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A STUDY OF THE EVOLUTION OF THE ATMOSPHERE OF VENUS

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ABSTRACT

This is a final report for NASA Grant No. NGR33-006-062 for the period 1 January 1972 to 31 December 1972. Principal emphasis of study has been the escape mechanism which results in "blow-off" of an atmosphere. The planets and satellites have been studied in this respect from an evolutionary standpoint. Studies were made of comets and the solar wind because of similarities with the problem treated here. Both static and dynamic studies have been made of upper atmospheric regions for neutral and for fully ionized media. Variation with more than one dimension is essential and has been incorporated.

This report is the final report of NASA Grant No. NGR33-006-062, entitled "A Study of the Evolution of the Atmosphere of Venus." The program was for one year starting 1 January 1972. The Principal Investigator has been Dr. Stanley H. Gross of the Electrical Engineering and Electrophysics Department of the Polytechnic Institute of Brooklyn. The program has been concerned with the escape of gases from planetary atmospheres, in particular possible primordial atmospheres dominated by light species. Escape of such gases is mainly by the "blow-off" mechanism. One application of interest is the apparent loss of water on Venus and its cosmological significance.

Studies under the program were divided into two areas: statics and dynamics. Static-like studies of upper atmospheres have been more or less traditional, due to the emphasis on solar UV absorption, diffusion and thermal conduction processes. One dimensional problems (with altitude or radius only) are assumed, and the complication of motion and three dimensions were recognized but not well treated. The structure of the thermosphere and temperature profile are determinable from static models, as well as exospheric temperatures for thermal escape studies. It is reasonable to compare such temperatures with temperatures corresponding to gravitational potentials for estimating escape efficiencies. This was done under this program and much of the contents is described in two papers published in the Journal of the Atmospheric Sciences (Smith and Gross, 1972; Gross, 1972), and these form a part of this report.

Further studies were made of the Galilean Satellites of Jupiter and Titan, the largest satellite of Saturn. These also utilize static models that permit some degree of comprehension of observations of these satellites. It is planned to present the results of this study at the DPS meeting of the AAU in March 1973 in Tucson, Arizona. A copy of the Abstract entitled "Evolutionary Aspects of the Atmospheres of Titan and the Galilean Satellites" is attached and forms part of this report.

Dynamical studies have consisted of two parts. One has been concerned with the development of escape flux equations for neutral media. The problem is similar to that originally made for the Solar Wind. Since the latter expands as a result of energy from within, whereas atmospheres expand from the absorption of energy from without, the analysis of this effort incorporates UV absorption and thermal conductivity rather than resort for simplitіcy to a polytrope. Equations have been developed to the point where further analysis will require computer evaluation.

Another part of the dynamical study of escape mechanisms has been concerned with ionized media. Here the development has assumed fully ionized gases. The equations are similar to that for neutral media except for the complications of electromagnetic terms. Much more work is required for this effort, particularly for partially ionized media.

In view of some similarity of rapid escape due to blow-off and cometary tail formation, some effort during the program was concerned with comets and their properties. One goal of the program is to study and analyze tail flow in this respect as well.

Flow from planets, comets or satellites, because of the directional aspect of the sun with respect to solar UV and the solar wind, necessitates treatment of a problem in which there is variation with at least two dimensions. Spherical symmetry is not realistic, and analysis, as contrasted with much of the work on the solar wind (or even the Earth's polar wind), must include the effects of angular variation in the models as well as radial variation. Introduction of the angle coordinate produces considerable complexity. The dynamical studies referred to above have included effects of variations with all three dimensions.

Much more analysis is required, and the efforts under this program are being continued as part of NASA Grant NGR33-006-068.

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The Evolution of Water Vapor in the Atmosphere of Venus

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ABSTRACT

The atmosphere of Venus appears to be deficient in water vapor by a factor of about 10^4 compared with the total amount of water on Earth.

The feasibility of loss of water vapor from the Venus atmosphere is examined, assuming H_2O as the sole initial constituent. A steady-state model is constructed, and the photochemistry establishes the distribution of important products in the upper atmosphere. Calculations of exospheric temperatures yield values as high as 100,000K. Such large temperatures result from the large abundance of atomic hydrogen in the exosphere, and imply a dynamic outflow of all constituents from the upper region of the atmosphere. Such an outflow would cause the escape of all hydrogen and some of the oxygen resulting from dissociation of H_2O. Little loss of CO_2 would result due to its low abundance in the upper region permitting its accumulation to the present observed value.

It is concluded that if Venus formed from the same mix of materials as Earth, much tectonic activity and fairly rapid outgassing must have occurred during the early phase of its history to account for the loss of water vapor.

1. Introduction

The scarcity of rare gases in the Earth's atmosphere (Brown, 1949) and the apparent low abundance of neon on Venus rules against the atmospheres of these planets being primordial remnants and in favor of outgassing from the interior as their source (Rasool, 1968; Vinogradov *et al.*, 1968). Since these planets are of about the same size and are located close to each other in the solar system, it is most probable that they formed from the solar nebula with about the same composition. Tectonic activity would therefore be similar, and exuded gases would consist of the same average composition as observed on Earth due to volcanoes, fumaroles, hot springs, etc. Thus, H_2O would be of the greatest abundance (on the order of 300 atm), followed by CO_2 (on the order of 70–100 atm) and N_2 ($\sim$1 atm) (Rasool and de Bergh, 1970). On Earth, water vapor condensed forming the oceans and CO_2 was locked up in the crust in the form of carbonates, the crust-atmosphere interactions being aided by the presence of oceans. The Venusian atmosphere appears to contain most of the exuded CO_2, some 70–100 atm (Avduevsky *et al.*, 1971), but very little water vapor (Vinogradov *et al.*, 1968; Belton, 1968). Being at a temperature of 747 ± 20K, the surface of Venus is too hot for all 300 atm of water vapor to condense to form oceans. The absence of water vapor from the atmosphere and its improbability of being at the surface implies that Venus at the present time is deficient in water by a factor of the order of 10^4 in comparison with Earth.

Explanations for the loss of water on Venus have been based on dissociation of water molecules in the upper atmosphere and subsequent escape of hydrogen (Rasool, 1968; McElroy and Hunten, 1969). Both rapid and gradual outgassing have been discussed in this context (Rasool and de Bergh, 1970).

Here we report on the results of a study in which we attempted to gain some insight into the details of the dissociation and loss of H_2O. Water vapor is assumed to be the sole constituent in the atmosphere, and the complications of other constituents, such as CO_2, are neglected. Interest is in the structure of the mesosphere, thermosphere and exosphere of this model, with particular emphasis on the extent of dissociation and the escape of dissociation products. A complete solution for the entire atmosphere from the surface is not given. Rather, approximations are made for the purpose of facilitating the solution of the upper atmospheric structure by assuming various mesospheric temperatures and by taking the temperature as constant throughout the mesosphere. The photochemistry of a water vapor atmosphere is analyzed, demonstrating the likely make-up of the upper atmosphere. The thermal conduction equation is solved to determine the exospheric temperature from which the escape rate may be estimated. However, exceedingly high exospheric

TABLE 1. Chemical reactions involving the most important dissociation products of H_2O.

Process	Reaction	Cross section or rate value*	Reference	Remarks
Photodissociation	$H_2O+h\nu \rightarrow OH+H$	$\sigma(H_2O)$	(Thompson *et al.* 1963; Watanabe and Zelikoff, 1953)	$\lambda \leqslant 2420$ Å
	$O_2+h\nu \rightarrow O+O$	$\sigma(O_2)$	(Thompson *et al.*, 1963; Watanabe *et al.*, 1953)	$\lambda \leqslant 1760$ Å
Atom-atom interchange	$OH+OH \rightarrow H_2O+O$	$1.38\times10^{-11}\, e^{-1000/RT}$	(Schofield, 1967)	
	$OH+O \rightarrow H+O_2$	2.06×10^{-11}	(Schofield, 1967)	
	$OH+H \rightarrow H_2+O$	$9.3\times10^{-12}\, e^{-7530/RT}$	(Schofield, 1967)	
	$OH+H_2 \rightarrow H_2O+H$	$6.3\times10^{-11}\, e^{-5490/RT}$	(Schofield, 1967)	
	$O+H_2 \rightarrow OH+H$	$2.1\times10^{-11}\, e^{-9400/RT}$	(Schofield, 1967)	
Recombination	$O+O \rightarrow O_2+h\nu$	1.5×10^{-20}	(Bates and Nicolet, 1950)	Rate very uncertain. Reaction probably not important
	$O+O+M \rightarrow O_2+M$	$6\times10^{-33}(T/300)^{-\frac{1}{2}}$	(Schiff, 1969; Barth, 1961; Harteck and Reeves, 1961; Kaufman and Kelso, 1961)	$T^{-\frac{1}{2}}$ dependence assumed
	$H+H+M \rightarrow H_2+M$	$2\times10^{-32}(T/300)^{-\frac{1}{2}}$	(Schofield, 1967; Kaufman, 1969)	$T^{-\frac{1}{2}}$ dependence assumed

* Units: $cm^3\ sec^{-1}$ for atom-atom interchange; $cm^6\ sec^{-1}$ for recombination.

temperatures are found indicating the likelihood of a blow-off of upper atmospheric gases rather than the thermal escape or evaporation usually associated with planetary atmospheres. The significance of these results is discussed.

2. Photochemistry

In a model atmosphere with H_2O as the sole constituent, it is very likely that the average temperature of the mesosphere will be in the range 200–300K as a result of infrared radiation from below and any warming due to constituents such as O_3. The photochemistry of H_2O at such temperatures involves many reactions due to the numerous dissociation products of H_2O such as H_2, O, O_2, OH, HO_2, O_3 and H_2O_2. On studying the chemistry, it is found that the most important constituents and reactions involve H_2O, H, H_2, O, O_2 and OH. A constituent such as HO_2 is involved in the chemistry, but its density is very small compared with the important products of dissociation. Many of the reactions are temperature-dependent, so that somewhat different results are to be expected for various mesospheric temperatures. The most important reactions are summarized in Table 1 together with their rate coefficients and source references. The rate for radiative association of O_2 is uncertain, and, at most, modifies the density of atomic and molecular oxygen at higher altitudes. The solar input in the UV range, corrected for the distance of Venus, is based on the data of Detwiler *et al.* (1961). Estimates of the time to reach equilibrium amounts to the order of 10^6 years.

The photochemical distributions for temperatures of 200, 250 and 300K are shown in Figs. 1–3, respectively. Equilibrium number densities are shown vs an initial H_2O number density, assumed to be in hydrostatic equilibrium. (These figures are plotted vs initial H_2O density instead of altitude to enable simpler comparisons, and because the actual altitude requires the solution for the lower part of the atmosphere.) The distribution is independent of whether the outgassing

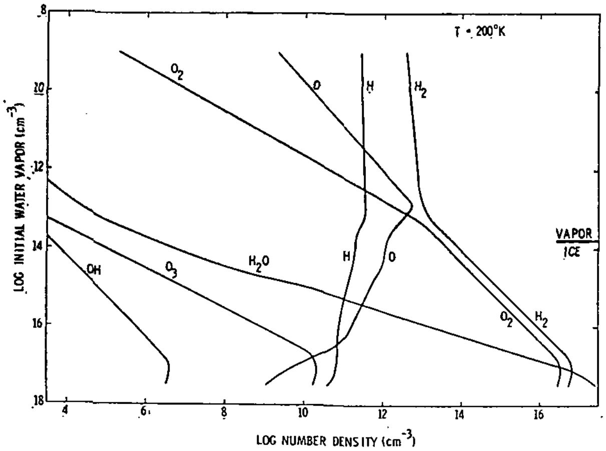

FIG. 1. Distribution of atmospheric constituents as a function of initial water vapor density for $T=200K$.

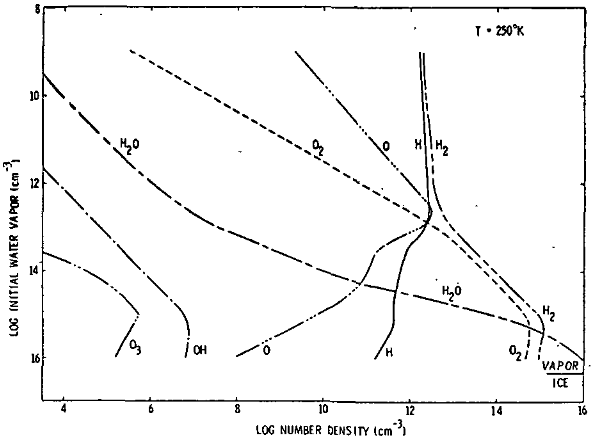

FIG. 2. Same as Fig. 1 except for $T=250K$.

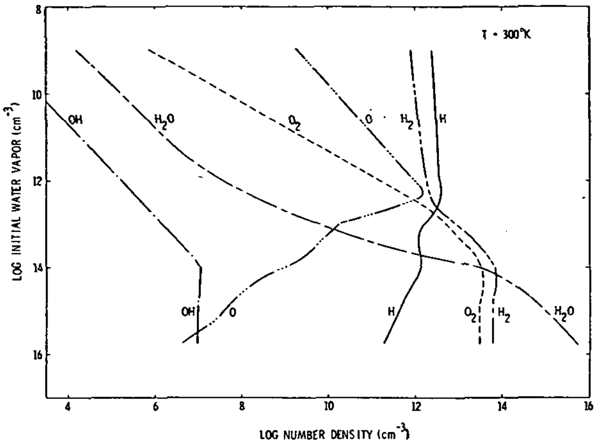

FIG. 3. Same as Fig. 1 except for $T=300$K. Ozone distribution is negligible and not shown.

rate is rapid or slow, as long as sufficient water vapor molecules are available and absorb solar UV at wavelengths less than 2420 Å. The photochemical range is for initial water vapor densities of 10^{18} to about 10^{13} molecules cm^{-3}. For initial H_2O densities in excess of 10^{16} cm^{-3} and temperatures of 250 and 300K, the equilibrium water vapor is almost entirely undissociated, whereas for $T=200$K the corresponding density is 10^{17} cm^{-3}. Thus, below about 10^{17} molecules cm^{-3}, H_2O is essentially undissociated down to the surface.

Figs. 1 and 2 also exhibit the ozone distribution. Ozone is minor in all three cases. Its greatest density in the range plotted is about 10^{10} particles cm^{-3} for $T=200$K, and for $T=300$K it is entirely negligible. The extent of O_3 formation depends on the balance between production due to recombination of O and O_2, and loss primarily by reactions with other constituents. The important O_3 reactions are listed in Table 2. In performing these calculations it was assumed that the density of oxygen in the ^1D state is half the total density of atomic oxygen. If the ^1D state is quenched by reactions with other constituents, the maximum density of O_3 would be no more than a factor of 5 greater than the values shown in the figures. Enough ozone may be present for $T=200$K to raise the temperature above this value.

Also shown in Figs. 1–3 are the vapor pressure lines for H_2O. For 200K the vapor-ice line is at 5.8×10^{13} particles cm^{-3}. For densities greater than this value H_2O would precipitate at 200K. The corresponding densities at 250 and 300K are 2.2×10^{16} and 8.8×10^{17} cm^{-3}. It would appear, then, that the assumption of 200K is unrealistic, whereas 250 and 300K provide more meaningful photochemical distributions as shown. However, the temperature will not be constant throughout the entire region, a minimum occurring at the mesopause. The 200K case would be more realistic if the mesopause is above the level where the initial H_2O is 5.8×10^{13} cm^{-3} and the temperature below remains above the precipitation temperature for the density at each level. In any event, the average temperature in the region would probably be above 200K, but less than or equal to 300K, and the results must be considered in this context.

3. Thermospheric distribution

The distributions in Figs. 1-3 for altitudes above the level of about 10^{13} initial H_2O molecules cm^{-3} are not photochemical distributions. The graphs show the decrease in density of each constituent, assuming diffusive equilibrium as the dominant process at the mesospheric temperature for each graph. The transition is accomplished by merging the photochemical and diffusive equilibrium regions into each other. The assumed temperatures are unrealistic for the thermosphere. The actual temperature will increase with altitude, and the constituents will decrease far less rapidly than shown on the graph. (Temperatures will be discussed further in Section 4.) However, the general nature of the distribution is still exhibited by the figures in spite of the assumed temperatures. Atomic hydrogen dominates in this region for 300K and molecular hydrogen for 200K. For 250K both H and H_2 are nearly equal in density in the regions shown. The nature of the distributions of H and H_2 as a function of temperature stems from the temperature dependence of the reactions of Table 1. Additional atomic hydrogen is included as a result of the photoionization of H_2 and subsequent reactions shown in Table 3. At high enough altitudes H will dominate in all cases for a diffusive equilibrium region. Atomic oxygen peaks in all three cases at a density somewhat less than 10^{13} particles cm^{-3} at an initial water vapor level between 10^{12} and 10^{13} particles cm^{-3}. The density of molecular oxygen is less than that of atomic oxygen at heights greater than the level where atomic oxygen peaks.

TABLE 2. Important ozone reactions.

Ozone reactions	Reaction rate coefficient	Reference
Production reaction $O(^3P)+O_2+M\rightarrow O_3+M$	Average of $4.1\times10^{-35}\,e^{1800/RT}$ and $2.3\times10^{-35}\,e^{2005/RT}$	(Schofield, 1967)
Loss reactions		
$O(^1D)+O_3\rightarrow O_2+O_2$	3×10^{-10}	(Schiff, 1969)
$H+O_3\rightarrow O_2+OH$	2.6×10^{-11}	(Schofield, 1967; Hunt, 1966)

TABLE 3. Principal molecular hydrogen reactions in diffusive equilibrium region.

Photoionization

$$H_2+h\nu \rightarrow H_2^+ + e \quad (\lambda \leqslant 804\ \text{Å})$$

Secondary product formation and recombination

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$
$$H_3^+ + e \rightarrow H_2 + H$$

4. Thermosphere and exospheric temperatures

The solution for the static model structure of a thermosphere heated by solar EUV is now a fairly standard problem, having been accomplished by a number of investigators (see, for example, Chamberlain, 1962; Gross and Rasool, 1964; McElroy, 1968). One integrates the heat conduction equation from the mesopause taking into account IR cooling, which in turn depends upon the particular constituents. The thermal conductivity equation is

$$\frac{d}{dz}\left(\kappa\frac{dT}{dz}\right)=Q-L, \tag{1}$$

where z is altitude, T temperature, κ thermal conductivity, Q the heat absorbed per unit volume from solar UV and x-ray energy, and L the heat energy lost by IR radiation per unit volume.

The UV heat loss Q is given by

$$Q=\alpha\epsilon\sum_i n_i(z)\int_{\lambda_1}^{\lambda_2} F_\infty(\lambda)\sigma_i(\lambda)e^{-\tau(\lambda,z)}d\lambda, \tag{2}$$

where:

ϵ is the efficiency factor representing the fraction of solar EUV and x-ray energy converted to heat

$F_\infty(\lambda)$ the incident solar energy flux of wavelength λ

$\tau(\lambda,z)$ the optical thickness of the atmosphere at wavelength λ and altitude z due to the absorption above

$$\left[=\sum_i \sigma_i(\lambda)\int_z^\infty n_i(\zeta)d\zeta\right]$$

$n_i(z)$ the number density of the ith absorbing constituent at altitude z

$\sigma_i(\lambda)$ the absorption or ionization cross section of the ith constituent at wavelength λ

α a numeric factor that takes on values appropriate for the rotation rate of the planet and the nature of the calculation (planetary average or sub-solar point computation, for example)

λ_1, λ_2 the lower and upper wavelength limits of the solar radiation band of importance.

The IR heat loss L depends on the cooling constituent and nature of the transition in the infrared portion of that constituent's spectrum. Atomic O is a radiator at 62 μ for the models of Figs. 1–3, and some cooling could result from H_2O molecules (6.26 μ) at the level of a mesopause, though the number density is small. One finds that the extent of cooling is not very significant and that most of the heat absorbed and conducted downward is due to atomic and molecular hydrogen. The EUV range is for wavelengths $\leqslant 911$ Å, and flux values, corrected for the distance of Venus, were taken from Hinteregger and Hall (1965). The cross sections for H and H_2 were taken from Gross and Rasool (1964).

The mesopause level may be estimated by equating the downward flux of heat and the height-integrated volumetric cooling rate for H_2O radiation (Gross and Rasool). The level of vibrational relaxation may be found from the relaxation time. The difficulty in making these computations is the uncertainty in the relaxation time (see, for example Herzfeld and Litovitz, 1959, and Goody, 1964). It is difficult to determine the temperature dependence of these data. However, using the value quoted by Goody for water vapor, which is at a temperature of 220K, one can show (with some uncertainty) that the level of vibrational relaxation at $T=300$K is at the total density level 3×10^{12} particles cm^{-3} and the mesopause is at the total density level of 10^{12} particles cm^{-3}. The corresponding particle density levels for $T=200$K are 10^{15} and 10^{14}–10^{15}, respectively. Vapor pressure effects are certainly important as well, particularly for a 200K temperature, adding to the uncertainty in the computation of the mesopause for this case.

In our calculations of the thermosphere we sought the temperature profile averaged over the dayside for a slowly rotating planet. Two values for the efficiency factor were used. Stewart and Hogan (1969) empirically found 0.27 for solar EUV for best agreement with the measured ionosphere of Venus, but weighted averages using the theoretical treatment of Henry and McElroy (1968) led to a value of 0.59. Thus, calculations were made for efficiencies of 0.3 and 0.6. From the calculated temperature profile obtained by integrating the heat conduction equation, one obtains the exospheric temperature by seeking the high-altitude asymptotic limit, and this temperature may then be used to estimate thermal escape rates for each constituent.

The computational method for finding the thermospheric distribution and temperature starts by assuming an initial distribution of constituents, such as the upper parts of Figs. 1–3. This distribution is inserted into the heat conduction equation (1), and a temperature profile is found. The temperature profile changes the distribution of the constituents, and a second solution of the temperature equation yields a new temperature profile which then yields a new distribution of constituents. The process is continued until the temperature and particle distributions converge to a consistent solution. Boundary values are usually assumed at a level such as the mesopause.

When this process was attempted for the atmospheric models that were studied, exceedingly high exospheric temperatures were found. The lowest value is obtained for the model with a 300K mesopause temperature with an efficiency of 0.3. For this model the computed value is 20,000K. The highest temperature is obtained for the model with a 200K mesopause temperature with an efficiency of 0.6. For this case the computed temperature is 100,000K. The value of the gravitational acceleration used in these calculations was 870 cm sec^{-2}. For lower values of the gravitational acceleration higher temperatures are obtained. Such high values of the temperature are indicative of very large escape rates and portend difficulties in attempting to find a convergent static solution for the thermosphere as explained in another paper by one of the authors (Gross, 1971).

The high temperatures result from three factors: 1) the large quantity of hydrogen in the upper atmosphere of the models studied, 2) the distance of Venus from the sun, and 3) the mass of the planet or its gravitational acceleration. That these physical factors may produce such conditions, in contrast with the present atmospheres of the terrestrial planets ($T_\infty \approx 1000-1500$K for Earth, ~700K for Venus, ~300–500K for Mars) may be appreciated from an approximate expression (Gross, 1971) derivable from Eq. (1):

$$T_\infty \approx \left\{ \frac{s}{A} \frac{\alpha \epsilon k}{mg} \int_{\lambda_1}^{\lambda_2} d\lambda F_\infty(\lambda)[\ln \tau_m(\lambda) + \gamma] \right\}^{1/s}. \quad (3)$$

Here, T_∞ is the exospheric temperature, τ_m the optical thickness at the level of the mesopause of the major constituent absorbing solar EUV (hydrogen for the models of Figs. 1–3), k Boltzmann's constant, m the mass of the major EUV absorber, g the gravitational acceleration, and γ Euler's constant (0.5771). The terms s and A are derived from an approximate expression for the thermal conductivity in terms of the temperature, i.e., $\kappa = AT^s$, where A and s are constants for the particular gas, hydrogen in this case.

The important parameters controlling the exospheric temperature are indicated in (3). The exospheric temperature T_∞ varies as $m^{-1/s}$, as $g^{-1/s}$ and, through the flux F_∞, as $R^{-2/s}$, where R is the distance from the sun. Atomic hydrogen has a mass 1/44 that of CO_2, so that if all other things were equal the temperature for an atomic hydrogen atmosphere would be $(44)^{1/s}$ times that for CO_2. However, the thermal conductivity and its variation with temperature of these two gases are different. For hydrogen $s = 0.75$ and $A = 250$ ergs $\text{cm}^{-1}\,\text{sec}^{-1}(^\circ\text{K})^{-1.75}$ (Dalgarno and Smith, 1962), whereas $s = 1.37$ and $A = 6.6$ ergs $\text{cm}^{-1}\,\text{sec}^{-1}(^\circ\text{K})^{-2.37}$ (Hilsenrath *et al.*, 1960). For the same solar flux integral in (3), heating efficiencies and rotation factor, (3) leads to values of $\sim 10^5$ K for atomic hydrogen and 400 to ~700K for CO_2.

5. Discussion

The equivalence of thermal energy and gravitational potential energy may be used to define an escape temperature for a constituent of the atmosphere at any level. The escape temperature of atomic hydrogen from Venus is 6600K when computed for the surface radius. Under these conditions the mean thermal velocity equals the escape velocity. For much higher temperatures the top of the atmosphere will "blow-off" (Opik, 1963), depleting the thermosphere of all gases. However, the outflow is limited by conditions at the base of the region, particularly when photochemistry supplies the constituent causing the heating. The limiting process is upward diffusion, eddy and molecular, from the chemical source region below. The complete description of the entire region entails the solution of a problem in dynamics rather than statics (Gross, 1971).

Atomic hydrogen is rapidly lost from the thermosphere in this way, as well as a percentage of atomic oxygen that is also supplied by dissociation of H_2O. The process may account for some of the loss of oxygen (Rasool, private communication), in view of its present small content in the atmosphere of Venus (Vinogradov *et al.*, 1968; Kuzmin, 1970). Very little of the more massive CO_2 is in the hydrogen-dominated thermosphere, most of it being below the mesopause. The loss of CO_2 due to the outflow would be small, and, as outgassing continued, the CO_2 content would increase to its present level and dominance.

Once CO_2 and any of its photochemical products control the thermosphere by being the principal absorbers of solar EUV, the exospheric temperature considerably decreases to values found today, and any hydrogen present at the top of the atmosphere escapes via thermal evaporation rather than by a "blow-off". The rapid escape stage must have ceased once the outgassing and rise of H_2O (and its products) could no longer supply thermospheric densities of atomic hydrogen on the order of 10^{10} particles or greater, an amount required to obtain an optical thickness of the order of unity or more to wavelengths <911 Å.

If the outgassing rate has been essentially the same over the entire life of the planet ($\sim 4.5 \times 10^9$ years), and a major proportion of the exuded H_2O was lost by dissociation and blow-off, then it appears to these authors that the present content of H_2O in the lower atmosphere is too small to support such a hypothesis. The lower atmosphere would store H_2O and supply hydrogen to the thermosphere, where hydrogen would continually build up and dominate the region. If Venus has released a major amount of H_2O from its surface, it must have occurred in a time shorter than its age. A simple calculation shows that the EUV energy in the sun's present radiation would provide sufficient energy to cause the number of H atoms in 300 atm of H_2O to escape in less than 10^9 years. Periods of more intense solar activity at wavelengths <400 Å would decrease this time accordingly. The time decreases, as well, in a linear fashion with the assumed extent of outgassed H_2O. The possibility that Venus had such fractions as $\frac{1}{2}$ or $\frac{1}{3}$ of Earth's H_2O cannot be discounted. Outgassing and loss of H_2O in a time much less than the age of the planet is also consistent with the explanation given by McElroy and Hunten (1969) of Lyman α in the outer atmosphere as measured by Barth *et al.* (1967) on Mariner 5.

Further studies of the dynamics of the problem would provide useful inputs to these considerations.

6. Conclusions

If Venus has exuded gases similar to Earth then its atmosphere would have been dominated by water vapor early in its history. Such an atmosphere would become dissociated in the mesophere producing atomic and molecular hydrogen, atomic and molecular oxygen, some OH and O_3, and very small quantities of minor gases such as HO_2. Molecular and atomic hydrogen would dominate the thermosphere, and atomic hydrogen would be the main constituent at high enough altitudes. Absorption of solar EUV by hydrogen results in a very high temperature thermosphere, producing expansion and blow-off of the top of the atmosphere with attendant loss of hydrogen and some oxygen. Carbon dioxide would be mostly below the mesopause and could accumulate to the present level as H_2O is dissociated and lost by rapid escape. The process could account for the major loss of H_2O by Venus.

It is likely that such a process occurred in the past when tectonic activity and outgassing may have been high. The entire loss of some 300 or less atmospheres of H_2O could conceivably have taken place during the first one or two billion years.

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On the Exospheric Temperature of Hydrogen-Dominated Planetary Atmospheres

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On the Exospheric Temperature of Hydrogen-Dominated Planetary Atmospheres

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ABSTRACT

All the planets may have been surrounded originally by atmospheres dominated by hydrogen or one of its compounds. While only the major planets have retained much of their initial atmospheres, the terrestrial planets appear to have lost these gases. Calculations of exospheric temperatures for these smaller planets preclude loss of hydrogen by the selective process of thermal escape, since exceedingly high values are found for these planets. Instead, a general outflow or "planetary wind" is expected to deplete rapidly the thermosphere of all constituents. Low values are obtained for the major planets and their retention of hydrogen is understandable.

Expressions are given for the exospheric temperature of a two-component diffusive equilibrium model which consists of a lighter molecule dominating the thermosphere and absorbing solar EUV, and a heavier constituent providing radiative cooling in the vicinity of the mesopause. The model approximates well the assumed atmospheres, but the resulting expressions may have wider application.

The dynamics of an expanding atmosphere are discussed. A three-dimensional outflow against the back pressure of the solar wind may be configured like a comet's tail.

1. Introduction

The atmospheres of the major planets consist mostly of hydrogen. The atmospheres of the terrestrial planets are mainly composed of other gases: CO_2 for Mars and Venus, N_2 and O_2 for the Earth, and, if any gas at all, CO_2 for Mercury (Rasool *et al.*, 1966). Nevertheless, it is very likely that the early atmospheres of the smaller planets were dominated by H_2 or its compounds, either from their primordial gaseous envelopes or as a result of outgassing from the interior. Thus, all or most of the planets may have had atmospheres in which hydrogen or its compounds played an important role.

If this is true, it is necessary to explain the present gaseous makeup of the atmospheres of the smaller planets. It is common to invoke the process of selective thermal escape, at least for the loss of H_2, in which constituents of lighter mass evaporate more rapidly than heavier particles. This process is assumed to have taken place during the life of the solar system. Outgassed constituents, such as CO_2 and N_2, are then presumed to dominate after the loss of hydrogen leading to the present state, though the process is not entirely clear.

This note provides results from studies of hydrogen-dominated atmospheres in which exospheric temperatures were calculated to estimate the evaporative loss rates of the constituents. Exceedingly high values were obtained for the terrestrial planets, whereas very low values were found for the major planets. Retention of major abundances of H_2 in the atmospheres of the large planets is understandable from these results. However, the very high values for the smaller planets preclude a thermal escape mechanism. Instead, they lead to a "blow-off" of the top of the atmosphere, the outflow being non-selective and carrying all constituents within the thermosphere (Opik, 1963). Because of a similarity of the dynamics to that of the solar wind, the blow-off may be likened to a "planetary wind." A complete solution for the flow and exospheric temperature requires specification of boundary conditions at the top and bottom of the thermosphere.

2. The thermosphere and the exospheric temperature

The structure of the thermosphere is usually found by solving a heat conduction equation for a stationary atmosphere. The method is now well known, having been carried out by a number of investigators (Chamberlain, 1962; Gross and Rasool, 1964; McElroy, 1968; and others). Both heating by absorption of solar UV and x-ray energy, and cooling by IR radiation, are included in the analysis. The lower boundary of the region is taken as the mesopause. The formulation is complex in detail and requires computational methods for solution. Here, however, an analytic solution for the exospheric temperature of a so-called "two-component" model in diffusive equilibrium is presented. The complete temperature structure for this model is also derived.

The two-component model consists of two gases, one being a constituent of lighter mass that absorbs solar EUV and heats the thermosphere, and the other being a constituent of greater mass that cools the atmosphere, primarily in the region about the mesopause. Such a model appears to represent suitably the upper portion of planetary atmospheres dominated by molecules containing hydrogen. Hydrogen, the lightest gas, is the main constituent in the thermosphere, and the absorber of solar EUV, whereas a heavier molecule, which may also contain hydrogen, is a cooling particle, and may even dominate in the lower regions of the atmosphere. Though the assumption of a two-component model is not necessarily precise in all cases, its choice leads to some simplifications and yields results that are reasonably valid, even when more constituents are incorporated. The resulting formulas also provide insight into the nature of the factors controlling the temperature and particle distributions.

The analysis of a thermosphere starts from the thermal conductivity equation

$$-\frac{d}{dz}\left(K\frac{dT}{dz}\right)=Q-L, \qquad (1)$$

where z is the altitude, T the temperature, K the thermal conductivity, Q the heat absorbed per unit volume from solar UV and x-ray energy, and L the heat energy lost by IR radiation per unit volume.

For a number of EUV absorbers Q is given by

$$Q=\alpha\epsilon\sum_i n_i(z)\int_{\lambda_1}^{\lambda_2} F_\infty(\lambda)\sigma_i(\lambda)e^{-\tau(\lambda,z)}d\lambda, \qquad (2)$$

where $\sum_i$ represents the discrete sum over i absorbers, ϵ is the efficiency factor representing the fraction of solar EUV and x-ray energy converted to heat, $F_\infty(\lambda)$ the incident solar energy flux at wavelength λ, $\tau(\lambda,z)$ the optical thickness of the atmosphere at wavelength λ and altitude z due to the above absorption, i.e.,

$$\tau(\lambda,z)=\sum_i \sigma_i(\lambda)\int_z^\infty n_i(\zeta)d\zeta,$$

$n_i(z)$ is the number density of the ith absorbing constituent at altitude z, $\sigma_i(\lambda)$ the absorption or ionization cross section of the ith constituent at wavelength λ, α a numeric factor that takes on values appropriate for the rotation rate of the planet and the nature of the calculation (planetary average or sub-solar point computation, for example), and λ_1, λ_2 the lower and upper wavelength limits of the solar radiation band of importance.

For the two-component model i takes on the values 1, 2, where 1 is used to designate lighter mass quantities and 2 is for the heavier particles. This model further assumes that the contribution to Q is entirely due to the lighter constituent, i.e., $i=1$ in (2). Hereafter, the subscript 1 will be dropped from $\sigma(\lambda)$.

In general, L depends on the cooling constituents and the nature of the transitions in the IR portions of their spectra. Approximate formulas have been given by a number of investigators (Bates, 1951; McElroy *et al.*, 1965). For the two-component model, cooling is due only to the heavier constituent for which $i=2$ in the above nomenclature.

Thermospheric cooling arises primarily as a result of collisional activation of higher states. Although only a small percentage of all collisions cause such transitions, and only some are deactivated radiatively, the cooling loss is proportional to the densities of the colliding constituents. Other factors enter, however, such as the temperature and the optical thickness to the radiation. Nevertheless, when the cooling constituent is a small percentage of the total number density in the region where most of the cooling occurs and when its number density decreases with altitude more rapidly than the remaining constituents, one may consider the cooling as arising solely from a local region at the base of the thermosphere. All factors are relatively constant in this region except the density of the cooling molecule. Under such circumstances L may be taken as proportional to the number density of the radiating particles, with a proportionality factor essentially constant for the height interval where cooling is relevant.

Although other situations may arise, in general, the assumed model is in accordance with this description; thus, we may take

$$L=\beta n_2(z), \tag{3}$$

where β is treated as a constant, though it truly contains factors that vary somewhat with altitude. Eq. (3) overestimates cooling at lower altitudes (usually below the mesopause) where the optical thickness to the cooling radiation is greater. However, the exospheric temperatures that are derived here are not significantly affected by these approximations.

On substituting (2) for Q (with $i=1$) and (3) for L in (1), one may integrate with respect to z from level z to infinity, taking $dT/dz=0$ for $z\rightarrow\infty$, to obtain

$$K_1\frac{dT}{dz}=\alpha\epsilon\int_{\lambda_1}^{\lambda_2}F_\infty(\lambda)[1-e^{-\tau(\lambda,z)}]d\lambda-\beta\int_z^\infty n_2(z)dz. \tag{4}$$

Here the thermal conductivity is taken as due primarily to the major constituent, the lighter particles.

The mesopause level is defined by the level $z=z_m$, where $dT/dz=0$, so that

$$\beta\int_{z_m}^\infty n_2(z)dz=\beta n_2(z_m)H_2(z_m)\,.$$

$$=\alpha\epsilon\int_{\lambda_1}^{\lambda_2}F_\infty(\lambda)[1-e^{-\tau(\lambda,z_m)}]d\lambda. \tag{5}$$

The integration of $n_2(z)$ in (5) is obtained from the distribution for $n_2(z)$:

$$n_2(z)=\frac{n_2(z_m)T_m}{T}\exp\left[-\int_{z_m}^z\frac{d\zeta}{H_2(\zeta)}\right], \tag{6}$$

where T_m is the temperature at the mesopause and H_2 is the scale height (kT/m_2g), k is Boltzmann's constant, m_2 the mass of the heavier constituent and g the acceleration of gravity. On substituting (5) and (6) in (4), one obtains

$$K_1\frac{dT}{dz}=\alpha\epsilon\int_{\lambda_1}^{\lambda_2}F_\infty(\lambda)\Bigg\{1-e^{-\tau(\lambda,z)}-[1-e^{-\tau(\lambda,z_m)}]$$

$$\times\exp\left[-\int_{z_m}^z\frac{d\zeta}{H_2(\zeta)}\right]\Bigg\}d\lambda. \tag{7}$$

Eq. (7) may be integrated to obtain the temperature by changing the independent variable from z to the optical thickness $\tau(\lambda,z)$. Since absorption of EUV is assumed to be entirely due to the lighter mass particle, we have

$$d\tau(\lambda,z)=-\sigma(\lambda)n_1(z)dz=-\frac{\tau(\lambda,z)}{H_1(z)}dz, \tag{8}$$

where $H_1(z)$ is the scale height of the lighter constituent and $n_1(z)$ is given by an expression like (6) with subscripts 1 in place of superscripts 2. The wavelength dependence of τ requires that integration with respect to τ be performed before integration with respect to λ. The procedure involves dividing (7) by the scale height $H_1(z)$, replacing the conductivity K_1 by the approximation $K_1=A_1T^{s_1}$ (where A_1 and s_1 are the constants for the gas), integrating with respect to z on interchanging the order of integration (λ and z), and then replacing the z integral by a τ integral. The result on integrating (7) is then

$$T_{(z)}{}^{s_1}=T_m{}^{s_1}+\frac{s_1\alpha\epsilon k}{A_1m_1g}\int_{\lambda_1}^{\lambda_2}d\lambda F_\infty(\lambda)\Bigg\{E_1[\tau_m(\lambda)]$$

$$+\ln[\tau_m(\lambda)]-E_1[\tau(\lambda,z)]-\ln[\tau(\lambda,z)]$$

$$-\frac{m_1}{m_2}[1-e^{-\tau_m(\lambda)}]\left[1-\left[\frac{\tau(\lambda,z)}{\tau_m(\lambda)}\right]^{m_2/m_1}\right]\Bigg\}, \tag{9}$$

where $\tau_m(\lambda)\equiv\tau(\lambda,z_m)$, and $E_1(\tau_m)$ is the exponential integral (Abramowitz and Stegun, 1964). The exospheric temperature T_∞ is obtained by taking $z\rightarrow\infty$ or $\tau(\lambda,z)\rightarrow 0$, so that

$$T_\infty{}^{s_1}=T_m{}^{s_1}+\frac{s_1\alpha\epsilon k}{A_1m_1g}\int_{\lambda_1}^{\lambda_2}d\lambda F_\infty(\lambda)\Bigg\{E_1[\tau_m(\lambda)]$$

$$+\ln[\tau_m(\lambda)]+\gamma-\frac{m_1}{m_2}[1-e^{-\tau_m(\lambda)}]\Bigg\}, \tag{10}$$

where γ is Euler's constant, 0.5572....

For most of the wave band of importance, $\tau_m\gg1$ and $E_1(\tau_m)$ and $e^{-\tau_m}$ may be neglected. When $m_2\gg m_1$ (CO_2 and H, for example) m_1/m_2 may be neglected. For those planets where $T_\infty\gg T_m$, the first term on the left side of (10) may also be neglected. In its simplest form one obtains

$$T_\infty\approx\left\{\left(\frac{s_1\alpha\epsilon k}{A_1m_1g}\right)\int_{\lambda_1}^{\lambda_2}d\lambda F_\infty(\lambda)[\ln\tau_m(\lambda)+\gamma]\right\}^{1/s_1}. \tag{11}$$

Eq. (11) illustrates the important parameters. For $s_1=\frac{1}{2}$, T_∞ is inversely proportional to g^2 and $m_1{}^2$, and since F_∞ varies as R^{-2} (R being the distance from the sun), T_∞ would vary as R^{-4}. Thus, the exospheric temperature would be much higher for a lighter constituent than a heavier molecule. For atomic hydrogen $s_1=0.75$ (Dalgarno and Smith, 1962), whereas for CO_2, $s_1=1.37$ (Hilsenrath, 1960), and one sees that the root, $1/s_1$, will also contribute to differences in the temperature. Eq. (11) also contains a wavelength integral representing the solar flux weighted by the logarithm of the optical thickness at the mesopause. This integral may be taken as varying only with R^{-2} for planets with the same major constituent in their thermospheres. There will be some small variation due to changes in mesopause conditions as the distance from the sun is increased, but these are minimized as a result of the logarithm. The difference in the wavelength integral for different absorbing gases should also be minimal as a result of the logarithm and the prevalence of the same order of magnitude of the absorption coefficient over the wavelength bands of interest ($\lambda \lesssim 900$ Å). Best comparisons are made, however, when the models consist of the same constituents, although Eqs. (10) and (11) may be used for various gases if differences at the mesopause, in the thermal conductivity and absorption coefficients, are taken into account.

Direct use of (10) [or (11)] to compute T_∞ for atomic hydrogen yields exospheric temperatures for each of the planets, as shown in Table 1. These are given for a nominal efficiency $\epsilon=0.5$ (for other values of ϵ, $T\approx\epsilon^{\frac{1}{3}}$ for the terrestrial planets). The temperatures are planetary averages, and all planets are assumed, for uniformity, to rotate rapidly, in spite of present conditions; that is, $\alpha=\frac{1}{4}$.

TABLE 1. Escape temperature and exospheric temperature for hydrogen atmosphere.*

Planet	T_{esc} (°K)	T_m (°K)	T_∞ (°K)
Mercury	710	**	350,000
Venus	4400	**	43,000
Earth	5200	**	15,000
Mars	1040	**	18,000
Jupiter	155,000	83†	98
Saturn	57,000	62†	72
Uranus	20,000	35†	38
Neptune	26,000	31†	31.5

* $\epsilon=0.5$, $\alpha=\frac{1}{4}$, g approximately equal to surface values.
** Not pertinent to calculation.
† Radiative equilibrium values.

The mesopause temperatures assumed for the major planets are the radiative equilibrium temperatures as given by the Eddington approximation, and are also listed in Table 1. Radiative equilibrium temperatures were chosen in the absence of better information for these planets to aid in demonstrating the small differences between mesopause and exospheric temperatures. The differences are essentially the result of thermospheric heating by solar UV. For conditions that would produce other mesopause temperatures (e.g., due to gravitational contraction or turbulence), the exospheric temperature due to solar UV would be correspondingly modified.

Table 1 demonstrates that the presence of H_2 as the major constituent absorbing solar EUV leads to high temperatures for all the terrestrial planets, whereas the values for the major planets are very low. (Hydrogen at the top of the earth's present atmosphere will not cause very high temperatures, since most of the solar EUV is absorbed by a more massive constituent, nitrogen.)

The derivation of (10) and (11) assumes that g does not vary much over the sensible portion of the thermosphere. When very high temperatures are obtained, the thermosphere is considerably extended. Under these conditions g may no longer be treated as a constant, and the temperature will reach much higher values. It is this complication that leads to the general expansion of the thermosphere and a steady outflow or blow-off of the gases in that region when the temperature is high enough. These matters are treated further in Section 3.

3. Exospheric "blow-off" of an atmosphere

The gases in a thermosphere and an exosphere may be expected to move out radially away from the planet, rapidly escaping or "blowing-off" when the thermal energy per particle exceeds its gravitational potential energy (Opik, 1963); that is, when

$$(\tfrac{3}{2})kT > \frac{mMG}{r}, \qquad (12)$$

where m is the mass of the particle, M the mass of the planet, G the gravitational constant, and r the radius from the center of the planet at the position of the particle. The temperature necessary for equality, T_{esc}, which will be called the "escape temperature," may be calculated for each planet for a given gas, and values are given in Table 1 for hydrogen with r equal to the radius of the planet. These values should be compared with the exospheric temperatures listed there in regard to the likelihood of rapid expansion and outflow.

The steady-state outflow problem leads to the same equations originally used by Parker (1963) to describe the solar wind. For the planets, energy is from without, rather than from within; and Bernoulli's equation is obtained for a polytropic atmosphere. Because of these similarities, one may refer to this blow-off as a "planetary wind." One must stipulate boundary conditions at the lower and upper limits of the atmosphere. Back pressure at the infinite limit is supplied by the solar wind. The lower limit is at the base of the thermosphere, and boundary conditions are specified with some difficulty. Here, the pressure is relatively high, but the velocity is small, being due to diffusion (molecular and eddy). When there is sufficient heat input from solar EUV, the outflow may become rapid, whereas under more normal planetary conditions, as for the present planetary atmospheres, the vertical flow will be small at large distances, corresponding to ordinary thermal escape or evaporation.

The one-dimensional problem exhibits the blow-off. However, in three dimensions, with the planet and its atmosphere immersed in a solar wind, one may expect the flow to form a tail behind the planet, with the flow from the sun side curving around toward the anti-solar direction. This description is similar to the flow observed in a comet's tail as the comet approaches the sun.

4. Discussion

Comparison of the escape and exospheric temperatures in Table 1 clearly indicates the nature of the upper atmosphere of the outer solar planets, if they are dominated by hydrogen. All the exospheric temperatures of the terrestrial planets exceed their escape temperatures. (It should be noted that T_{esc} is calculated for the radius of the planet's surface. The higher the level of escape, the lower the escape temperature.) The present condition of the major planets is understandable from data in the table.

A high-temperature thermosphere leads to non-selective escape. The constituents lost from the thermosphere are replaced from below by continued photodissociation and diffusion. Some products of these processes remain and accumulate in the mesosphere and may be transported downward by convection and mixing. For example, O_2 from dissociation of H_2O may be partially lost in the thermosphere as well as transported down to the surface where it may be lost by the formation of oxides. Heavier gases not importantly associated with hydrogen photochemistry will be mostly below the thermosphere with little above the mesopause. Any non-selective outflow would hardly deplete such gases. Thus, CO_2 could accumulate on Venus (Smith and Gross, 1972). The heavier rare gases would be retained in the same fashion. Therefore, this non-selective escape process is still consistent with Brown (1949) in that low rare gas abundances imply outgassing as the source of the terrestrial atmospheres.

The possibility of a dynamic outflow of light gases from terrestrial planets bears on the problem of the evolution of the solar system. Its further study, including interaction with charged particles and comparison with research on cometary tails, may be fruitful.

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Evolutionary Aspects of the Atmospheres of Titan and the Galilean Satellites

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SPECIAL INSTRUCTIONS (if any):

Possible atmospheres for Titan and the Galilean satellites have been studied with respect to losses by escape. It is found that primordial atmospheres mostly of hydrogen and helium lead to exospheric temperatures exceeding escape temperatures causing rapid loss by the blow-off process. It is unlikely that present atmospheres could be mainly H_2. Present atmospheres would then be made up of Neon and Nitrogen, the latter from dissociation of NH_3. H_2O would undoubtedly be trapped as ice on cold surfaces and little oxygen would be available. Ne/N_2 atmospheres yield exospheric temperatures between 600°K and 1000°K for the Galilean satellites and 200°K-350°K for Titan, values too low to lose much N_2 and Ne via thermal escape. Light gases in the thermosphere would rapidly be lost. The study implies that H_2 on Titan is being replenished by a source such as outgassing with CH_4 likely playing a role. Higher temperatures, generally, for the Galilean satellites result in more efficient escape processes, possibly explaining the lack of detection of H_2 and CH_4. Nevertheless, their surfaces are still cold enough to form ice.

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