

HYDROGEN LOSS FROM THE TERRESTRIAL PLANETS

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INTRODUCTION

The idea of escape of light atmospheric gas is older than the kinetic theory, having been introduced by J. L. Waterston in 1846 (Chamberlain 1963). The thermal escape concept was revived by G. J. Stoney around the turn of the century and given a definitive form by Jeans (1925), whose name is usually associated with it. Spitzer (1952) was the first to realistically incorporate atmospheric structure into the problem. Observation in 1955 of Lyman- α scattering from the geocorona, the atomic-hydrogen cloud around the Earth, and many more recent satellite and space-probe measurements have led to a number of interpretive and theoretical papers, which Chamberlain (1963) and Tinsley (1974) have reviewed. Composition and structure of other atmospheres are discussed by Hunten (1971b) and Ingersoll & Leovy (1971).

Escape from a planet is intimately linked to the nature of the exosphere, the region in which the mean free path is so long that collisions can be neglected for many purposes. Most atoms in the exosphere are in free ballistic orbits; a few of the fastest ones may be on escape orbits. The bottom of the exosphere is the critical level, or exobase, defined as where the mean free path (in the horizontal direction) is equal to the scale height. The conventional approximation of the critical level is that the atmosphere is fully collisional below it and collisionless above; Chamberlain (1963) discusses the validity of this approximation. The planetary corona can be defined as the hydrogen component of the exosphere.

Global averages are used throughout most of the present review. The exosphere is actually asymmetric to a considerable degree, as are the escape processes. Nevertheless, the long mean free path permits a great deal of lateral flow, which helps to justify the approximation of spherical symmetry (McAfee 1967; Vidal-Madjar & Bertaux 1972; Tinsley 1974; Tinsley, Hodges & Strobel 1975).

Atmospheric escape is an interesting phenomenon, particularly for its effect on

the evolution of atmospheres. Loss of hydrogen creates free oxygen at significant rates, for example, twice the amount now in the Earth's atmosphere if the current rate has always been valid. On Mars, it is probable that the oxygen also escapes nonthermally, in such a way that the hydrogen loss is balanced. The recent appreciation of nonthermal processes has totally changed our picture of atmospheric escape. This has been accompanied by a simple means of describing the important diffusion effects that link the upper and lower atmospheres (Hunten 1973b). Space limitations have kept the descriptions brief; many sections must be regarded as little more than guides to the literature.

PROCESSES

In this section we discuss the various individual processes that enter into the picture of hydrogen loss: the escape mechanisms themselves, the production of H and H₂ from other molecules, and the ionization of H atoms.

Thermal or Jeans Escape

The escape flux ϕ_J is readily derived with the postulate of a critical level, a surface from which all the escaping atoms are regarded as originating. A convenient variable is the ratio of gravitational to thermal energy:

$$\lambda = \frac{GMm}{KTr} = \frac{V_{\text{esc}}^2}{U^2} = \frac{r}{H}. \quad (1)$$

G is the Newtonian gravitational constant, M the mass of the planet, m the mass of the atom, k Boltzmann's constant, T the temperature, r the distance from the center of the planet, v_{esc} the escape velocity at r , $U = (2kT/m)^{1/2}$, a thermal velocity, and $H = kT/mg$ the scale height (g is the acceleration of gravity at r). The Maxwell-Boltzmann velocity distribution is weighted by the cosine of the zenith angle and integrated over the upper hemisphere, and from v_{esc} to infinity, to give the flux:

$$\phi_J = n_c w_J = n_c BU(1 + \lambda_c) \exp(-\lambda_c)/2\pi^{1/2}. \quad (2)$$

Subscript c refers to the critical level; n_c is the number density of H atoms at the critical level, and w_J a velocity defined by the second equality, usually called the effusion velocity. The factor B , usually between 0.5 and 1, is discussed below.

Taking account of the variation of gravity with height, the barometric equation for an isothermal upper atmosphere reads

$$n = n_c \exp(\lambda - \lambda_c). \quad (3)$$

According to Equation 3, the density at infinity has the finite value $n_c \exp(-\lambda_c)$, another indication that escape must be important, unless λ_c is very large. Despite this defect in Equation 3, it is a useful approximation at the heights of primary interest. Corrections are discussed by Herring & Kyle (1961), Chamberlain (1963), and Hunten (1973b). Substitution of Equation 3 into Equation 2 gives

$$\phi_J = nBU(1 + \lambda_c) \exp(-\lambda)/2\pi^{1/2}. \quad (4)$$

Except for the slowly varying term $(1 + \lambda_c)$, Equation 4 does not contain any reference to the critical level; it may be evaluated at any convenient height with a temperature equaling that of the critical level that is connected to it by Equation 3. This result illustrates why the exact definition of the critical level is unimportant. The simplest possible definition may therefore be adopted: at the critical level, the mean free path is equal to the scale height, and the probability is $1/e$ that a particle travelling straight up can either escape totally from the planet or can go into a free elliptical orbit. In terms of the collision cross-section $Q \simeq 3.3 \times 10^{-15} \text{ cm}^2$, the total density at the critical level is given by

$$n_{ct} H_{ct} Q = 1. \quad (5)$$

For the Earth, the corresponding height is 450–500 km.

A detailed discussion of the validity of Equations 2 and 5 has been given by Chamberlain (1963). He confirms their accuracy and shows that they are intimately linked to the existence of the Maxwell-Boltzmann velocity distribution. Because hydrogen atoms in the high-velocity tail are escaping, this tail must be at least slightly depressed. Graphic illustrations of this effect are given by Öpik & Singer (1961).

Subsequently, several authors attempted to calculate the corresponding reduction of the escape flux. Brinkmann (1971) and Chamberlain & Smith (1971) finally obtained convergence. The effect depends on the ratio of masses of the escaping and background gases; with a large ratio, energy exchange during a collision is inefficient and the deviation larger. The deviation also increases as escape becomes more rapid, or λ_c smaller. Typical values for the Jeans ratio B (i.e., actual flux divided by Jeans flux) are 0.50 for Mars (H in CO_2), 0.72 for Earth (H in O), and close to unity for equal masses.

Equation 2, corrected in this way, gives a relation between the escape flux and the density n_c . Until recently, it was assumed that n_c was determined by the atmospheric structure and that the flux can thus be obtained. It is often the reverse, however; Hunten first realized this for Titan (Hunten 1973a), and it was later applied to the Earth (Hunten 1973b, Hunten & Strobel 1974, Liu & Donahue 1974a). The hydrogen flux can be determined by processes acting hundreds of kilometers below the critical level, and the Jeans equation then serves to adjust the density appropriately. This was recognized much earlier for hydrogen atoms above 100 km, but the full implications were not realized at the time.

In fact, both Hunten & Strobel and Liu & Donahue found the thermal escape flux is only one-third to one-half what was expected. Liu & Donahue (1974b,c) therefore proposed that escape of nonthermal atoms produced by charge exchange with fast protons, along with a smaller contribution by direct proton escape at polar latitudes compensated for the difference. These processes are discussed in the next two sections.

Charge Exchange

The Earth's plasmasphere contains a component of hot protons trapped in the magnetic field. According to Serbu & Maier (1970), the temperatures range from

5000° to 20,000°K and the density can be as large as 10^4 cm^{-3} at $r = 1.5$ Earth radii on the day side. These protons cannot escape, but they can exchange charge with exospheric hydrogen atoms:



The result is a thermal proton and a fast atom that is almost certain to escape unless directed at the Earth. The cross-section is large: $4 \times 10^{-15} \text{ cm}^2$. The significance of escape by charge exchange was pointed out by Cole (1966), and a crude quantitative estimate has been made by Tinsley (1973). He stresses that the Serbu & Maier ion densities may be somewhat too large. The rate of reaction, Equation 6, per unit volume is $kn(r)n^+(r)$, where k is the rate constant calculated by Dalgarno (1960) and n^+ is the proton density. Tinsley multiplied this rate by the geometrical factor, $(r/r_c)^2$, to normalize the flux to the critical level, and another factor, g , to account for the fraction of particles travelling in directions that will permit them to escape. Thus he obtained

$$\phi_E = \int g(r/r_c)^2 kn^+ dr \quad (7)$$

as the contribution to the charge exchange flux from $1.5R_E$ to infinity. Using a hydrogen density at the critical level of about $3 \times 10^4 \text{ cm}^{-3}$, which is appropriate to a thermal escape flux of $10^8 \text{ cm}^{-2} \text{ sec}^{-1}$ at 1250°K (the day side of this model), Tinsley found the corresponding charge exchange escape flux to be $4 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$, averaged over the globe, or four times the thermal flux. Thus, even if Tinsley's estimate is too high, it seems likely that the charge-exchange process is somewhat more important than the Jeans process.

Proton Escape

Because of the magnetic field, protons cannot normally escape from the Earth. There is one exception: at high magnetic latitudes, the field lines are "open," being drawn out into a long tail by the solar wind. Proton escape along these lines is so rapid as to constitute a "polar wind" (Banks & Holzer 1969). The flow is greatly aided by an upward electric field caused by the more mobile electrons escaping, combined with O^+ ions remaining in the ionosphere. Velocities typically approach 10 km/sec at $r = 2$ earth radii. For a particular choice of neutral-hydrogen density, Banks & Holzer obtain ion fluxes in the neighborhood of $5 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$. Liu & Donahue (1974b) estimate that the fraction of the global area is 6%, and the mean flux is therefore $3 \times 10^7 \text{ cm}^{-2} \text{ sec}^{-1}$. Modified estimates, adapted to specific conditions, are given below in the discussion of the Earth.

Solar Wind Sweeping and Accretion

The solar wind, for the present purpose, may be considered a fully ionized hydrogen plasma that carries an embedded magnetic field and sweeps past the planets at a typical velocity of 320 km/sec. At the Earth's orbit, the proton and electron densities are 8 cm^{-3} and the fluxes therefore $F = 2.5 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$ (Hundhausen 1972). At Venus and Mars, the densities and fluxes are 1.9 and 0.37 as great.

Because of the magnetic field, any ions created in the solar wind are swept away. The details of the process involve the motional electric field, which causes the new ions to move on a cycloidal trajectory. Such details are of interest near the limb of a planet, where the transverse motion may carry the ions into the atmosphere instead of downstream, but the total mass loss is affected very little (Wallis 1972; Cloutier, Daniell & Butler 1974). We therefore adopt the simple description of Michel (1971): new ions are caught up in the solar wind and swept away.

The geometry of the flow past the various planets is discussed below, along with the shielding of the Earth by the geomagnetic field. First, however, we discuss the creation of ions in the outer atmosphere.

ION PRODUCTION One limit on the loss rate from a planet is the rate at which ions can be created. The planetary hydrogen corona is optically thin to solar ionizing radiation, and the ionization coefficient J can be calculated by integrating the product of solar photon flux and the ionization cross-section over all frequencies. The result is $J = 5 \times 10^{-8} \text{ sec}^{-1}$ for the Earth; the mean lifetime of an atom is $1/J = 2 \times 10^7 \text{ sec}$, or about eight months. The column abundance of H above the exobase is about $5 \times 10^{12} \text{ atoms/cm}^2$ (Meier & Mange 1973), and the corresponding ion production rate is $2.5 \times 10^5 \text{ ions cm}^{-2} \text{ sec}^{-1}$. Allowance for shadowing on the night side reduces this number to around $1.5 \times 10^5 \text{ cm}^{-2} \text{ sec}^{-1}$ as a global mean. With the total escape rate over $10^8 \text{ cm}^{-2} \text{ sec}^{-1}$, the photoionization rate is trivial by comparison.

For the Earth, a much more potent process exists: ionization of O atoms followed by the charge exchange



Reaction 8 happens to be resonant, and can proceed in either direction at a rapid rate (Fehsenfeld & Ferguson 1972). Because the total production of O^+ is enormous compared to the photoionization of H, the net direction is very much to the right. The large polar wind flow discussed above essentially originates through Reaction 8. On Mars and Venus, any such processes are much less important, and the potential of ion escape is correspondingly much more limited.

SWEEPING The capacity of the solar wind to pick up atmospheric ions is limited (Biermann, Brosowski & Schmidt 1967; Cloutier, McElroy & Michel 1969). If the added mass flux exceeds the incident mass flux by a factor $\sigma \simeq 9/16$, a shock forms, and the solar wind is diverted around the planet. Michel (1971) has estimated the maximum possible mass addition to this diverted flow, using Figure 1 as a model. The lowest flow line to return to space is determined by the new atmospheric ions as just outlined; therefore the mass loss is essentially independent of atmospheric density. If all ions above the dividing level are lost, the height integral gives a factor H and the integral around the limb gives $2\pi r \sin \theta$. If F is the proton flux in the solar wind, the maximum swept-flux is σF , and the total number of protons carried away per second is $(\sigma F)(2\pi r H \sin \theta)$. This may be divided by $4\pi r^2$ to get the global-mean flux. Michel estimates that $\sigma \sin \theta$ is approximately 0.34; the result is therefore

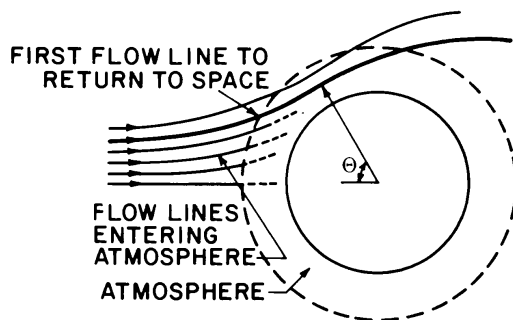


Figure 1 Michel's model for flow of solar wind past an unmagnetized planet. Probably the angle θ of closest approach is considerably smaller than the sketch.

$$\phi_s \simeq 0.34FH/2r = 0.17F/\lambda, \quad (9)$$

where $\lambda = r/H$ as before. For Venus, $\lambda \simeq 15$ at a temperature of 400°K , and ϕ_s therefore $5 \times 10^6 \text{ cm}^{-2} \text{ sec}^{-1}$. It is not much less for Mars, where F and λ are both reduced by a similar factor.

For Earth, the solar wind is deflected by the magnetosphere at a great distance, and the picture outlined here does not apply. Instead, we have the more potent processes discussed in earlier sections. The magnetosphere protects the atmosphere from a direct interaction, but evidently the indirect effects become much larger; in a sense, the magnetosphere gathers energy from a large cross section of solar wind and makes some of it available for escape.

ACCRETION In Figure 1, the solar wind flow below the dividing line runs into the planet; the separation of the flow lines is exaggerated for clarity. Without this distortion, the corresponding area upstream in the solar wind is probably much less than πr^2 . If the factor is ~ 0.1 , the number of protons accreted per second is $\sim 0.1\pi r^2 F$; the ratio of gain to loss is $\sim \lambda/7 \sim 1$. Most likely, then, for an unmagnetized planet with an atmosphere the gain of hydrogen from the solar wind is of the same order as the corresponding loss.

On the Earth, the loss seems to be dominant. Johnson & Axford (1969), in a discussion of the He^3 budget, adopted an auroral proton flux of $4 \times 10^5 \text{ cm}^{-2} \text{ sec}^{-1}$ (global mean). From the consistency obtained for He^3 , they suggested that this flux might indeed come from the solar wind. In any case, it must be close to an upper limit. A more relaxed limit can be obtained from the neon abundance on the Earth (Junge, Oldenberg & Wasson 1962). Even in the unlikely event that all this neon came from the solar wind, its influx would not exceed $3000 \text{ atoms cm}^{-2} \text{ sec}^{-1}$. With a Ne/H ratio of 5×10^{-5} (Cameron 1973), the hydrogen flux must be less than $6 \times 10^7 \text{ cm}^{-2} \text{ sec}$, and probably is much less. Even this figure, however, is significantly smaller than the estimated loss due to charge transfer.

Diffusion and Mixing

If hydrogen is escaping from the top of an atmosphere, it must be flowing up from its source at or near the surface. The details have only recently come under

scrutiny, and it has become clear that the flow plays an important, sometimes dominating, role in setting the total escape flux (Hunten 1973a,b; Hunten & Strobel 1974; Liu & Donahue 1974a–c). Earlier work directed at the Earth's thermosphere came close to the issue but did not make the final connection because of the practice of taking a lower boundary at 100–120 km (Bates 1959; Bates & Patterson 1961; Mange 1961; Kockarts & Nicolet 1962, 1963).

It is convenient to divide an atmosphere into two regions, the homosphere below and the heterosphere above; the boundary is the homopause. The homosphere is uniform in composition, except for condensable gases and some minor constituents involved in photochemistry. The stirring of the homosphere takes place by vertical motions on all sorts of scales, often loosely termed turbulence; correspondingly, the homopause is often called the turbopause. In the heterosphere, the prevailing situation is diffusive equilibrium; each stable constituent takes up its individual scale height corresponding to its own mass. Unstable or escaping constituents, flowing upward or downward, take up a dynamic distribution that can be obtained from the diffusion equation (as discussed below). This process is appreciably simplified if the constituent can be treated as minor, that is, as making a negligible contribution to the total density. This restriction, though adopted here, is not necessary (Hunten 1973a,b).

FLOW EQUATION A convenient flow equation can be formulated to include both (molecular) diffusion and mixing (or eddy diffusion) (Colegrove, Hanson & Johnson 1965, 1966):

$$\phi_i = -D_i n_i \left(\frac{1}{n_i} \frac{dn_i}{dz} + \frac{m_i g}{kT} + \frac{1 + \alpha_i}{T} \frac{dT}{dz} \right) - K n_i \left(\frac{1}{n_i} \frac{dn_i}{dz} + \frac{m_a g}{kT} + \frac{1}{T} \frac{dT}{dz} \right). \quad (10)$$

Subscript i denotes the flowing constituent (usually H or H₂ in this paper), and a the background atmosphere. The thermal-diffusion factor is α_i ; D_i is the diffusion coefficient and K is the eddy diffusion coefficient. Hunten (1973b) gives a collection of values for D_i , which is conveniently written $D_i = b_i/n_a$; b_i is a binary collision parameter, equal to $2.73 \times 10^{19} \text{ cm}^{-1} \text{ sec}^{-1}$ for H in air, and 1.46×10^{19} for H₂ in air (at 208°K). Typically, b (and D along with it) varies as $T^{0.7}$.

K is best described as a parameter to be determined empirically by fitting a solution of Equation 10 to observations of a suitable tracer. Hunten & Strobel (1974) recommend $K = 3 \times 10^5 \text{ cm}^2 \text{ sec}^{-1}$ near 100 km on Earth, giving high weight to observations of argon, but including helium and oxygen as well. For Venus and Mars, K seems to be close to $10^8 \text{ cm}^2 \text{ sec}^{-1}$, as discussed below.

D_i varies inversely as atmospheric density and therefore grows rapidly with height. The homopause is conveniently and consistently defined as the height where $D_i = K$. The corresponding density is $n_{ah} = b_i/K$. At any appreciable distance from this level, one or the other term in Equation 10 is dominant and the other usually neglected. Useful analytic solutions exist, some of which Hunten (1975) discusses. Hydrostatic equilibrium is obtained when $\phi_i = 0$. In the homosphere, the second term is dominant, and setting the parenthesis equal to zero gives a distribution of n_i parallel to that of n_a . In the heterosphere, the converse is true, and vanishing of the first parenthesis gives the state of diffusive equilibrium.

LIMITING FLOW For the present purpose, a useful transformation of Equation 10 was introduced by Hunten (1973a,b). The mixing ratio $f_i = n_i/n_a$ is used, and a limiting flux, ϕ_l , is defined as follows:

$$\begin{aligned}\phi_l &= \frac{b_i f_i}{1 + f_i} \left[(m_a - m_i) \frac{g}{kT} - \frac{\alpha_i}{T} \frac{dT}{dz} \right] \\ &\simeq \frac{b_i f_i}{H_a} \left(1 - \frac{m_i}{m_a} \right) \\ &\simeq \frac{D_i n_i}{H_a} \left(1 - \frac{m_i}{m_a} \right).\end{aligned}\tag{11}$$

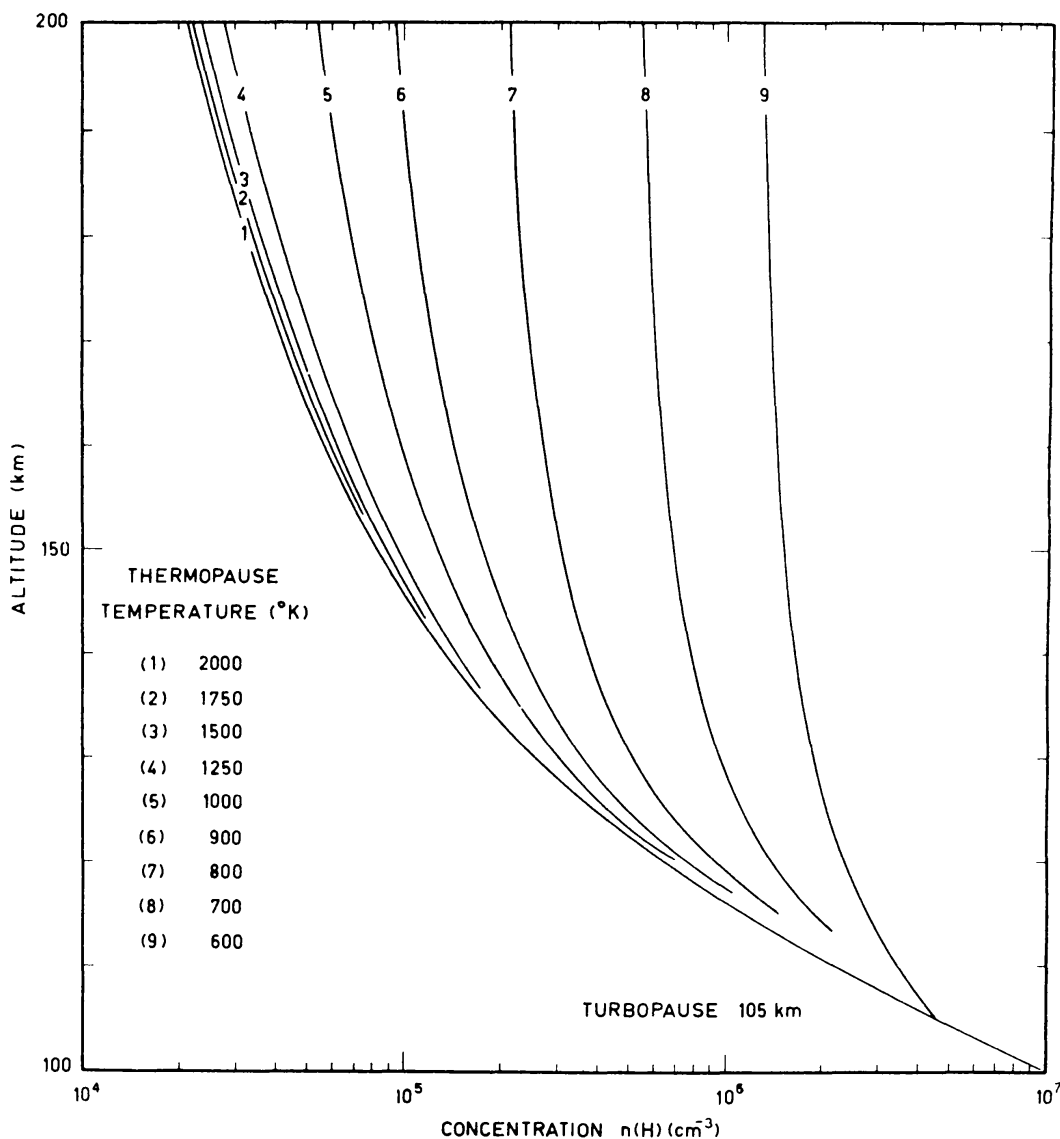


Figure 2 An early model (Kockarts & Nicolet 1963) showing limiting flow of atomic hydrogen. The envelope at the left is the limiting-flow line, and the various curves go into diffusive equilibrium at different points. Only thermal escape is considered.

The approximations hold for a small temperature gradient. A further approximation for a light gas such as H or H₂ is

$$\phi_l \simeq b_i f_i / H_a, \quad (12)$$

and the corresponding limiting velocity is

$$w_l = \phi_l / n_i \simeq b_i / n_a H_a = D_i / H_a.$$

After some manipulation, Equation 11 in Equation 10 gives

$$\phi_i = \phi_l - (K + D_i) n_a \frac{df_i}{dz}. \quad (13)$$

Consequently, there must be a gradient of mixing ratio unless $\phi_i = \phi_l$, although in many cases the gradient is negligibly small. If $\phi_i > \phi_l$, the gradient is negative and the mixing ratio f_i decreases upwards, tending to choke off the flow. Thus, ϕ_l is really a limiting flux, to be exceeded appreciably only where K or n_a is large enough to keep df_i/dz close to zero. These ideas are mainly applied just above the homopause, where both quantities are small. If escape from the top of the atmosphere is easy (normally true for the Earth), the upward flux tends to be only slightly smaller than ϕ_l . Equation 13 then implies $df_i/dz \simeq 0$: the hydrogen takes up almost the same vertical distribution as the background atmosphere. Physically this effect arises because the limiting velocity w_l is inversely proportional to n_a . However, there remains a small upward increase of f_i , and a corresponding increase of ϕ_l by Equation 12. At some height the difference $\phi_l - \phi_i$ becomes large and so does df_i/dz : the hydrogen reverts to diffusive equilibrium with a very large scale height. This behavior is illustrated in Figure 2, calculated by Kockarts & Nicolet (1963). The lower envelope of the curves represents limiting diffusion. (These computations include only the Jeans escape process.)

The consequences of the limiting-flow principle are far-reaching. Given an efficient escape process (e.g. a high-enough exospheric temperature), the maximum possible escape flux can be obtained immediately if the mixing ratio of available hydrogen at the homopause is known (Equations 11 or 12). For hydrogen on Earth (as discussed below and illustrated in Figure 2), the appropriate conditions are usually realized.

The meaning of limiting flow can be illustrated with a transformed heterospheric model of Figure 3 (Hunten 1971a). The whole region has uniform density n_{ah} , its height is therefore H_{ah} , and the critical level is slightly below the top. The diffusion coefficient is $D_h = b/n_{ah} = K$ (from the definition of the homopause); the subscript

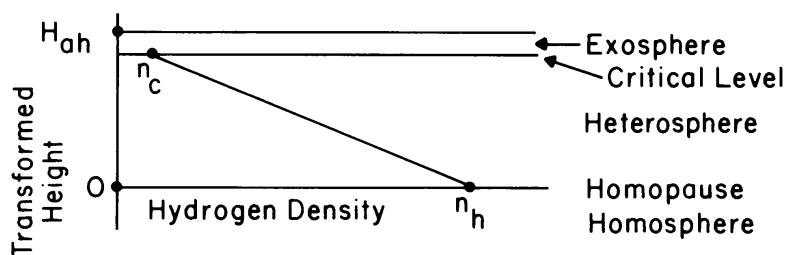


Figure 3 Constant-density model of the heterosphere.

i has been dropped for simplicity. The straight line shows the hydrogen distribution, still with the assumption of easy escape, so that $n_c \ll n_h$. The density drop across the slab is therefore n_h , and the elementary diffusion equation gives $\phi = -D_h dn/dz = D_h n_h/H_{ah} = b f_h/H_{ah}$, which is Equation 12. Diffusive equilibrium, on the other hand, corresponds to $n_c \simeq n_h$ and a much smaller flux.

CRITERION FOR LIMITING FLOW We now give an approximate criterion to decide whether or not limiting flow is likely. If the result is borderline, a more detailed examination is necessary. In the limiting-flow situation, $n_c \ll n_h$, as just discussed; in the classical or Spitzer (1952) situation, $n_c \simeq n_h$. We use the limiting velocity at the homopause, $w_h = D_i/H_a = K/H_a$. For the Earth, $w_h = 3 \times 10^5/6 \times 10^5 = 0.5$ cm/sec. Correspondingly, there is an effusion velocity w_c at the critical level; it includes the Jeans velocity w_J of Equation 2 and contributions from any other significant escape processes. The smaller of these two velocities indicates the controlling, or bottleneck, process, i.e. diffusion or escape (Hunten 1973b). In this simple discussion, it is assumed that the critical level and homopause are not very far apart, so that inverse-square effects can be neglected and the scale height of hydrogen taken as infinity.

ION FLOW Large upward and downward fluxes of protons take place on the Earth as ionospheric and magnetospheric conditions change, and the high-latitude flux has already been mentioned as an escape process. All these flows are limited in a manner closely analogous to the discussion above (Hanson & Ortenburger 1961, Banks & Holzer 1969, Banks & Kockarts 1973). The diffusion coefficient for protons is much smaller than for atoms because of the Coulomb interaction with ions and the efficient charge-transfer process (Equation 8).

TOTAL HYDROGEN For the homosphere, a useful flow equation can be written to describe "total hydrogen": the sum of all hydrogenous constituents weighted by the number of hydrogen atoms (Thomas 1973, Hunten & Strobel 1974). At heights where $D_i \ll K$, Equation 13 becomes approximately $\phi_i \simeq -K n_a (df_i/dz)$. We write one such equation for each component of total-H, weight as described above, and add. The result is

$$\phi_t = -K n_a \frac{df_t}{dz} = \text{constant.} \quad (14)$$

The total flux must be constant because there can be no sources or sinks of total-H. This result neglects molecular diffusion but nonetheless is accurate enough to indicate the true situation. Processes such as precipitation are not included, so this result is not valid in the troposphere.

Equations 12 and 14, applied to Earth, make predictions that detailed computation confirms (Hunten & Strobel 1974; Liu & Donahue 1974a,b,c). The total-H flux at 30 km is equal to the escape flux (apart from a small r^2 factor). This flux is small enough that df_i/dz is essentially zero throughout the homosphere, that is, f_i is constant from 30 to 100 km. If the chemical form of hydrogen is known at 100 km (the homopause), the limiting flux can be obtained by the expression

$\phi_i = b_i f_i / H$; this flux is therefore almost completely determined by the value of f_i in the stratosphere. The dominant form at 100 km is H_2 , which is converted to atoms in the heterosphere (Process 15 below).

Hydrogen Sources

At first sight, the only significant source of escaping hydrogen would seem to be H_2O , which is so abundant in our own environment. In fact, this is far from clear, even for the Earth, where CH_4 seems to be more important, perhaps dominant. On Venus an important source is HCl . On all planets H_2 must be considered, if only as an intermediate, and for primitive atmospheres NH_3 (as well as CH_4) must be included.

DISSOCIATION The stable molecules listed above must be broken up, either by solar photons or free radicals. Photolysis occurs mainly above 40–50 km on the Earth and all the way to the cloud tops on Venus and the surface on Mars. Computation of the rate for a given molecule requires integration over the wavelength of the cross-section multiplied by the attenuated solar flux. The result is a photodissociation coefficient J , as introduced above for ion production. Information on cross-sections is found in reviews by McNesby & Okabe (1964) and Hudson (1971). J coefficients are given by Kockarts (1971) for H_2O in air, by Nicolet (1971) for CH_4 in air, and by Hunten & McElroy (1970) for H_2O in CO_2 . Photolysis of CH_4 commonly produces H_2 directly; some of the events with H_2O at short wavelengths do the same. Dissociation rates (J multiplied by concentration) for H_2O and HCl on Venus are shown by McElroy, Sze & Yung (1973).

FREE RADICALS Methane is destroyed by reaction with OH and metastable $O(^1D)$, and H_2 and H_2O by the latter. These processes become dominant below about 50 km on Earth, where the $O(^1D)$ is produced by photolysis of O_3 . Densities are given (as diurnal means) by McElroy et al (1974). For the present purpose, the subsequent reactions after methane is first attacked are considered instantaneous, leading finally to two water molecules per methane molecule.

Hunten & McElroy (1970), considering the $O(^1D)$ processes for Mars, found that H_2O destruction is probably much less than direct photolysis. They found that a considerable amount of H_2 is produced in subsequent reactions, and its reaction with $O(^1D)$ is important, particularly at high latitudes where H_2O is frozen out and there would otherwise be no odd hydrogen.

Ozone is rarer on Venus, and the production rate of $O(^1D)$ correspondingly slower; it probably does not play a significant role. More likely, the chlorine atoms from HCl photolysis split up H_2 into atoms. This effectively accomplishes photolysis of H_2 , which is very slow by direct absorption. The reverse reaction also occurs (McElroy, Sze & Yung 1973; Sze & McElroy 1975).

At high altitudes on all three planets, an important question is how quickly H_2 can be broken up into atoms. As just mentioned, photolysis is very slow, and in any case attenuation by other gases inhibits it. On the Earth, a very efficient process operates at the high temperatures above 130 km (e.g. Hunten & Strobel 1974):



An H_2 molecule is thus split by formation of an O_2 molecule. High temperatures are required because the first step is slightly endothermic. Reaction with $\text{O}(^1\text{D})$ is also significant below 130 km.

The temperatures on Mars and Venus are now regarded as too low for Process 15 to operate, and the O densities are small as well. Instead, there is an ionospheric process (McElroy & Hunten 1969b):



The ion X^+ can be CO_2^+ , CO^+ , O^+ , or N_2^+ , but not O_2^+ or NO^+ . O_2^+ is currently favored over CO_2^+ as the major ion on both planets, and on Mars at least the conversion of H_2 may be incomplete (Liu & Donahue 1975b). One model of Venus shows considerable, but not complete, conversion (Kumar & Hunten 1974).

ODD AND EVEN HYDROGEN The constituents discussed above are long-lived, and discussions of their behavior must include eddy and diffusive transport. Their unstable products, however, have short lifetimes and are conveniently lumped together as “odd hydrogen”: they are H , OH , and HO_2 . H_2O_2 , which is sometimes included, is effectively a dimer of OH and rapidly splits into $2(\text{OH})$ through photolysis. Conversion of odd back to even hydrogen (H_2 and H_2O) occurs through the reactions



(or $\text{OH} + \text{OH}$, or $\text{H}_2\text{O} + \text{O}$)

The importance of the radical HO_2 is obvious, but unfortunately its reaction rates are difficult to measure. The rate coefficient of Reaction 17 has been measured as $2 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$, but there are strong theoretical reasons for expecting it to be an order of magnitude smaller (Kaufman 1975). The branching ratio of Reaction 18 has not been measured. The first branch shown is particularly important because it is a major source of H_2 , which dominates the flow on all three terrestrial planets. Estimates for the partial rate coefficient range from $1.5 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ (Hunten & McElroy 1970) to $1 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ (McElroy & Donahue 1972). Liu & Donahue (1974c) find that simultaneously low values for both reaction rates give predictions for the Earth's mesosphere that disagree with observations (cf Figures 5–7 below).

These uncertainties are tolerable for Earth because the escape is controlled to a first approximation by limiting flow of total hydrogen. For other problems and other planets the consequences are more serious.

CONDENSATION The availability of H_2O at heights where it can be converted to odd hydrogen and to H_2 is very much limited by condensation on all three terrestrial planets. For Earth and Mars, the process is freezing out at low temperatures; for Venus, it seems to be absorption in the clouds of concentrated H_2SO_4 .

An important but subtle question is the existence and behavior of cold traps, which are named for their counterparts in laboratory vacuum systems but are not nearly as well understood. Air, in passing through a cold region, loses its vapor by condensation and precipitation and subsequently contains only that amount corresponding to the vapor pressure at the minimum temperature. For many problems, including that of escape, the important quantity is the mixing ratio, rather than the partial pressure. A cold trap is therefore most significant if it operates at a high total pressure. For example, the Earth's mesopause is much colder than the tropopause, but the latter is much more important as a trap, and condensation at the mesopause, which forms noctilucent clouds, occurs only under special conditions.

At balloon heights on the Earth, the volume mixing ratio of H_2O is about 4×10^{-6} or 4 ppm (Mastenbrook 1968, Hunten & Strobel 1974). The reason for this remarkably low value is not really understood, although a cold trap at the tropical tropopause may be involved (Urey 1959). Perhaps even more remarkable is that the stratosphere is almost certainly a source of H_2O by oxidation of CH_4 (Bates & Nicolet 1965), and even probably by oxidation of H_2 . Recent models agree in finding a large downward flux of H_2O (around $5 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$) out of the stratosphere (Hunten & Strobel 1974, Liu & Donahue 1974c). Since the methane is biological in origin, and perhaps also the H_2 , the present escape rate from Earth is apparently controlled by biological processes. This control is only possible, however, because of the efficient cold trap for H_2O .

For Mars, the observed amount of water vapor fluctuates greatly, but a typical value is a few precipitable microns, or $10^{19} \text{ molecules cm}^{-2}$ (Hunten 1971b). The vertical distribution is unknown, but Hunten & McElroy (1970) argued on the basis of typical temperature profiles that the vapor must be largely confined to the bottom 5 km. They estimated the production rate of odd hydrogen, suggesting a mean of $2 \times 10^9 \text{ cm}^{-2} \text{ sec}^{-1}$. Recently Liu & Donahue (1975b) arrived at a similar picture after first trying a scheme in which water vapor was abundant as high as 40 km; they could not tolerate the large OH production at this height.

Parkinson & Hunten (1972) pointed out that surface condensation is probably important for other components of the hydrogen system, notably H_2O_2 and HO_2 . Hunten (1974) has further discussed this suggestion. The vapor pressure of H_2O_2 is similar to that of H_2O ; the fact that it freezes out at high Martian latitudes is likely to be an important drain on odd hydrogen during the winter and perhaps an important source in spring. HO_2 also freezes out, though information is mainly confined to temperatures lower than those reached on Mars. When the deposit is warmed, gases released at O_2 , H_2O_2 , and H_2O .

The visible clouds of Venus are almost certainly concentrated sulfuric acid, around 85% H_2SO_4 by weight or 50% molar (Young 1975). This material's strong affinity

for water explains the extreme dryness of the Venus stratosphere (around 1 ppm H_2O); this had previously been puzzling because Venus seems to lack any sort of cold trap (McElroy & Hunten 1969a). A lower limit to total-H on Venus is the HCl abundance, 0.6 ppm (Connes et al 1967). The H_2 abundance is unknown and could conceivably raise this figure by a factor of more than 10.

THE PLANETS

With the background developed above, we now discuss the Earth, Venus, and Mars in turn.

Earth

As outlined earlier, three principal mechanisms contribute significantly to hydrogen escape. Before discussing the details, we summarize our present views of their relative importance, using an exospheric temperature of 1000°K . The classical Jeans process is responsible for only 20% of the loss rate. Charge exchange with plasma-spheric protons dominates, accounting for over 70%. Polar ion flow accounts for 7%. The total flux is governed fairly accurately by the limiting-flow principle of Hunten (1973b). Each component of the flux is very nearly proportional to the H density n_c at the critical level. But the Jeans flux is also very sensitive to temperature (Equation 2). An increase of exospheric temperature increases this component and depresses n_c . The other two components are therefore reduced, and the same total flux will be maintained. Its value is $(2-3) \times 10^8 \text{ atoms cm}^{-2} \text{ sec}^{-1}$.

RECENT PROGRESS As mentioned above, the principle of limiting flow for thermospheric hydrogen was implicit in the work of Bates, Patterson, Mange, Kockarts, and Nicolet around 1960 and had been formulated for ion flow by Banks and his collaborators. But a formal statement came out of work on Titan by Hunten (1973a), then expanded to other planets (Hunten 1973b). Somewhat oversimplified, it reads as follows:

“The mixing ratio f_i of total-hydrogen is the same at the homopause and in the lower stratosphere. The escape flux is then closely approximated by $\phi \simeq bf_i/H_a$. (Equations 11 and 12), where b is the collision parameter for H_2 molecules.”

Thus, once f_i has been set in the stratosphere, the escape flux is determined by the mix of H and H_2 at the homopause. For the principle to work, all forms of hydrogen must be convertible to H and H_2 at the homopause, H_2 must convert to H below the critical level, and H must escape freely. All these conditions are normally satisfied on the Earth, with a possible exception at low exospheric temperatures (discussed below).

A detailed aeronomical model of the region from 50 km to the critical level was next studied by Hunten & Strobel (1974). The only escape was by the Jeans process (which had been omitted in all previous models of this kind). The general ideas were rather accurately verified: the escape flux was independent of variations in reaction rates and solar ultraviolet flux and nearly independent of eddy diffusion coefficient. H_2 was found to outweigh H at the homopause; variations in the ratio

were the main contributor to variations in escape flux. Almost simultaneously, a similar, independent study by Liu & Donahue (1974a), who also varied the exospheric temperature, found the expected reduction of flow for temperatures below 1000°K. Otherwise, the flux was $1.8 \times 10^7 \text{ cm}^{-2} \text{ sec}^{-1}$ for each 1 ppm of stratospheric hydrogen.

In different ways, both papers noted a discrepancy between stratospheric and exospheric observations. In the stratosphere, f_t is 9–14 ppm; the Jeans flux at 1100°K is close to $5 \times 10^7 \text{ cm}^{-2} \text{ sec}^{-1}$ from observations of H density and temperature. Hunten & Strobel took $f_t = 9$ ppm and computed a flux of $1.5 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$. They noted the discrepancy but concluded that it was probably within the combined errors. Liu & Donahue started with the escape flux and computed a total-H mixing ratio; with an upper limit of $1 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$ for the flux, f_t could not exceed 5 ppm. The agreement between the two investigations is excellent. Liu & Donahue, however, concluded that the discrepancy was real. The stratospheric measurements could have been faulty, but more probably other escape mechanisms were at work.

Another discrepancy discussed in both papers relates to an observed variation of Jeans flux with solar activity (Vidal-Madjar, Blamont & Phissamay 1973; Blamont, Cazes & Emerich 1975). Such a variation seemed natural on the old Jeans-Spitzer picture, but it does not accord with the computations when thermal escape is the only loss process.

Liu & Donahue (1974b) therefore investigated polar ion flow and charge exchange as supplementary processes, showing that charge exchange in particular seemed to be large enough to resolve the discrepancies. Shortly thereafter and independently, Bertaux (1974, 1975) made the same suggestion, but without quantitative estimates. He was influenced by his satellite results, which showed a variation of Jeans flux with solar activity, and he realized the conflict with the limiting-flow principle.

THE PRESENT POSITION A consistent picture, including all three loss processes, was given by Liu & Donahue (1974c). The partitioning of the constant total flux among the three processes was done, somewhat arbitrarily, as follows.

The total flux was taken as $\phi_t = 2.68 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$, corresponding to $f_t = 14.8$ ppm at 50 km: 0.5 ppm of H₂, 0.25 ppm of CH₄, and 6.4 ppm of H₂O. All three fluxes are proportional to n_c , which must be determined consistently. The factor was taken as $n_c w_J = \phi_J$, calculated from Equation 2 with a Jeans ratio of $B = 0.73$. The charge-exchange flux ϕ_E varies as the column amount of hydrogen and therefore as $n_c H_c$. Tinsley's estimate, $\phi_E = 2 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$, refers to a temperature of 1000°K, correspondingly gives $\phi_J = 5 \times 10^7 \text{ cm}^{-2} \text{ sec}^{-1}$. These assumptions produce

$$\phi_E = 2 \times 10^8 \frac{n_c H_c}{(n_c H_c)_{1000}} \cdot \frac{\phi_J}{5 \times 10^7} \text{ cm}^{-2} \text{ sec}^{-1}. \quad (19)$$

The polar wind component is proportional to a slowly varying function of temperature, ϕ_{P0} , adapted from computations of Banks & Holzer (1969), thus giving

$$\phi_P = \phi_{P0} \frac{\phi_J}{5 \times 10^7} \simeq 0.36 \phi_J. \quad (20)$$

where $\phi_{p_0} \simeq 1.8 \times 10^7 \text{ cm}^{-2} \text{ sec}^{-1}$ is approximately valid over the temperature range considered. The sum $\phi_J + \phi_E + \phi_P$ is set equal to ϕ_t , and ϕ_J is found (Equation 5 of Liu & Donahue 1974b). The three components are shown in Table 1, and ϕ_J is plotted as the solid line in Figure 4. The other lines are deduced from observations. The agreement is excellent, perhaps better than could be expected in view of the rather crude nature of the theoretical estimates.

As mentioned above, Bertaux (1974, 1975) independently conceived a similar explanation for his OGO-5 data, shown (with a correction by the Jeans ratio) by the dotted line in Figure 4. Previously Vidal-Madjar, Blamont & Phissamay (1974) had remarked on a variability of ϕ_J during the lifetime of OSO-5, ascribing it to a variation with solar activity in the hydrogen density at 100 km. This, as we now know, is not a viable explanation for variations in ϕ_J . In fact, Vidal-Madjar and his colleagues were probably observing the same type of phenomenon found by Bertaux. Their results are shown by the dashed line in Figure 4.

The treatment outlined here is rather intuitive and needs considerable sharpening. Tinsley's estimate of ϕ_E is also crude—a better treatment and a careful assessment of the hot-proton densities in the plasmasphere would be highly desirable. But the basic result seems fairly secure, namely, the total H-atom escape flux is $(2-3) \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$ and accords with measured abundances of hydrogen compounds in the stratosphere. The escape rate accepted in much of the literature since Donahue's (1966) review was too small by a factor of 5–10.

It is still unclear how low the exospheric temperature must drop to produce a substantial deviation from the limiting flux. Liu & Donahue (1974a) note that brief diurnal decreases have little effect because of a substantial hydrogen reservoir between the diffusion region and the escape region. The most appropriate diurnal-mean temperature is near the maximum. The charge exchange process, which dominates in any case at the lower temperatures, is most likely adequate to maintain limiting flow under all common circumstances.

The polar wind and charge-exchange mechanisms are not individually worldwide but have nearly complementary distributions: they correspond respectively to

Table 1 Partitioning of the total escape flux among the three mechanisms at various exospheric temperatures T_c .

T_c (°K)	ϕ_J	ϕ_E	ϕ_P
900	2.6	22.2	1.4
950	3.67	21.2	1.9
1000	5	20	1.8
1100	7.05	16.5	2.9
1200	8.7	13.5	3.6
1500	13.5	8.9	4.4
1900	18.2	5.6	2.9

J stands for Jeans, *E* for charge exchange, *P* for polar wind. Units are $10^7 \text{ cm}^{-2} \text{ sec}^{-1}$. From Liu & Donahue (1974b).

regions of open and closed magnetic-field lines. In their respective regions, the two fluxes are comparable, with the polar component being probably somewhat larger. Some lateral flow from lower latitudes may therefore be required. The site of the flow is the lower exosphere, and it has been studied considerably (e.g. McAfee 1967, Vidal-Madjar & Bertaux 1972, Tinsley 1974). As summarized by Liu & Donahue (1974b), most of the flow into the polar cap comes from a ring about 20° wide just outside it. The cap can thus draw on the limiting flow through a much larger region. The previous focus in lateral-flow studies has been the smoothing of the expected large diurnal variation due to the Jeans flux alone. This variation now

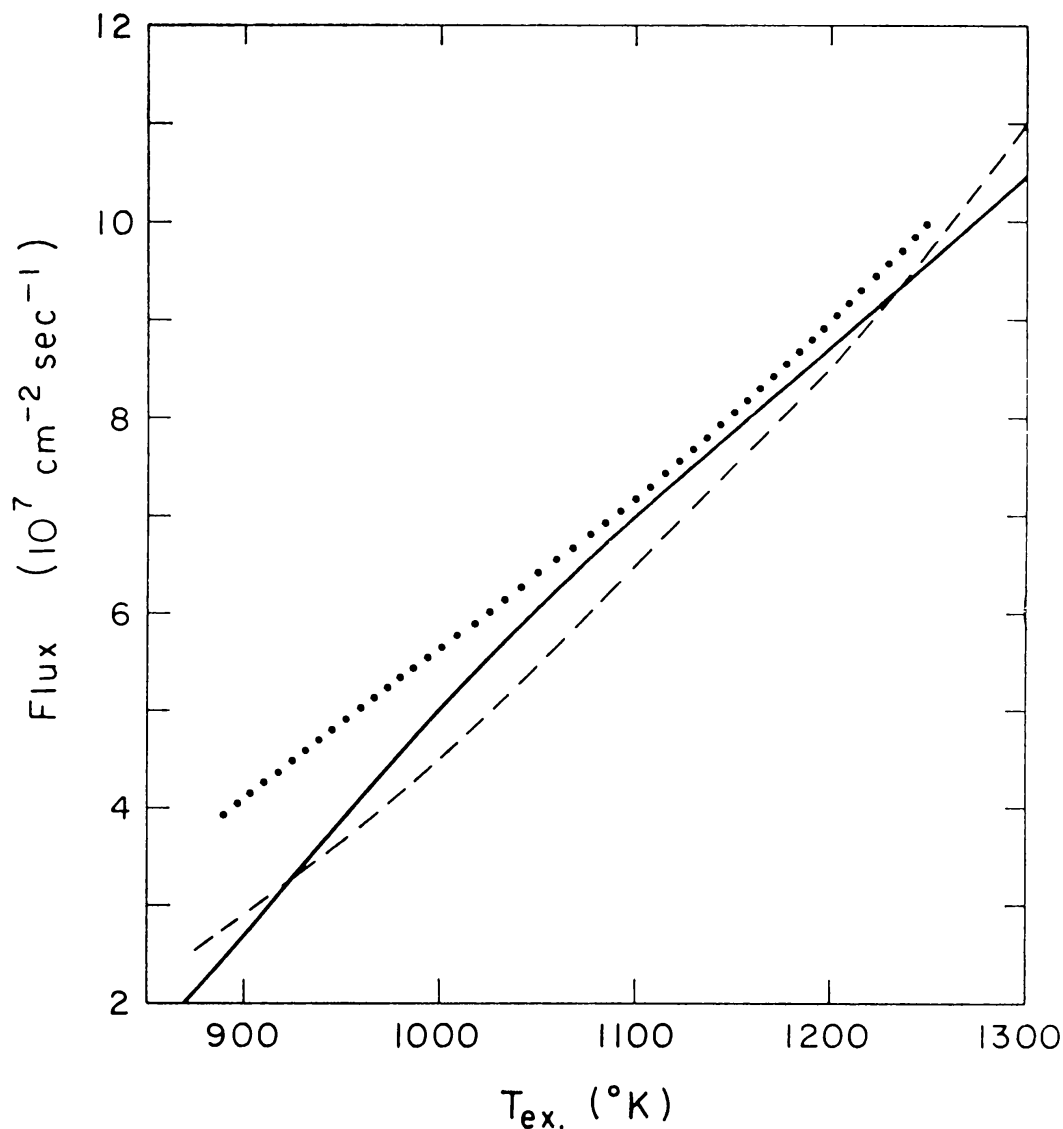


Figure 4 Jeans escape fluxes from Earth as functions of exospheric temperature. The dotted line was observed by Bertaux (1975), the dashed line was observed by Vidal-Madjar, Blamont & Phissamay (1974), and the solid line was calculated. From Liu & Donahue (1974c), with permission of the American Meteorological Society.

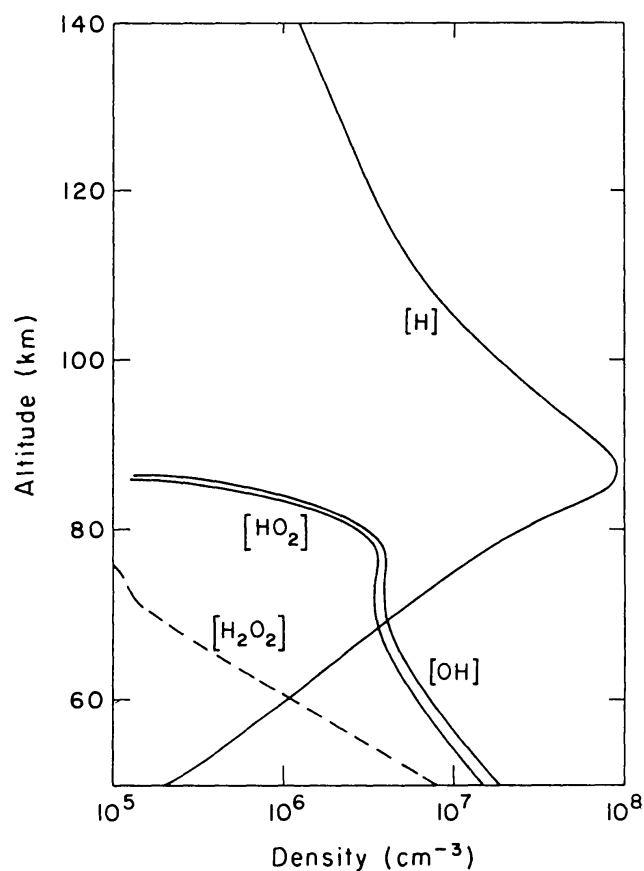


Figure 5 Densities of several hydrogenous constituents in the model of Liu & Donahue (1974c). Reprinted with permission of the American Meteorological Society.

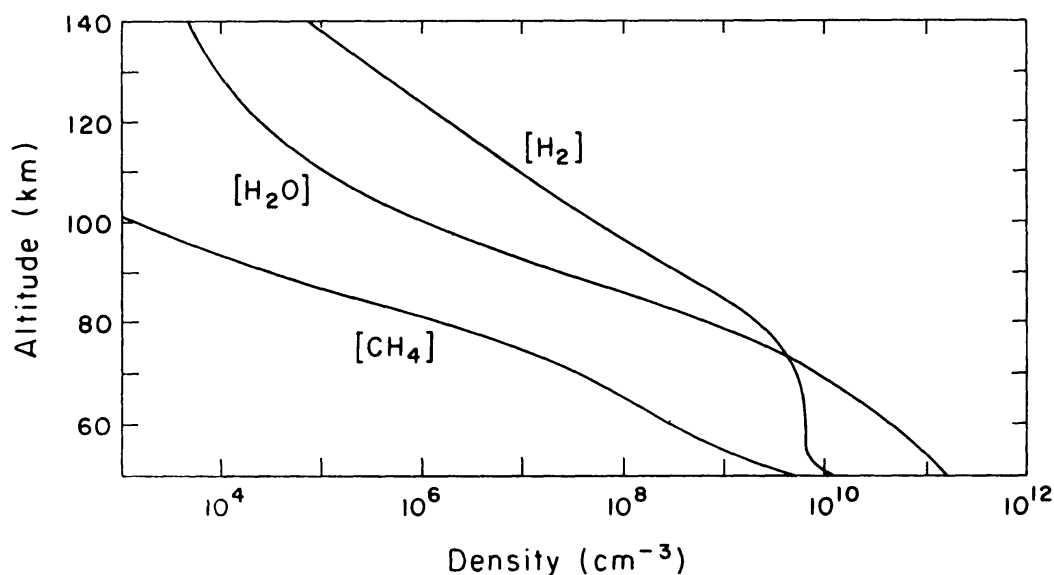


Figure 6 Densities of the other hydrogenous constituents in the model of Liu & Donahue (1974c). Reprinted with permission of the American Meteorological Society.

seems less important, and flow towards the polar regions has to be considered, along with the diurnal variation of the charge-exchange flux.

Figures 5–7 show the densities of hydrogen species and the fluxes for the model of Liu & Donahue (1974c). Particularly noteworthy near the top of Figure 7 is the conversion of the H_2 flux into an H flux by Process 15.

These developments have very much depended on research directed to other planetary bodies. Limiting flow of H in the thermosphere has been known for over 15 years, but the generality of the principle was brought out in Hunten's (1973a) study of Titan. This work was stimulated by observations interpreted in terms of substantial amounts of H_2 in the methane atmosphere of that body. The detailed models of Hunten & Strobel and of Liu & Donahue were both developed out of earlier studies of H_2O photolysis and hydrogen escape on Mars (Hunten & McElroy 1970, McElroy & Donahue 1972). Again, these papers dealt with observed water vapor absorptions and Lyman- α resonance scattering. The influence of planetary studies on our understanding of the Earth is real and important.

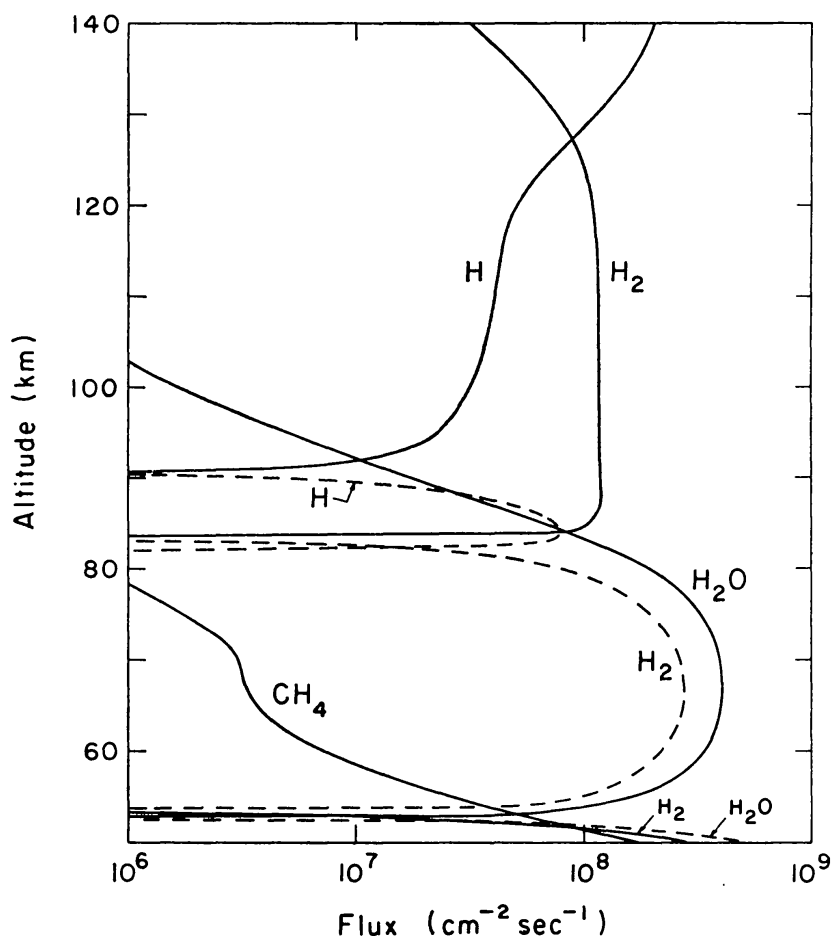


Figure 7 Fluxes in the model of Liu & Donahue (1974c). Solid lines represent upward fluxes and dashed lines represent downward fluxes. Reprinted with permission of the American Meteorological Society.

THE EARLY ATMOSPHERE The revised escape rate of hydrogen has interesting consequences for the Earth's oxygen budget. If the present rate is representative, the corresponding production of free oxygen in 4.5×10^9 years would be 500 g cm^{-2} , or about twice what is now in the atmosphere. Other components of the budget are indicated in Table 2, from Hunten (1973a). The amount of oxygen to produce the Fe_3O_4 now in the crust is nearly 60 times the atmospheric amount. If the oxygen in carbonates also came from the atmosphere, the factor is 270. Hydrogen escape would have had no particular difficulty producing even these amounts in the distant past if the stratosphere had been sufficiently richer in hydrogenous molecules. For example, a flux 10^3 greater than at present would result from a mixing ratio $f_t \simeq 0.4\%$, and would produce all the oxygen in Table 2 in 10^9 years. Loss of hydrogen from CH_4 and NH_3 , if required, is equally plausible.

More conservatively, if the escape rate had been somehow maintained at no more than its present value in the early atmosphere, there would still be around 5% of the present O_2 in the atmosphere by 500–1000 million years ago. At that time, presumably, life was still in a glycolytic stage in the ocean, and respiration with photosynthetic conversion of CO_2 to O_2 had not begun. We can now assume considerably more O_2 than was previously available for the transition to respiratory forms of life. The timetable for the development of life and the conversion of CO_2 to O_2 becomes much more comfortable.

Venus

The basis of nearly all ideas about hydrogen on Venus is the measurements by the Lyman-alpha ($L\alpha$) photometer on Mariner 5 (Barth et al 1967). These results are shown, along with the recent ones of Mariner 10, in Figure 8 (Broadfoot et al 1974). These data are remarkable in two ways: they imply a small H density, and they cannot be represented by a normal exospheric density distribution. They require at least two components, either two masses or two temperatures, in a ratio of 2–3 (Wallace 1969). Suggestions, never very credible, that the inner component might result from stray light were thoroughly refuted by Mariner 10. This spacecraft, however, was not operated in such a way as to be sensitive to the outer component, which was much better observed by Mariner 5.

The first interpretations relied on a computed exospheric temperature of 700°K by McElroy (1968), which gave a good fit to the outer component of $L\alpha$. The inner

Table 2 Oxygen and hydrogen budgets for the primitive Earth

	CO_2	Fe_2O_3	Atmosphere	Totals
Material now present (kg cm^{-2})	72	137	1.035	
O_2 required (kg cm^{-2})	52	13.7	0.24	
H_2O mass (kg cm^{-2})	59	15.4	0.27	
H_2O liquid depth (m)	590	154	2.7	750
H_2 from H_2O (cm^{-2})	2.0×10^{27}	5.2×10^{26}	9×10^{24}	2.5×10^{27}
H_2 from CH_4 , NH_3 (cm^{-2})	2.0×10^{27}	—	5.2×10^{25}	2.5×10^{27}

component would then have a mass of 2. Barth, Wallace & Pearce (1968) identified it with H_2 and suggested that the $L\alpha$ arose by photodissociation at wavelengths short enough to excite one of the atoms. This proposal, also presented (Barth 1968) at the Second Arizona Conference on Planetary Atmospheres, was vigorously attacked by Donahue (1968) in his conference review because of the problem it presented of disposing of the very large number of hydrogen atoms created from H_2 in the model. Later McElroy & Hunten (1969a) showed that the upper limit to the H_2 density in such a model was about 10^7 cm^{-3} at 150 km compared to about 10^{10} cm^{-3} in Barth's model. The obvious alternative seemed to be deuterium atoms (Donahue 1968, 1969; McElroy & Hunten 1969a), which could in principle be greatly enriched in the upper atmosphere. In present-day language, H was to be in an extreme limiting-flow situation and D close to diffusive equilibrium. For this situation to be possible, the eddy-diffusion coefficient K would have to be small, less than $10^5 \text{ cm}^2 \text{ sec}^{-1}$, to give a small homopause velocity w_h . The special assumptions about K and T_c caused no little uneasiness, but the real deathblow to the deuterium hypothesis came from a rocket flight by Wallace et al (1971). Their spectrometer, able to resolve the isotope splitting of $L\alpha$, showed no sign of the required D component.

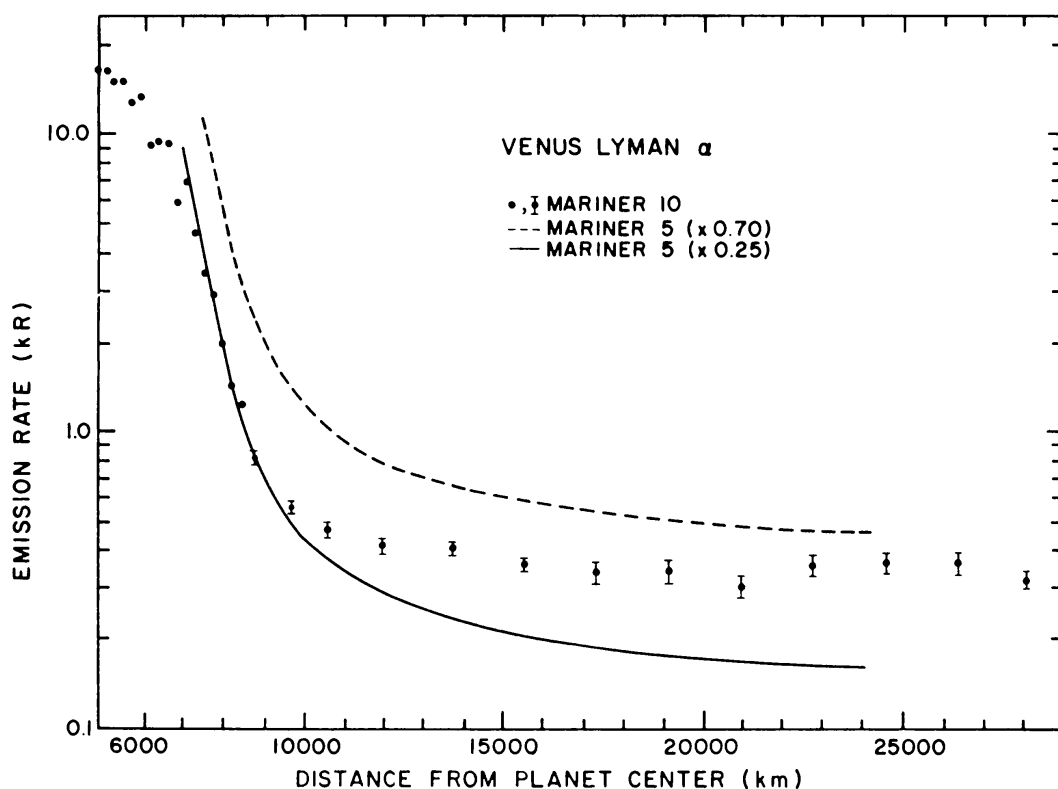


Figure 8 Lyman alpha observations on the day side of Venus. The dashed curve is from a recalibration of Mariner 5, and the solid curve represents an arbitrary further shift needed to match Mariner 10. From Broadfoot et al (1974), with permission of the American Association for the Advancement of Science.

Another problem with Venus was pointed out by J. C. G. Walker (unpublished work) and emphasized by Hunten (1973b) in terms of his limiting-flow principle: a considerable amount of H_2O and HCl exists near the cloud tops of Venus, in addition to an unknown amount of H_2 . The mixing ratio of HCl is 0.6 ppm (Connes et al 1967) and about 1 ppm for H_2O (Young 1972, Fink et al 1972). Thus, there are at least 2.5 ppm of total hydrogen near the cloud tops. The HCl photochemical system of Prinn (1971) would add a mixing ratio of H_2 equal to 10 ppm. Then, according to limiting diffusion, if the limiting flow applied to H , the escape flux of H could not be less than $3 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$ and might need to be as large as $25 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$. The small H densities permitted by the $L\alpha$ data allowed only $10^6 \text{ cm}^{-2} \text{ sec}^{-1}$ for the Jeans process. Hunten (1973b) discussed this dilemma and concluded that the most likely solution was that the exospheric temperature is 350°K . In this case, the component of low scale height would be hydrogen, limiting diffusion would not apply because of the low exospheric temperature, and the destruction of H_2 by O would be inhibited. Then, with an eddy coefficient, K , of $5 \times 10^6 \text{ cm}^2 \text{ sec}^{-1}$, the H_2 density would be at its upper limit of 10^7 cm^{-3} in the thermosphere when the mixing ratio in the lower atmosphere is 4 ppm. Fast atoms from dissociation of H_2 might then provide the "hot" component of $L\alpha$.

This suggestion was taken up by Kumar & Hunten (1974) in work that was completed just before Mariner 10 encounter. Their model ionosphere, at 350°K exospheric temperature, gave a fair fit to Mariner 5 data, although it is considerably poorer with Mariner 10. They did, however, identify some possible sources of hot H atoms with strengths of the required order. They are ion- H_2 reactions of the form of Equation 16, where X^+ is O^+ or CO_2^+ . The corresponding destruction of H_2 limited its density at the critical level to well under 10^5 cm^{-3} . Previously suggested sources of hot H had been judged inadequate by McElroy & Hunten (1969a), including photodissociation of H_2 , which had been advocated by Barth (1971). Sze & McElroy (1975) list many additional possibilities.

Both the ionospheric model and the semiquantitative discussion of H required an eddy coefficient K of $1 \times 10^8 \text{ cm}^2 \text{ sec}^{-1}$. Its effect is to maintain small densities of H and O atoms in the thermosphere and exosphere. The escape flux can only be guessed, because the velocity distribution of the nonthermal atoms is unknown. (The escape rate of the thermal component is negligible.) Kumar & Hunten suggested that 10–30% of the hot atoms might escape, but the figure could be 50% or possibly even higher. The flux would therefore be $(1-5) \times 10^6 \text{ cm}^{-2} \text{ sec}^{-1}$, still far below the limiting value. Most of the H atoms produced in the ionosphere must flow back down to be chemically combined again at deeper levels.

Mariner 10 confirmed that the exospheric temperature in 1974 was around 400°K , both from the $L\alpha$ data reproduced in Figure 8, and from a similar analysis of helium radiation (Broadfoot et al 1974). These results inspired Liu & Donahue (1975a) and Sze & McElroy (1975) to take up the problem.

For the purposes of this review the two treatments are essentially equivalent. Sze & McElroy include chlorine photochemistry and obtain results that apply all the way down to the cloud tops, but chemical details matter little above 90 km, where transport is dominant. Liu & Donahue (1975a), for example, assumed $f_t = 2.6 \text{ ppm}$

for total-H at the cloud tops. To keep the exospheric H density down at the observed value then required either a large K , a large escape flux, or some combination. The escape flux was simply an arbitrary parameter, assumed to result from a nonthermal mechanism of unknown nature. In the two extreme cases, the nonthermal escape gives limiting flux over a considerable height range; the large K keeps H_2 and H to a small scale height, in a constant mixing ratio with the CO_2 , to high altitudes. It also can be thought of as sweeping downwards the H atoms from H_2 destruction. Depending on the specific assumptions, K had to be up to a few times $10^8 \text{ cm}^2 \text{ sec}^{-1}$. For substantially smaller K , the nonthermal flux had to be nearly $10^8 \text{ cm}^2 \text{ sec}^{-1}$.

Both papers concluded that the high K was the more likely answer and drew the corollary that the O abundance in the upper atmosphere is therefore small, because of the same downward sweeping that acts on H.

The probable weakness of any nonthermal escape process is due to the small observed H densities in the exosphere. The assessment by Walker, Turekian & Hunten (1970) is still valid for the most part, and many of the ideas have been discussed above under the individual processes. Ion production is simply too slow in the absence of the large O^+ amounts that are so effective for charge exchange on Earth. Venus has no plasmasphere because it lacks a magnetosphere. Solar wind sweeping of H_2^+ ions was the strongest potential process turned up by Walker et al; their limit was $1.3 \times 10^7 \text{ H atoms cm}^{-2} \text{ sec}^{-1}$, too small by an order of magnitude to be significant in the present context. In any case, it is inconsistent with the Michel limit, Equation 9, by at least a factor of 3, and it ignores the corresponding accretion.

We should remember as a cautionary warning that the dominant escape process from Earth has only recently been worked out after many decades of belief in Jeans escape. Nevertheless, it seems very improbable that Venus has a nonthermal escape flux anything like $10^8 \text{ cm}^{-2} \text{ sec}^{-1}$. A total flux of order $10^6 \text{ cm}^{-2} \text{ sec}^{-1}$ is much more likely.

Mars

Lyman-alpha emission from the Martian corona was observed by Mariners 6 and 7 (Barth et al 1969). Subsequent analysis established the Jeans escape flux as $1.8 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$, with $n_e = 3 \times 10^4 \text{ cm}^{-3}$ and $T_e = 350^\circ\text{K}$ (Anderson & Hord 1971). The Jeans ratio of 0.50 (Chamberlain & Smith 1971) was not included in this result, which therefore becomes $9 \times 10^7 \text{ cm}^{-2} \text{ sec}^{-1}$. An aeronomical model by Hunten & McElroy (1970) showed that such fluxes could plausibly be accounted for, with photolysis of the observed H_2O amounts as the source. (Barth has told us that, years before his observation, he had been advised not to waste his time—the gravity of Mars was too small to hold appreciable amounts of atomic hydrogen.) As Hunten & McElroy pointed out, the corresponding O_2 production would give the amount in the atmosphere ($\sim 0.1\%$) in only 10^5 years. This mixing ratio had to be assumed, but was later confirmed (Carleton & Traub 1972, Barker 1972, review by Hunten 1974). Hunten (1973b) showed that the model results were in excellent accord with the limiting-flow principle based on the H_2 mixing ratio. The relation

of the H_2 to the H_2O is subtle, however, and the evaluation of the total-H mixing ratio requires the H_2O near the surface to be excluded. Also, the model assumed an ionosphere rich enough in CO_2^+ to convert nearly all the H_2 to escaping H.

Considerable interest in the topic was generated when McElroy (1972) noticed an important nonthermal escape process for oxygen that should be roughly in balance with the hydrogen loss. The escape energy from a height of 200 km is $\frac{1}{8}$ eV per atomic mass unit, or 2 eV for an oxygen atom. More than this energy is given in the dissociative recombination of any likely oxygenated molecular ion, CO_2^+ , CO^+ , or O_2^+ . This is true even if the atom is electronically excited within the ground configuration. (For Earth and Venus, the escape energy is too large for the process to work.) Thus essentially half of all ions created above the exobase of Mars produce an oxygen atom that escapes—that is, all the recombination events that produce an atom that travels outward. Hence, it is easy to calculate the nonthermal escape flux simply by calculating the appropriate ionization rate or resorting to a model for the ionosphere. The result is that 7×10^7 O atoms escape per square centimeter per second. Within the errors, the O flux is equal to half the hydrogen thermal escape flux of 9×10^8 atoms $\text{cm}^{-2} \text{sec}^{-1}$.

It is difficult to accept as an accident such a coincidence of escape fluxes. McElroy (1972) and McElroy & Donahue (1972) suggested that a connection through the chemistry governs the recombination of CO_2 on Mars. They argued that the escape of oxygen regulates the production of H_2 and hence of atomic hydrogen and that the escape flux of hydrogen is constrained to follow that of oxygen. Qualitatively, if the two were unbalanced—for example, if the O escape rate were too low—the O_2 , and hence the O_3 density, would be larger than normal, and the excess $\text{O}(^1\text{D})$ would attack H_2 , thus increasing its destruction rate. At the same time, the reaction of H with O_2 would increase the amount of HO_2 and OH while decreasing that of H. The overall result would be a decrease in the product of H and HO_2 and therefore a decrease in the rate of production of H_2 . Hence H_2 production would decrease, its destruction increase, and the rate of H escape decrease. Two photochemical systems are available; each differs in some details but either one is able to operate as described (McElroy & Donahue 1972, Parkinson & Hunten 1972, Hunten 1974).

However, we are faced here with a paradox in view of Hunten's limiting-flow principle. The H escape from Mars is copious and one would expect the state to be one of limiting diffusion in which the concentration of total-H in the lower atmosphere controls escape. It is difficult to understand how the escape rate of atomic oxygen would determine the total mixing ratio of hydrogen in the lower atmosphere. A possible way out is defining total-H to exclude H_2O near the surface, as suggested above. The rationale would seem to be the very loose coupling between H_2O and the H_2 that actually is the buffer and the carrier of hydrogen to high altitudes.

Liu & Donahue (1975b) have recently investigated the question in detail. They solved the coupled diffusion equations from the surface to the exobase for all constituents expected to be important: CO_2 , CO, O_2 , H_2O , odd hydrogen (H, OH, HO_2), H_2O_2 , and odd oxygen ($\text{O} + \text{O}_3$). Water was assumed to issue from the

surface at a rate equal to the oxygen escape by dissociative recombination. The ionospheric structure was also computed. Too little CO_2^+ was found in the ionosphere to give complete conversion of H_2 to H ; most of the ions were converted to O_2^+ , which does not attack H_2 . Near the exobase, the number density of H_2 remained 4 times larger than that of H . The ratio of escape fluxes (at 320°K) was a factor of 8 the other way, or a factor of 4 in terms of total atoms being lost. The total- H escape flux of $1.1 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$ is nicely in balance with the O flux, $0.53 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$. The uncorrected Jeans equation was used, but the same effusion velocity could be restored by a small increase of the adopted exospheric temperature. The essential point is that balanced fluxes were found, even with an arbitrary choice of effusion velocity.

Because H_2 remains abundant at the exobase and is too heavy to escape freely, the requirement for limiting flow is not satisfied and the feedback from the O escape can readily operate; the apparent paradox is resolved.

Clearly, this result is sensitive to the computed positive-ion composition of the ionosphere. It should therefore be accepted with some caution until this composition has been confirmed. Possibly the feedback could still work under limiting-flow conditions by controlling the abundance of H_2 . As suggested above, total-hydrogen would have to be defined as excluding H_2O .

Liu & Donahue (1975b) also ran two models with the atmospheric O_2 abundance increased by factors of 1.5 and 2. The H_2 abundance was found to decrease by somewhat larger factors. These results verify the most important step in the postulated feedback chain and strongly support its validity. The general conclusion is that on Mars it is not just hydrogen, but rather water, that escapes. These processes may be important in keeping the Martian surface as dry as it is.

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