right]. \quad (36)$$

With H_1 twice H_2 , this ratio becomes

$$\left(\frac{n_2}{n_1} \right)_0 = \left(\frac{n_2}{n_1} \right)_{R_c} 1.3 \exp \left[-\frac{R_c}{H_1} \right] = 5 \times 10^{-5} \left(\frac{n_2}{n_1} \right)_{R_c}. \quad (37)$$

So with the deuterium to hydrogen ratio 10 at R_c , the mixing ratio implied for D and H is 5×10^{-4} . The tap water ratio on earth is 1.4×10^{-4} .

4. Water on Venus

This brings us finally to the intriguing lack of water on Venus. In discussions of planetary hydrogen escape, attention often is focussed on the mechanism of escape from the exosphere. In a real atmosphere the escape probability per atom from the base of the exosphere has little to do with the total escape flux. This is controlled rather by the source strength in the lower atmosphere and this is determined in practice by the rate of photodissociation of hydrogen compounds each as H_2O . Thus, water vapor must be convected up from the planet's surface to the upper atmosphere with the mixing ratio determined by the value it can achieve at the temperature minimum. When the water finally reaches the altitude at which it is exposed to solar photons shorter in wavelength than 1860 \AA it begins to dissociate. In the presence of other gases it must compete for photons below about 1800 \AA with O_2 and below 1700 \AA with CO_2 . Some of the hydrogen atoms produced may be lost by recombination, the rest will diffuse upward. When they reach the base of the exosphere they escape. The global escape flux will equal the upward flux resulting from photodissociation and the hydrogen density between the source and escape regions will adjust itself to maintain this flux. For a given production rate, if the escape probability increases because of increased exospheric temperature or because of the sweeping effect of the solar wind, the density at the escape level will simply decrease to keep the flux constant. Thus, the fact that the hydrogen 500 km above the surface of Venus is exposed to the solar wind will have little effect

on the rate at which that planet loses hydrogen. What counts is how rapidly the hydrogen is liberated from compounds further down.

If in the course of 4.5×10^9 yr Venus has lost as much hydrogen as is stored in the form of water on the earth's surface, it has lost about 1.5×10^{28} atoms cm^{-2} . This calls for an escape flux of about 10^{11} atoms $\text{cm}^{-2} \text{sec}^{-1}$ during a large part of the planet's life. In turn, this means that the dissociation rate also must have attained that value. At present on earth the rate is about 10^8 atoms $\text{cm}^2 \text{sec}^{-1}$. It is interesting that there is sufficient solar flux at Venus to dissociate about 2×10^{11} water molecules $\text{cm}^{-2} \text{sec}^{-1}$ if the water did not need to compete with such gases as O_2 and CO_2 for the photons (Sagan, 1967). The threshold for CO_2 absorption is about 100\AA beyond that for O_2 and the absorption coefficient almost two orders of magnitude smaller. Thus, if the O_2 abundance in the mesosphere of Venus is much smaller than on earth, the photodissociation rate per H_2O molecule is much higher there. Nevertheless, given the existence of temperatures in the neighborhood of 200K in the upper atmosphere, the water vapor content could never become high enough in the upper atmosphere for water to consume a large fraction of the solar photons below 1700\AA . It is difficult to see how the photodissociation rate could approach the level of 10^{11} molecules $\text{cm}^2 \text{sec}^{-1}$ unless the atmosphere was free even of CO_2 . Only if the atmosphere were radically different in the past is it possible to understand how Venus could once have possessed as much water as earth now has.

5. The ionosphere

It appears that there will be little difficulty in accounting for the daytime ionosphere observed on Venus by Mariner 5 (Kliore *et al.*, 1967) in terms of an F1 model with CO_2^+ the major ion (McElroy, 1968). In this case we must ask why the same model runs into trouble on Mars.

The nocturnal Cytherian ionosphere with a maximum of 10^4 electrons cm^{-2} at 6200 km should present some very serious problems. The lowest layer, some 10 km wide, appears to be CO_2^+ . If it is, the total rate of loss of these ions is given by

$$(\text{CO}_2^+)n_{e0}\text{H}_e = 4 \times 10^7 \text{ ions cm}^{-2} \text{sec}^{-1}. \quad (38)$$

The problem is how to account for such an ionization

rate. If, for example, a mechanism involving transport of He^+ from the day side is involved, a daytime ionization rate for He far in excess of (38) will be required. On earth the rate is only $2 \times 10^6 \text{ cm}^{-2} \text{sec}^{-1}$.

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