

NONTHERMAL ESCAPE OF THE ATMOSPHERES OF VENUS, EARTH, AND MARS

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Abstract. Atmospheric loss from planetary atmospheres is an important geophysical problem with implications for planetary evolution. This is a multidisciplinary research field that requires an expertise in a wide range of subjects including statistical mechanics, fluid mechanics, plasma physics, collision theory, and surface science. This paper is a review of the current state of our understanding of atmospheric loss from the terrestrial planets. A detailed discussion is provided of the basic concepts required to understand the processes occurring in the high-altitude portion of a planetary atmosphere referred to as the exosphere. Light atomic species with sufficient translational energy can escape from an atmo-

sphere. The translational energy required for escape could be thermal energy and proportional to the ambient temperature or the result of some collisional processes energizing the species above thermal energies. These collisional processes, which include charge exchange and dissociative recombination between energetic ions, neutrals, and electrons, are referred to as nonthermal escape processes. We highlight the similarities and differences in the important escape mechanisms on the terrestrial planets and comment on application of these mechanisms to evolutionary theories of the terrestrial atmospheres. The emphasis in this paper is directed toward the need to consider the exosphere as collisional.

1. INTRODUCTION

One of the more challenging multidisciplinary problems in geophysics and atmospheric science is the study of the evolution and escape of planetary atmospheres. An atmosphere is bound incompletely to a planet by the planetary gravitational field. At very high altitudes, atomic species of low mass, such as hydrogen and helium, can attain speeds in excess of the escape speed of the planet and escape, provided they suffer no further collision. The escape flux referred to as thermal escape or *Jeans* [1925] escape depends on the ambient temperature and occurs over a range of altitudes where the atmosphere is approximately collisionless, which is in the vicinity of the exobase. The exobase is the altitude for which the mean free path of atmospheric constituents is equal to the density scale height and is defined in detail in section 2. The region above the exobase is referred to as the exosphere. For Earth the exobase is at approximately 500 km, and the exosphere, in the vicinity of the exobase, is predominantly atomic oxygen with hydrogen and helium as minor species. Heavier species such as oxygen, nitrogen, and carbon can escape from the atmospheres of the terrestrial planets as a result of collisional

processes that are referred to as nonthermal escape mechanisms. An example of such collisional processes are collisions between hot protons and cooler hydrogen atoms resulting in energetic hydrogen atoms that can escape. There are many other nonthermal processes including photodissociation, sputtering [Johnson, 1994], and solar wind pickup. *Hunten* [1982] has provided a comprehensive list of the various types of nonthermal processes that occur in planetary atmospheres. Since the particle densities of the exosphere are small, an approximate model of the exosphere [Chamberlain, 1963] assumes that exospheric atoms move, without colliding, under the influence of the planetary gravitational field.

The study of exospheric processes and escape mechanisms from the planets is of considerable interest to planetary scientists in their effort not only to better understand the present state of planetary atmospheres but also to model atmospheric evolution. This is a multidisciplinary study which involves coupling of different atmospheric regions in addition to the interaction of the exosphere with the solar wind plasma and the planetary surface. The expertise of scientists in atmospheric chemistry and dynamics, ionospheric plasma properties, geology and planetary surface morphology, planetary magnetic fields, the solar wind plasma, and other fields is required.

There have been several excellent reviews which provide a good overview of the basic concepts involved in

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the study of exospheres. The review by *Chamberlain* [1963] provides a very detailed theoretical description of the collisionless exosphere. Several additional reviews have been written by *Hunten and Donahue* [1976], *Tinsley* [1978], *Fahr and Shizgal* [1983], *Hunten* [1982, 1990], and *Mahajan and Kar* [1990]. This review is motivated by the need to emphasize the importance of nonthermal processes in planetary exospheres and to reconsider current exospheric models. This review is appropriate at this time in view of upcoming missions to Mars and the important observational constraints on theoretical models that the new data will provide. Our aim in this paper is to provide the geophysics community with a background of the basic concepts in exospheric physics as well as an understanding of the important outstanding research problems. While some of the topics covered in the previous reviews are repeated for completeness, the main emphasis of this paper will be collisional phenomena and nonthermal processes. We provide an up-to-date review, and we cite primarily the most recent papers since about 1980 which impact on current research in this area. We refer the reader interested in the historical development of the subject to the reviews mentioned previously and the exhaustive reference lists contained in those works.

The present understanding of planetary exospheres is determined largely by satellite and ground-based observations which are predominantly measurements of the emissions of exospheric constituents. These include Lyman α and Lyman β emissions of atomic hydrogen at 121.6 nm and 102.6 nm, respectively, emission of helium at 58.4 nm, and emission of atomic oxygen at 130.4 nm. These observations of the exosphere together with in situ mass spectrometric measurements provide density and temperature profiles of neutral and charged constituents. For example, data from the Pioneer Venus large probe neutral mass spectrometer indicated an enrichment of the deuterium to hydrogen (D/H) ratio in the exosphere of Venus by a factor of 100 relative to the terrestrial value [*Donahue et al.*, 1982]. As discussed in section 3, this enrichment of deuterium relative to hydrogen is believed to arise from the enhanced escape of hydrogen due to nonthermal processes. Nonthermal processes refer to collisions between exospheric species and translationally energetic species (both ions and electrons), generally of ionospheric origin. This includes processes such as the collision of hot plasmaspheric protons with exospheric hydrogen, $H^+ + H \rightarrow H^* + H^+$, which effectively converts the energetic protons to translationally excited hydrogen atoms H^* , with speeds in excess of the escape speed. Such nonthermal processes provide an important escape mechanism and also make possible the escape of heavier species, such as oxygen, nitrogen, and carbon, for which the thermal escape rate is very small. An important nonthermal process in the exospheres of Mars and Venus is the dissociative recombination of O_2^+ with electrons, that is, $O_2^+ + e^- \rightarrow O^* + O^*$, with the product oxygen atoms

translationally excited. Some of the exothermicity of the reaction appears as translational energy of the product atoms, and a large population of energetic or hot atoms is produced.

Hot oxygen atoms resulting from dissociative recombination were predicted to occur on both Mars and Venus by *McElroy et al.* [1982a] and *Rodriguez et al.* [1984]. The presence of hot oxygen on Venus was confirmed by the 130.4-nm measurement of the ultraviolet spectrometer on the Pioneer Venus Orbiter [*Nagy et al.*, 1981]. A hot corona of atomic oxygen has also been observed for the terrestrial exosphere [*Yee et al.*, 1980]. Theoretical estimates of the nonthermal character and extent of these hot oxygen coronae in the exospheres of the terrestrial planets have been provided by several researchers [*Nagy and Cravens*, 1988; *Nagy et al.*, 1995; *Ip*, 1988, 1990; *Lammer and Bauer*, 1991; *Shematovich et al.*, 1994]. Enhanced loss of hydrogen with respect to deuterium, as implied by the D/H ratio observed by the Pioneer Venus Orbiter, if coupled with an appropriate loss of oxygen, may be indicative of the loss of water. The observed Pioneer Venus Orbiter D/H ratio has led to suggestions that an Earth equivalent ocean of water existed on Venus in the distant past and has dissipated as a result of this loss of atomic hydrogen and oxygen. Other isotopic fractionations, such as the enrichment of ^{15}N over ^{14}N on Mars, can be explained on the basis of similar nonthermal processes.

Nonthermal processes have also been employed in order to understand a discrepancy in the terrestrial helium budget [*Axford*, 1968; *Bates and McDowell*, 1959; *Lie-Svendson et al.*, 1992]. The production of 4He is predominantly from the radioactive decay of ^{238}U , with an estimated flux of $F_{prod} \approx (0.9-1.9) \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$ [*Torgerson*, 1989]. For helium the exospheric escape energy on Earth is approximately 2.5 eV, and for a density of 10^6 cm^{-3} and temperature of 1000 K at the exobase the thermal Jeans flux is $F_J = 0.4 \text{ cm}^{-2} \text{ s}^{-1}$ (see section 2), so that $F_{prod}/F_J \approx (2.3-4.8) \times 10^6$. Clearly, the calculated rate of outgassing of 4He is far greater than the loss due to thermal Jeans escape, and the atmospheric helium content should be far above what is observed. Furthermore, as helium is chemically inert, there are no reactive processes to account for the observed discrepancy. In order to reconcile this, there must exist additional loss processes which remove helium from the atmosphere. *Lie-Svendson et al.* [1992] and *Lie-Svendson and Rees* [1996a, b] recently studied several potential nonthermal mechanisms and suggested that the exothermic charge exchange reaction $He^+ + N_2 \rightarrow He + N_2^+ + 9 \text{ eV}$, originally proposed by *Maier* [1968], could produce He atoms of sufficient energy for escape.

Given the importance of nonthermal collisional processes to many exospheric situations, it is very clear that exospheric conditions are determined to a large extent by collisional processes and the collisionless models have to be reconsidered. Nonthermal mechanisms are discussed at length in section 3, with emphasis on the need

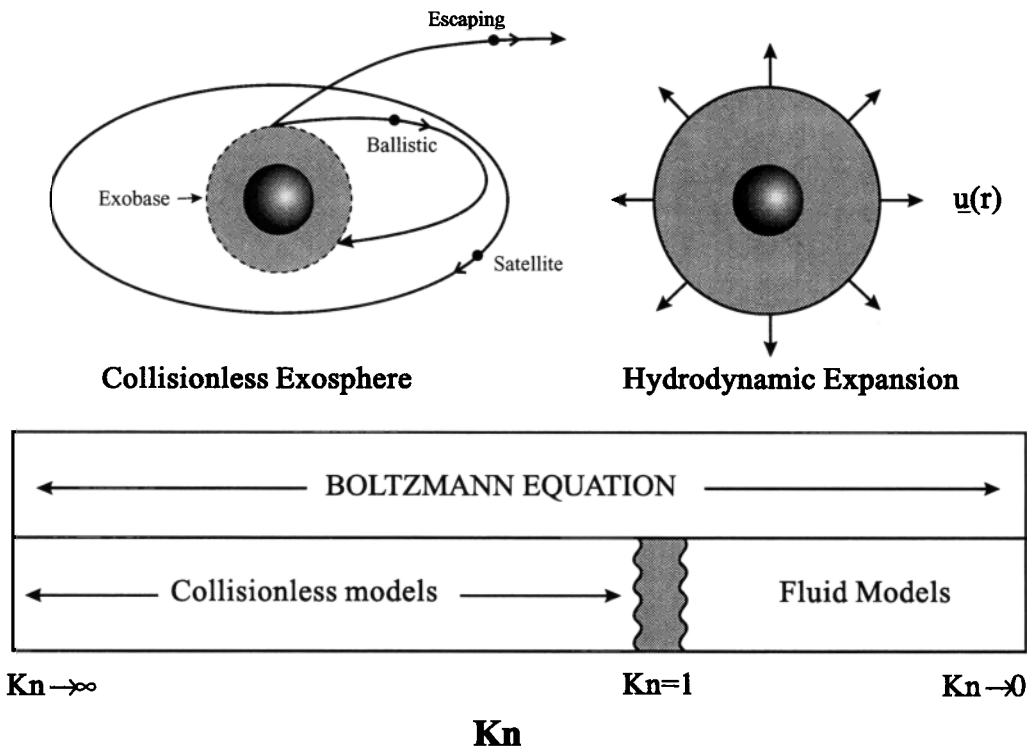


Figure 1. Regimes of validity for hydrodynamics and kinetic theory versus the Knudsen number, $Kn = l/H$. The hydrodynamic expansion of the atmosphere with radial velocity $u(r)$ is shown on the right. The collisionless exosphere [Chamberlain, 1963], characterized by different particle classes, is depicted on the left. Collisionless kinetic theory models are valid in the limit $Kn \rightarrow \infty$, whereas hydrodynamic models are valid when the mean free path is very small and $Kn \rightarrow 0$. The Boltzmann equation of kinetic theory is valid for the whole range of Knudsen number.

to reconsider theoretical models of the exosphere to include collisional processes in a consistent manner. In particular, the classic model of thermal or Jeans escape will be addressed in terms of a collisional approach, in contrast to the standard view of a thermal evaporative process from an exobase.

Thermal and nonthermal escape mechanisms are based on kinetic theory and individual particle dynamics. An alternative model of atmospheric loss whereby the atmosphere is viewed as a dense fluid which expands radially outward has also been employed. This approach is analogous to the solar and polar wind expansions [Chamberlain, 1961; Parker, 1965; Banks and Holzer, 1968; Axford, 1968; Brandt, 1970; Hundhausen, 1972; Lemaire and Scherer, 1973]. The polar wind refers to the loss of terrestrial H^+ and He^+ along open magnetic field lines at high latitudes. These fluid-like expansions are based on the hydrodynamic equations of fluid mechanics. Such models have recently been employed to explain the observed isotopic fractionations on Mars and Venus [Hunten et al., 1987; Zahnle and Kasting, 1986; Zahnle et al., 1990; Pepin, 1991, 1992, 1994]. An important theoretical problem is the reconciliation of kinetic theory and hydrodynamic models of an expanding exosphere. An analogous problem in other areas of geophysics, notably models of the solar and polar winds [Lemaire and

Scherer, 1973; Fahr and Shizgal, 1983], and planetary magnetospheres also exists, although the conditions there are more nearly collisionless than for the dense (primordial) atmospheres. Figure 1 is a depiction of these different physical situations. The diagram on the left shows a planet surrounded by a thick atmosphere, above which is a collisionless exosphere with particles executing escaping, ballistic, and satellite orbits [Chamberlain, 1963; Fahr and Shizgal, 1983]. The diagram on the right shows a fluid-like atmosphere expanding radially outward. The bottom portion of Figure 1 refers to the different theoretical approaches employed to describe atmospheric loss and is discussed later.

The important interaction of the solar wind with the exospheres of Venus and Mars, with no or vanishingly small planetary magnetic fields, is presented in section 4. The solar wind plasma can penetrate deep into the extended exospheres of these planets, ionize the neutral species there, and sweep them up in the embedded interplanetary magnetic field. Several processes, including scavenging, mass loading, and sputtering, are discussed in detail. Nonthermal escape of helium from Mars arising from the interaction of the solar wind and the Martian ionosphere has been discussed by Barabash et al. [1995]. The solar wind penetrates deep into the

corona, and He^+ ions are picked up and swept out of the atmosphere.

The impact of nonthermal processes in planetary exospheres on the development of evolutionary models is discussed in section 5. As already mentioned, the Pioneer Venus Orbiter measurements of D/H enrichment on Venus have led to the suggestion of a layer of water tens to hundreds of meters thick in the distant past [Donahue, 1995]. For Mars a similar history of past water abundance has been suggested [Squyres and Kasting, 1994], based on estimates of water abundance and surface morphology from satellite data [Pollack et al., 1987], Earth-based spectroscopy of HDO [Owen et al., 1988], and measurements of isotopic fractionation of gases trapped in shergottite-nakhlite-chassignite (SNC) meteorites [Pepin, 1991; McSween, 1994]. However, the processes which have led to the loss of water on Mars and Venus appear to be somewhat different. Venus probably had its water primarily in the form of water vapor [Hunten, 1993] because of the higher atmospheric and surface temperatures. This large amount of atmospheric water vapor would have created a dense population of atomic hydrogen via photodissociation, and conditions would have been favorable for bulk hydrodynamic loss. This process has been suggested to explain both the observed isotopic fractionation of noble gases and the removal of large amounts of hydrogen and thus, possibly, water. Unless exospheric temperatures were higher in the past than today, it appears that thermal escape is, in general, negligible on Venus. On Mars, nonthermal and thermal processes may have both played a large role in removing much of the original water, possibly aided by impact erosion early in the planet's history [Hunten, 1993; Squyres and Kasting, 1994]. It is still uncertain whether the relative escape rates of H and O correspond stoichiometrically to the escape of water [Fox, 1993a]. Another important indication of atmospheric evolution is the observed patterns of isotopic fractionation in the noble gases of the terrestrial atmospheres. Their deviation from the patterns found in the solar wind and meteorites impart important information and constraints on the history of atmospheric evolution [Hunten et al., 1987; Zahnle et al., 1990; Pepin, 1991].

This review is important in view of the upcoming international effort to observe both the surface and atmosphere of Mars. The Martian neutral atmosphere, ionosphere, and the solar wind plasma interaction will be measured by instruments aboard satellites to Mars toward the end of the decade. These include Planet B [Tsuruda and Yamamoto, 1995] and Mars 96 and 98 [Zakharov, 1994]. Some of the planned missions to Mars involve experiments to obtain signatures of the hot coronae in the Martian exosphere [Nagy and Cravens, 1988]. Additional measurements will be obtained with the Hubble Space Telescope and instruments aboard the Mars Surveyor and Pathfinder orbiter/lander pairs to be launched in 1996 and 1998, respectively. These satellite missions will collectively yield important information on

nonthermal processes and will provide the impetus for the further development of theoretical models of atmospheric evolution and planetary climate change.

In section 2 we present a brief overview of exospheric theory [Chamberlain, 1963]. This is a kinetic theory description, based on particle distribution functions, and could be extended to include collisional processes as discussed by Fahr and Shizgal [1983]. The important idea of diffusion-limited flux in the lower part of the atmosphere as controlling the escape is also presented. In section 3 the important role of nonthermal processes, which is the main emphasis of the paper, is discussed. Section 4 is devoted to the important interaction of the solar wind with the extended corona of energized or hot atoms of Mars and Venus. The implications of atmospheric loss to the understanding of the evolution of the atmospheres of the terrestrial planets and climate are briefly discussed in section 5.

2. AN OVERVIEW OF THE EXOSPHERIC PROBLEM: A TUTORIAL

2.1. Collisionless Exosphere: Thermal Escape

The basic concepts of planetary atmospheric escape were given by Jeans [1925] and extended to the collisionless thermal escape model by Chamberlain [1963] and Chamberlain and Hunten [1987]. The lower region of the atmosphere where turbulent mixing of gases leads to a homogenous composition is called the homosphere. Above this region, turbulence becomes less important relative to molecular diffusion as a form of vertical transport, and the vertical distribution of individual atmospheric gases is determined by their respective masses. In this region, called the heterosphere, the density profile $n_i(r)$ of the i th constituent is determined by the balance of gravity and gas pressure. The equation for hydrostatic equilibrium [Bauer, 1973; Banks and Kockarts, 1973], $dp_i = GMn_i m_i dr/r^2$, together with the ideal gas law, $p_i = n_i kT$, can be integrated to give the barometric density variation with radial distance r ,

$$n_i(r) = n_i(r_0) \exp \left[\frac{r}{H_i(r)} - \frac{r_0}{H_i(r_0)} \right] \quad (1)$$

where G is the gravitational constant, M is the planetary mass, m_i is the molecular mass of the i th species, and r_0 is some reference level. A constant temperature T is assumed in the derivation of (1). Each species is distributed according to its own scale height, defined by

$$H_i(r) = kTr^2/GMm_i = kT/m_i g(r) \quad (2)$$

where k is the Boltzmann constant and $g(r)$ is the gravitational acceleration. If we set $r = r_0 + z$ and expand the first term of the exponential up to linear terms in z , we find the exponential density profile,

$$n_i(r) = n_i(r_0) \exp \left[-\frac{z}{H_i(r_0)} \right] \quad (3)$$

The atmospheric scale height in (2) should be distinguished from the pressure scale height $H_{p_i} = d \ln n_i/dz + d \ln T/dz$ which includes the effect of a varying temperature. The exobase or critical level r_c is defined as the altitude for which the mean free path, the average distance between particle collisions, given by

$$l = 1/\sqrt{2}n\sigma \quad (4)$$

is equal to the barometric scale height of the major constituent, that is, $l(r_c) = H(r_c)$. In (4), σ is the energy independent collision cross section for collisions with the major constituent, and n is the total density.

In the standard model [Jeans, 1925; Chamberlain, 1963] the atmosphere above the exobase is considered collisionless, while below, it is collision dominated. Particles that reach the exobase from below and move upward with speeds in excess of the escape speed given by

$$v_{\text{esc}} = \sqrt{2GM/r} \quad (5)$$

will escape from the gravitational field of the planet. This model assumes that above the exobase the particles move on collision-free trajectories determined by the planetary gravitational field. The classification of exospheric species into classes of particles such as ballistic, satellite, and escaping based on this model is discussed at length by Chamberlain [1963] and Fahr and Shizgal [1983] and is not repeated here. In these models a Maxwellian distribution of particle velocities

$$f^{\text{max}}(v) = n(m/2\pi kT)^{3/2} \exp[-mv^2/2kT] \quad (6)$$

is assumed to exist at the exobase. The escape flux of particles moving radially outward at the critical level is determined by averaging over the outward directed velocity for speeds greater than the escape speed, that is,

$$F_J = 2\pi \int_{v_{\text{esc}}}^{\infty} \int_{\theta=\pi/2}^{\theta=0} f^{\text{max}} \cos \theta v^3 d(\cos \theta) dv \quad (7)$$

so that the thermal or Jeans escape flux is given by

$$F_J = \frac{n_c}{2} \sqrt{\frac{2kT_c}{m\pi}} (1 + \lambda_c) e^{-\lambda_c} \quad (8)$$

In (8), T_c and n_c are the temperature and density of the escaping species at the exobase, respectively, and the escape parameter λ_c is defined by

$$\lambda_c = E_{\text{esc}}/kT_c \quad (9)$$

where the total energy for escape is $E_{\text{esc}} = \frac{1}{2}m v_{\text{esc}}^2$. The escape speeds and escape energies for H and O from the terrestrial planets are shown in Table 1. Mars, the smallest of the three, has the lowest escape energy. The escape flux is determined by the ratio of the escape energy relative to the thermal energy, that is, by λ_c in (9). Table 2 compares the values of λ_c for the terrestrial planets. The very large value for Venus arises from the

TABLE 1. Planetary Escape Velocities and Energies

Planet	r_c , km	v_{esc} , km s ⁻¹	$E_{\text{esc}}^{\text{H}}$, eV	$E_{\text{esc}}^{\text{O}}$, eV
Earth	500	10.8	0.61	9.69
Venus	200	10.2	0.54	8.64
Mars	250	4.8	0.12	1.91

low exospheric temperature. For Venus, thermal escape is insignificant at present, and nonthermal processes (section 3) play a dominant role. However, Donahue [1986] has discussed the escape of primordial atmospheres from planetesimals for which λ_c is small and Jeans flux is significant.

It is important to note that in (7) the three-dimensional velocity integral is carried out only over the upper half of the velocity space ($\theta \geq 0$). Since the Maxwellian distribution function is isotropic, the flux would be zero if the lower hemisphere of the velocity space was included. This model of atmospheric escape is an oversimplification. The actual distribution function at the exobase is not Maxwellian, because the escape process preferentially removes energetic particles and nonthermal processes introduce them. The distribution that leads to an outward flow must include an anisotropic part so that the drift velocity is given by

$$\mathbf{u}(r) = \int f_{\text{anisotropic}}(r, \mathbf{v}) \mathbf{v} dv \quad (10)$$

where $f_{\text{anisotropic}}(r, \mathbf{v})$ depends on the velocity direction as well as the speed. It is reasonable to expect that escaping particles originate not only from a single altitude at the exobase but from a range of radial positions in the vicinity of the exobase. Hence the escape flux is $\mathbf{F}(r) = n(r)\mathbf{u}(r)$, where $\mathbf{u}(r)$ is given by (10) and depends on the radial position. The total escape flux is determined by the integral of $\mathbf{F}(r)$ over a range of radial distances in the vicinity of the exobase. This picture of atmospheric escape, which considers both thermal and nonthermal escape as collisionally induced phenomena, is discussed at greater length in section 3.

2.2. Hydrodynamic Escape

The thermal escape mechanism described by (8) is often referred to as evaporative escape. This implies a process with a flow speed, $u(r) = F_J/n(r)$, which is very small relative to the speed of sound, $v_s = \sqrt{\gamma kT/m}$, where

TABLE 2. Planetary Exospheric Values for Hydrogen Escape

Planet	r_c , km	T_c , K	λ_c	F/n_c , cm s ⁻¹
Earth	500	1000	7.06	7.94×10^2
Venus	200	275	22.89	1.65×10^{-4}
Mars	250	300	4.65	3.39×10^2

$\gamma = c_p/c_v$, the ratio of specific heats. For Earth's exosphere we find, using the data in Table 2 and with $v_s \approx 300 \text{ m s}^{-1}$, that $u/v_s \approx 0.027$. This can be compared with the expansion of the solar atmosphere, which at Earth orbit is supersonic with a ratio of $u/v_s \approx 1\text{--}1.5$ [Chamberlain, 1961; Parker, 1965; Axford, 1968; Brandt, 1970; Hundhausen, 1972; Lemaire and Scherer, 1973]. The exospheric model developed by Chamberlain [1960] for the solar wind expansion gave a bulk flow at Earth orbit that was less than observed. Lemaire and Scherer [1973] showed that an exospheric model of the solar wind with the correct self-consistent electric field gave a supersonic flow speed in accord with observations. A detailed review of the solar and polar wind theories is beyond the scope of this review and has been presented elsewhere [Lemaire and Scherer, 1973; Fahr and Shizgal, 1983].

The solar and polar winds are generally considered to be fluid-like or hydrodynamic and can be described by considering the equations of hydrodynamics rather than the particle picture of the collisionless exosphere. The theory of hydrodynamic escape of an atmosphere, as it applies to the solar wind, is described in standard references [Parker, 1958; Brandt, 1970; Hundhausen, 1972]. Similar hydrodynamic models have been used to describe the loss of a planetary atmosphere for which the escape parameter λ_c is small and the flow speed is large [Watson et al., 1981; Kasting and Pollack, 1983]. Such large flow speeds may have existed during early planetary atmospheric formation, when hydrogen rich proto-atmospheres are exposed to high levels of solar EUV flux. Hydrodynamic models of atmospheric escape have been used to explain the enrichment of the isotopes of the noble gases [Hunten et al., 1987; Zahnle and Kasting, 1986; Zahnle et al., 1990].

The basis for the hydrodynamic formulation used to describe atmospheric expansions is the equations of conservation of mass, momentum, and energy [Chapman and Cowling, 1964; Kundu, 1990]. It is a contraction of the kinetic theory description based on the lower-order moments of the nonequilibrium distribution function. The lower-order moments of the distribution function are the density, $n(\mathbf{r}, t) = \int f(\mathbf{r}, t) d\mathbf{v}$; the bulk velocity, $\mathbf{u}(\mathbf{r}, t) = (1/n) \int \mathbf{v} f(\mathbf{r}, t) d\mathbf{v}$; and the temperature $\frac{3}{2}nkT(\mathbf{r}, t) = \int (m/2)[\mathbf{v} - \mathbf{u}(\mathbf{r}, t)]^2 f(\mathbf{r}, t) d\mathbf{v}$. This corresponds to the five-moment models used by St. Maurice and Schunk [1979] for a similar description of ionospheric phenomena. For steady flow in a spherical geometry the conservation equations without mass or energy sources or sinks are

$$\frac{1}{r^2} \frac{d}{dr} (r^2 \rho u) = 0 \quad (11)$$

$$\rho u \frac{du}{dr} = -\frac{dp}{dr} - \rho \frac{GM}{r^2} \quad (12)$$

$$\frac{1}{r^2} \frac{d}{dr} \left[r^2 \rho u \left(\frac{1}{2} u^2 + \frac{3p}{\rho} \right) \right] = -\frac{1}{r^2} \frac{d}{dr} (r^2 p u) - \rho u \frac{GM}{r^2} \quad (13)$$

where the mass density $\rho(r) = n(r)m$. In (12), $p(r) = n(r)kT(r)$ is the hydrostatic pressure, assumed to be given by the equation of state [Kundu, 1990]. If in (12) $du/dr = 0$, the atmosphere is not expanding, and we have the equation of hydrostatic equilibrium used to derive (1) and (3). Equations (12) and (13) do not include viscous effects and an anisotropic pressure tensor related to velocity gradients [Chapman and Cowling, 1964; Kundu, 1990]. For a planetary atmosphere, energy transport occurs both from the lower atmosphere and as solar EUV absorption in the middle-to-upper atmosphere [Watson et al., 1981]. Many aspects of hydrodynamic models applied to planetary atmospheres have been discussed by Hunten [1979], Watson et al. [1981], Zahnle and Kasting [1986], Kasting and Pollack [1983], and Zahnle et al. [1990].

In Figure 1 we contrast the kinetic and hydrodynamic approaches to atmospheric escape with regard to the Knudsen number, $Kn = l/H$. In the collision-dominated regime at low altitude the mean free path is small, $Kn \ll 1$, and the hydrodynamic approach is valid. In the collisionless regime at high altitude the mean free path is extremely long, $Kn \gg 1$, and the independent particle model with different particle classes is a good approximation. In order to describe phenomena over the whole range of Kn values the Boltzmann equation must be employed. However, the solution of the Boltzmann equation over the whole range of Knudsen number is difficult, especially for $Kn \approx 1$.

2.3. Diffusion-Limited Flux

The escape of particles from the exobase is, under certain circumstances, determined by the flux from lower altitudes in the atmosphere. If the flux from below is low, then the density at the critical level is adjusted so that the escape flux at the exobase is consistent with the flux at lower altitudes. This important concept has been reviewed by Hunten [1990], who provided a detailed account of the historical development of what is referred to as diffusion-limited flux. We follow the presentation of Hunten [1973a, b] and Hunten and Donahue [1976]. The vertical flux ϕ of a minor component (denoted by 1) diffusing through a background component (denoted by 2) is given by Banks and Kockarts [1973],

$$\phi = -Dn_1 \left(\frac{1}{n_1} \frac{dn_1}{dz} + \frac{1}{H_{e1}} \right) - Kn_1 \left(\frac{1}{n_1} \frac{dn_1}{dz} + \frac{1}{H_{e2}} \right) \quad (14)$$

where the equilibrium scale heights are defined by

$$\frac{1}{H_{e1}} = \frac{m_1 g}{kT} + \frac{(1 + \alpha) dT}{T dz} \quad (15)$$

$$\frac{1}{H_{e2}} = \frac{m_2 g}{kT} + \frac{1 dT}{T dz}$$

The first term of the right-hand side of (14) represents a flux due to molecular diffusion, where D is the molecular diffusion coefficient and α is the thermal diffusion coefficient. The second term describes the contribution of turbulent mixing to the vertical flux, where K is the eddy diffusion coefficient. In the homosphere, $K \gg D$, and in

the heterosphere, $D \gg K$. At the boundary of these two regions called the homopause, $K \approx D$ so that both terms must be considered. The phenomenon of turbulent mixing is not well understood [Rodrigo *et al.*, 1990], and values for the eddy diffusion coefficient K are uncertain, whereas the molecular diffusion coefficient D can be calculated rigorously from kinetic theory [Chapman and Cowling, 1964]. In some applications the eddy diffusion coefficient serves as an adjustable parameter. Values of K have also been estimated from the distribution of minor species [Von Zahn *et al.*, 1980].

The flux ϕ can be expressed as a function of the mixing ratio, defined as $f = n_1/n_2$, and the gradient of the mixing ratio with altitude, df/dz . If we take the logarithmic derivative of $n_1 = fn_2$, we have that

$$-\frac{1}{n_1} \frac{dn_1}{dz} = \frac{1}{H_f} + \frac{1}{H_2} \quad (16)$$

where we have used $H_f = -f^{-1} df/dz$. If we now define the binary diffusion parameter, $b_1 = Dn_2$, and substitute for $n_1^{-1} dn_1/dz$ from (16) into (14), we have that

$$\phi = b_1 f \left(\frac{1}{H_2} - \frac{1}{H_1} \right) + \frac{1}{H_f} (Kn_1 + b_1 f) \quad (17)$$

If we use $f = n_1/n_2$ and replace H_f by its definition, we have that

$$\phi = \phi_l - \frac{df}{dz} (Kn_2 + b_1) \quad (18)$$

In (18),

$$\phi_l = \frac{b_1 f}{H_2} \left(1 - \frac{m_1}{m_2} \right) \quad (19)$$

is the limiting flux, which for a light gas diffusing in a heavier background simplifies to

$$\phi_l \approx b_1 f / H_2 \quad (20)$$

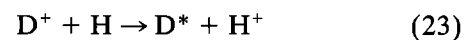
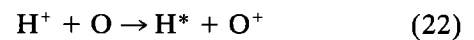
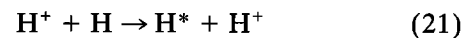
Jeans escape at the exobase requires an adequate supply of atoms from below, and in some instances the escape flux is controlled by diffusion at lower altitudes. If diffusive equilibrium exists and both density profiles are barometric, then $df/dz > 0$ for $m_2 \gg m_1$, and $\phi < \phi_l$. If the two components are completely mixed and they follow the same density distribution, then f is constant and $\phi = \phi_l$. The exact situation for a particular planetary atmosphere will be somewhere between these two extremes. Hunten [1973b] and Hunten and Donahue [1976] have provided a criterion as to whether a particular situation corresponds to the limiting flow situation or not. Applied to Earth, the limiting flux given by (19) corresponds to a flow speed at the homopause of $w_h = D/H_2 \approx 1.4 \text{ cm s}^{-1}$. Table 2 shows that the flow speed for Jeans escape is approximately $8 \times 10^2 \text{ cm s}^{-1}$. In this case it is clear that diffusion is the controlling process. The flux throughout the atmosphere and at the exobase is equal to the value at the homopause level which is

specified by the mixing ratio there. If, for example, exospheric temperature is changed, the density at the exobase, n_c , adjusts so that $F_j = \phi_l$. The density distribution of the minor species essentially follows the distribution of the background since f is nearly constant. If there is a loss mechanism in addition to thermal escape (see section 3), then the sum of all escape fluxes would be equal to the limiting flux. As conditions change, such as the exospheric temperature, the contributions from each mechanism will adjust, but the sum would remain the same.

3. COLLISIONAL NONTHERMAL PROCESSES AND ATMOSPHERIC ESCAPE

The kinetic theory of nonthermal escape has been previously reviewed by Fahr and Shizgal [1983], who provided a very detailed account of the literature to that date. Hunten [1982, 1990, 1993] has also presented a personal and historical account of the introduction of nonthermal processes to explain the observations of planetary exospheres. In this paper we will highlight the advances that have been made since about 1980 and refer the reader to the previous reviews for the literature prior to that date. However, there is some overlap with the previous reviews in order to make the discussion presented here reasonably complete.

Nonthermal processes generally refer to collisional processes between exospheric constituents with charged species to produce atoms that are translationally energetic and incompletely thermalized. The charge exchange reactions of energetic protons or deuterium ions with hydrogen or oxygen



are prototype nonthermal processes. On Earth the protons are of ionospheric and/or plasmaspheric origin and at a temperature of about 2000–10,000 K, whereas exospheric hydrogen is at about 750–1250 K. Reaction (21) converts the cooler hydrogen into a nonthermal population of translationally energetic hydrogen atoms H^* that can escape with an enhanced rate relative to the thermal Jeans escape rate. We present in the first part of this section an overview of several such nonthermal processes that occur in the atmospheres of the terrestrial planets. A more detailed discussion of the important current theoretical issues follows later. The discussion of the important nonthermal process involving direct interaction of the solar wind with the upper atmospheres of Mars and Venus is deferred to section 4, as the physics of this process is somewhat different from the collisionally induced processes discussed in this section.

On Venus the charge exchange reactions (21) and

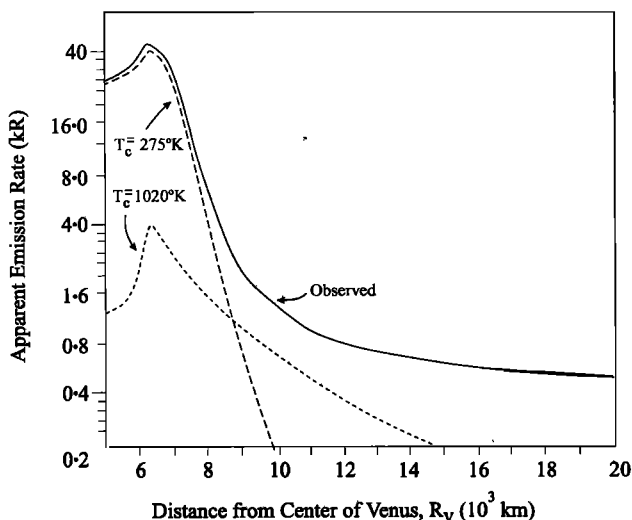


Figure 2. Dual hydrogen corona of Venus obtained by Mariner 5. The observed emission in kilorayleighs versus radial position is fitted to a thermal component at 275 K and a nonthermal component at 1020 K (adapted from Anderson [1976]).

(23) are the dominant escape mechanisms since the thermal escape is very slow because of the low exospheric temperature; see (8) and Table 2. Reaction (22) is not important because the proton density and temperature are low near the exobase where the oxygen density is significant [Cravens *et al.*, 1980; Hodges and Tinsley, 1986]. The existence of a population of energetic H atoms on Venus was confirmed by observations with the ultraviolet photometer on Mariner 5 [Barth *et al.*, 1967; Anderson, 1976]. The Lyman α emission indicated an altitude dependence characterized by two very different

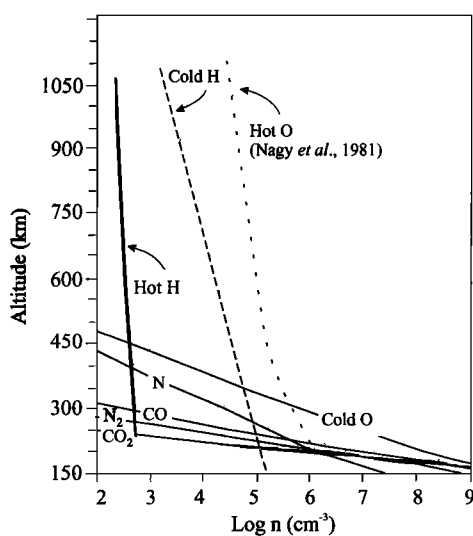
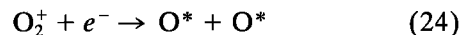


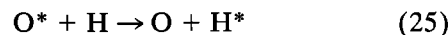
Figure 3. Altitude profiles of neutral atmospheric constituents of Venus. The extended coronae of H and O were calculated with theoretical models (adapted from Luhmann [1986, Figure W] with kind permission from Kluwer Academic Publishers).

scale heights as shown in Figure 2. The scale heights corresponded to different H atom populations, a thermal component at about 150–275 K and density 10^5 cm^{-3} and a hot component at approximately 800–1500 K and a density of 10^3 cm^{-3} [Stewart *et al.*, 1979; Takacs *et al.*, 1980].

In addition to the charge exchange reactions (21) to (23) other mechanisms can produce energetic atoms. The dissociative recombination of O_2^+ ,



is an important reaction for producing energetic atomic oxygen on Earth, Venus, and Mars [McElroy and Yung, 1976; Yee and Hays, 1980; Knudsen, 1973, 1990; Zhang *et al.*, 1993a]. Reaction (24) indirectly produces additional energetic hydrogen and/or deuterium by virtue of the elastic energy transfer collisions



This combination of processes has been considered as important escape mechanisms for H and D from Venus [McElroy *et al.*, 1982b]. The hydrogen escape rate resulting from reaction (25) is estimated by Rodriguez *et al.* [1984] to be about $8 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$, whereas the escape rate resulting from reaction (21) is $2.8 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ [Hodges and Tinsley, 1986]. The energy transfer reaction (25) could be a significant contribution to the escape flux for low ionospheric temperatures. A summary of the situation for Venus as obtained from theoretical models is shown in Figure 3. The density profiles of hot H and O are shown relative to the profiles of the thermal components and other constituents. In Figure 4 we show for the Martian exosphere the calculated density profiles of hot H and O relative to the cold components. The details of the theoretical models are discussed later in this section. It is clear that both Venus and Mars have extended coronae of hot oxygen. There is an important interaction of the exospheres with the solar wind as discussed in section 4. Reaction (24) is also believed to be the important mechanism for the production of translationally energetic oxygen on Earth. A hot oxygen geocorona has

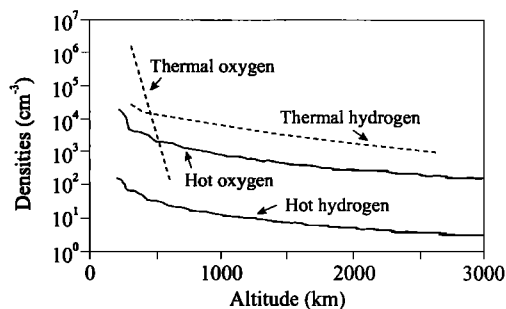


Figure 4. The hot corona of Mars. Calculated thermal and hot hydrogen and oxygen density profiles (adapted from Nagy *et al.* [1990, Figure 6]).

TABLE 3. Variation of the Charge Exchange and Jeans Flux With Exospheric Temperature

T_{∞} , °K	r_c , km	$n_{O^+}^c$, 10^7 cm^{-3}	$n_{H^+}^c$, 10^4 cm^{-3}	$F_{H^+,H}^A$	F_J	$F_{H^+,H}/F_J$	$F_{H^+,H} + F_J$
750	370	6.35	20.0	1.36	0.16	8.50	1.52
1000	450	5.00	8.7	0.82	0.73	1.10	1.55
1250	535	3.89	3.5	0.48	1.21	0.40	1.69
1500	615	3.17	1.6	0.30	2.33	0.13	2.63

Adapted from *Shizgal and Lindenfeld* [1982].

^aAll fluxes are in units of $10^8 \text{ cm}^{-2} \text{ s}^{-1}$; $\sigma_{O,H} = 33 \times 10^{-16} \text{ cm}^2$; $\sigma_{H^+,H} = 50 \times 10^{-16} \text{ cm}^2$; $n_{H^+} = 2 \times 10^4 \text{ cm}^{-3}$; and $T_{H^+} = 4000 \text{ K}$.

been verified by measurements of the $O^+(^2P)$ emission at 731.9 nm by *Yee et al.* [1980] with estimates of the density of hot oxygen of 10^5 cm^{-3} at 550 km.

Similar processes may act to form hot coronae of other species. The dissociative recombination process



can create a population of energetic nitrogen on Mars [*Brinkmann*, 1971; *Fox and Dalgarno*, 1980, 1983; *Ip*, 1988, 1990; *Lammer and Bauer*, 1991; *Fox*, 1993b]. The mass spectrometers on the Viking landers measured an isotopic ratio of 6.0×10^{-3} for $^{15}\text{N}/^{14}\text{N}$, which is about 1.62 times the terrestrial value of 3.68×10^{-3} . This isotopic enhancement or fractionation of the heavier isotope with respect to the lighter one is due to the fact that the energy given to the products is just enough for the ^{14}N to escape but too small for the heavier ^{15}N . Measurements of such isotopic fractionations yield significant information about early planetary volatile budgets and form important constraints on the development of evolutionary models of the terrestrial atmospheres [*Hodges*, 1993a; *Pepin*, 1994; *Jakosky et al.*, 1994; *Richards et al.*, 1994]. Another well-known example is the enhancement of the D/H ratio on Venus over the terrestrial ratio recorded by the mass spectrometer on the Pioneer Venus Orbiter. With D/H values of 1.6×10^{-2} on Venus and 1.56×10^{-4} on Earth the ratio on Venus exceeds that on Earth by a factor of 100 [*Kasting and Pollack*, 1983]. We address the evolutionary aspects of this and other isotopic fractionations in section 5.

Nonthermal processes have been considered theoretically at some length by numerous researchers. The charge exchange reaction (21) was originally suggested by *Cole* [1966] and was reconsidered by *Chamberlain* [1977], *Tinsley* [1978], *Kumar et al.* [1978], *Shizgal and Lindenfeld* [1979], *Cravens et al.* [1980], *Hodges et al.* [1981], *Hodges and Tinsley* [1981], *McElroy et al.* [1982b], *Shizgal* [1985, 1987], *Hodges and Breig* [1991, 1993], and *Hodges* [1993a, 1994].

An important feature of the charge exchange process on Earth is the temperature dependence of the charge exchange induced escape relative to the Jeans escape. The thermal flux (equation (8)) clearly increases with an increase in the exospheric temperature T_c . This is in conflict with the results obtained by *Liu and Donahue* [1974a, b, c] and *Hunten and Strobel* [1974] and verified recently by *Yung et al.* [1989] which demonstrated clearly

that the flux of hydrogen in all forms is equal to approximately $1.5 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ independent of T_c . It is now recognized [*Chamberlain*, 1977; *Shizgal and Lindenfeld*, 1982; *Bertaux*, 1975; *Hodges et al.*, 1981; *He*, 1995] that the charge exchange induced escape flux from reaction (21) decreases with increasing exospheric temperature, whereas the Jeans flux increases with increasing exospheric temperature. The sum of the two fluxes is constant at about the limiting flux value at the homopause and independent of exospheric temperature.

This has been demonstrated very clearly by *Shizgal and Lindenfeld* [1982], who employed a simple collisional model to obtain an expression of the charge exchange induced flux that can be compared with the thermal escape flux. They showed that the charge exchange induced escape F_{ce} is given by

$$F_{ce} = \hat{n}_H + \sqrt{2kT_c/\pi m_H} e^{-\lambda_c} [(1 + \tau) - \sqrt{1 + \tau} e^{-\lambda_c}] / \tau \\ = 2k_{ce} \hat{n}_{H^+} n_H \quad (28)$$

where the important parameter is $\tau = T_c/T_{H^+} - 1$ and \hat{n}_{H^+} is an effective density [*Shizgal and Lindenfeld*, 1982]. For sufficiently large T_{H^+}/T_c temperature ratios, (28) gives a rate coefficient of the form

$$k_{ce} = 3.6 \times 10^{-6} \text{ s}^{-1} / (1 - T_c/T_{H^+}) \quad (29)$$

For $T_{H^+} = 4000 \text{ K}$ and $T_c = 1000 \text{ K}$, this gives a value of $4.8 \times 10^{-6} \text{ s}^{-1}$ close to the estimate of $4.3 \times 10^{-6} \text{ s}^{-1}$ obtained by *Bertaux* [1975]. The variation of the charge exchange flux versus exospheric temperature from *Shizgal and Lindenfeld* [1982] is shown in Table 3 which should be compared with the observations of *Bertaux* [1975] reproduced in Figure 5. The main result in both cases is the increase of the charge exchange flux and the decrease of the thermal flux with decreasing exospheric temperature, and the total flux remains essentially constant. This is consistent with the results of *Liu and Donahue* [1974a, b, c] and *Yung et al.* [1989], who demonstrated that the escape flux should be approximately $1.8 \times 10^{-8} \text{ cm}^{-2} \text{ s}^{-1}$. The independence of the escape flux can be related to the result that hydrogen escape is diffusion-limited.

The result in (28) is an oversimplification, but it does illustrate in a clear way the essential concepts involved in nonthermal escape. This result has been employed recently to interpret ground-based Balmer α observations

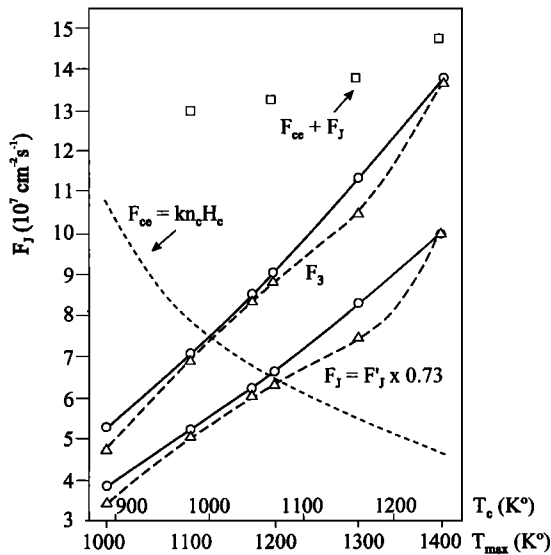


Figure 5. The terrestrial Jeans escape flux F_J and charge exchange flux F_{ce} versus exospheric temperature T_c . The two curves for F_J , indicated by solid and dashed curves, are for slightly different schemes used in the Lyman α data reduction. The total flux, $F_J + F_{ce}$, denoted by squares, is nearly constant over the temperature range considered (adapted from *Bertaux [1975]*).

of geocoronal hydrogen [*Kerr et al., 1993; He, 1995*]. A more realistic model which includes the actual density and temperature profiles was carried out by *Maher and Tinsley [1977]*. Their estimates of the escape fluxes for low and middle latitudes are $1.5 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$, in agreement with the value obtained by *Shizgal and Lindenfeld [1982]*.

The theoretical structure of the exosphere must be reconsidered in order to include these collisional nonthermal processes. The collisionless picture is not a true reflection of the actual exosphere, although one could consider the exosphere as almost collisionless with infrequent nonthermal collisional processes as a first-order perturbation, as done by *Chamberlain [1977]* and *Hodges and Tinsley [1981]*. The notion of an exobase that divides the atmosphere discontinuously between collision-dominated (hydrodynamic) and collisionless (kinetic) regimes has to be abandoned. The escape process should be considered as occurring from a range of altitudes above and below the exobase. These concepts were discussed by *Shizgal and Lindenfeld [1979]* and emphasized in the review by *Fahr and Shizgal [1983]*. They originate in the older works of *Biutner [1958]*, *Jensen [1963]*, and *Jockers [1970]* and are found in the recent papers by *Johnson [1992, 1994]*.

The basic concept for nonthermal escape is that translationally energetic species are produced by elastic or reactive collisions. These energetic particles are moving in all directions, but only those moving radially outward can escape, provided they do not suffer further collisions that change the direction and magnitude of

their velocity so as to preclude their escape. Since the density decreases approximately barometrically (see (3)), the rate of collisions decreases with increasing altitude, and hence the population of translationally energized particles decreases. However, with the decrease in the density the mean free path increases, and the probability of escape increases. Hence the rate of escape as a function of altitude attains a maximum value that occurs in the vicinity of the exobase. We can write the total escape flux as an integral over radial position, that is,

$$F_{\text{total}} = \int_{r_0}^{\infty} F(r) dr \quad (30)$$

In (30), r_0 is some radial position in the atmosphere where escape is zero, and $F(r)$ is the total production rate of energetic atoms escaping from radial position r and given by

$$F(r) = \int_0^{\infty} p(r, v) Q(r, v) dv \quad (31)$$

where $Q(r, v)$ is the velocity dependent production rate of energetic particles at radial position r . The other quantity, $p(r, v)$, is the probability that a particle with speed v at position r will escape and has a weak dependence on the speed. The explicit form of $p(r, v)$ is given by *Lindenfeld and Shizgal [1979]*. This quantity takes into account the effect of the overlying atmosphere above r and whether the particle will suffer a further collision mitigating escape. The probability for escape, $p(r, v)$, increases to unity with altitude, whereas the production of energetic particles through collisions, $Q(r, v)$, decreases with altitude. The production of fast particles for escape is enhanced by collisions, while the probability of escape is hindered by them. This involves the product $p(r, v)Q(r, v)$, and there is a maximum in the contribution to the total escape flux as shown by the dashed curve in Figure 6.

The rate of production of fast moving particles depends on the rate of binary encounters between the two colliding species and is given by

$$Q(r, v) = n_1(r)n_2(r)$$

$$\cdot \iint f_1(r, \mathbf{v}_1) f_2(r, \mathbf{v}_2) g \sigma^*(g, \Omega) d\Omega dv' \quad (32)$$

where the species densities are $n_1(r)$ and $n_2(r)$ and the species distribution functions are $f_1(r, \mathbf{v})$ and $f_2(r, \mathbf{v})$, respectively. If the distribution functions are Maxwellian (see (6)) as used in the calculation of the thermal escape, the altitude dependence also enters implicitly in terms of the temperature profile $T(r)$. A major difficulty is that the distribution functions of nonthermal species are far from equilibrium and the distribution functions are not Maxwellian. In (32), g is the relative velocity of the

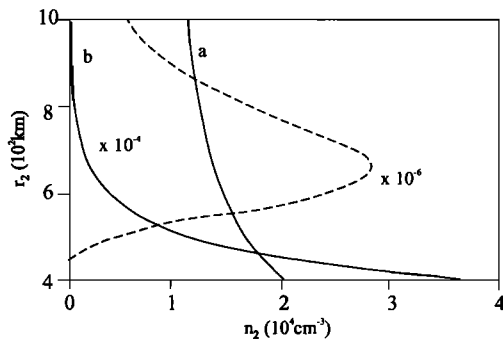


Figure 6. Altitude variation of the thermal escape flux. Solid curves are the density profiles of hydrogen (curve a) and background oxygen (curve b). The dashed curve shows the altitude dependence of the flux proportional to the product of the hydrogen and oxygen densities and the escape probability $n_{\text{H}}n_{\text{O}}P(r)$ (adapted from *Lindenfeld and Shizgal* [1979, Figure 6] copyright (1979) with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK).

colliding pair, Ω is the scattering angle that gives the orientation of the final relative velocity \mathbf{g}' relative to the initial relative velocity \mathbf{g} , and $\sigma^*(g, \Omega)$ is the differential scattering cross section, which describes the details of a binary collision. The details of such a reactive binary collision are shown in Figure 7 for the process (23). The distributions in (32) are for the incoming particles, and the integration is over the velocity of the product H^+ ion. Equation (32) thus gives the velocity dependent rate of production of energetic D^* . With the kinematics of the collision the velocities of the products (\mathbf{v}, \mathbf{v}') can be related to the velocities of the reactants ($\mathbf{v}_1, \mathbf{v}_2$) so that the final result $Q(r, v)$ is a function of the velocity of the translationally energetic D^* atom. It is the angular dependent differential cross section $\sigma^*(g, \Omega)$ that is required in (32), and which may play an important role in the velocity dependence of $Q(r, v)$. The angle independent total cross section is $\sigma_{\text{tot}}(g) = \int \sigma^*(g, \Omega) d\Omega$.

This formulation of nonthermal escape, developed by *Lindenfeld and Shizgal* [1979], *Shizgal and Lindenfeld* [1982], and *Shizgal* [1985, 1987] is rigorous provided that one has all the detailed information with regard to the density and temperature profiles, dynamical information

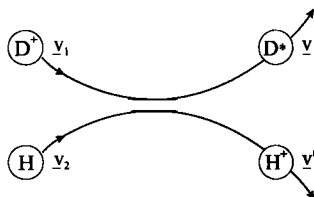
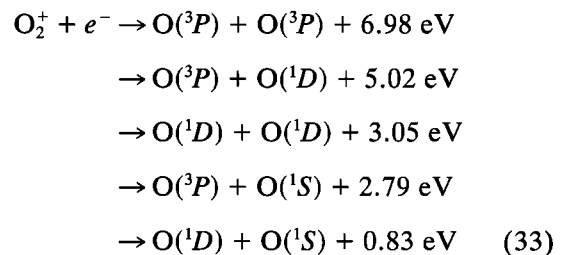


Figure 7. Schematic of a charge exchange binary collision. D^+ and H enter into a collision with velocities \mathbf{v}_1 and \mathbf{v}_2 , respectively. The products of the collision are H^+ and translationally energetic D^* with relative velocities \mathbf{v}' and \mathbf{v} , respectively.

with regard to the collision cross section, and the nature of the distribution functions that enter into the calculation of the escape flux. Density and temperature profiles are obtained from observation or atmospheric models. Collision cross sections are determined theoretically or from laboratory experiments. The distribution functions are determined from the solution of the Boltzmann equation or from Monte Carlo simulations. Observations are then required to put a constraint on the theoretical models that are constructed in this way.

In recent years it has become increasingly clear that the details of the collisional process are important to determine quantitative escape fluxes. For example, the details of the cross sections for dissociative recombination of O_2^+



remain uncertain [*Guberman*, 1988, 1991; *Fox*, 1993a]. Since the escape energy for oxygen from Mars is 1.91 eV (see Table 1), only the first two channels are important. Much of the dynamical information for such processes, such as the branching ratios of these processes, is lacking, and the details of the cross section for this process are necessary. An added complication is that the collision cross sections also depend on the vibrational state of the molecular ion [*Yung et al.*, 1989; *Guberman*, 1987, 1988, 1991; *Bates and Mitchell*, 1991; *Fox and Bougher*, 1991; *Gurwell and Yung*, 1993], and so the production of fast oxygen atoms will also depend on the vibrational distribution function (which is not shown explicitly in (32)). There are similar uncertainties in the corresponding dissociative recombination reactions of N_2^+ [*Fox*, 1993b]; the major channel for N_2^+ in the ground state is the one that yields $\text{N}(^4S)$ and $\text{N}(^2D)$. Further details can be found in the recent paper by *Fox* [1993b].

The theoretical treatment of the (H^+, H) charge exchange reaction is comparatively easy and can be considered to be quite standard, despite being implemented only recently [*Shizgal*, 1985, 1987; *Hodges and Breig*, 1991, 1993; *Hodges*, 1993b; *Clarke and Shizgal*, 1994]. For the charge exchange reactions (21) and (23), *Shizgal* [1985] pointed out that the approximation that only large impact parameters contribute to the cross section (that is, that the proton trajectory remains essentially linear during a collision and little energy is transferred) is incorrect. Detailed quantum mechanical differential cross sections for the charge exchange process are required to correctly describe the kinematics of the process [*Shizgal*, 1985, 1987; *Hodges and Breig*, 1991, 1993; *Hodges*, 1993a, 1994]. The approach based on the solution of the radial Schroedinger equation and the

calculation of the quantum mechanical phase shifts is standard and well known in the chemical physics community [Rodberg and Thaler, 1967; Shizgal, 1987]. The recent calculations by Hodges and Breig [1993] confirmed the earlier suggestions by Shizgal [1985] that the simple linear trajectory approximation is invalid for this system. Shizgal [1987] compared the escape fluxes for Venus calculated with the exact differential cross section with the results for the linear trajectory approximation. This was also examined by Clarke and Shizgal [1994] with respect to the relaxation properties of hot protons in a thermal bath of atomic hydrogen.

Gurwell and Yung [1993] considered the production of hot oxygen from dissociative recombination (24) and the subsequent energy transfer reactions (25) and (26). They employed accurate analytic fits to the differential cross sections for these processes. The importance of the angular distribution of the products, as determined by the differential cross sections, is emphasized in this paper. The distributions of hot hydrogen calculated in this way for Venus did not yield temperatures in good agreement with the observed two-temperature exosphere. An important consideration may involve the partial thermalization of the energetic atoms produced owing to collisions with other ambient species, such as atomic oxygen on Earth and CO₂ on Mars and Venus. This requires a statistical or kinetic theory treatment to take into account the thermalization process in competition with charge exchange reactions. Fahr and Shizgal [1983] and Johnson [1994] have emphasized the need to consider a detailed treatment of the collisional processes with the Boltzmann equation and realistic differential cross sections.

The rigorous kinetic theory treatment involves the solution of the Boltzmann equation for the system under consideration. The Boltzmann equation for the distribution function $f(r, v)$ of some species that could escape is given by

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_r f + \frac{\mathbf{F}}{m} \cdot \nabla_v f = \mathcal{J}[f] + Q(r, v) \quad (34)$$

The left-hand side of (34) describes the time and space evolution of the distribution function in the absence of collisions, as determined by diffusion (the term in $\mathbf{v} \cdot \nabla_r f$) and the planetary gravitational field $(\mathbf{F}/m) \cdot \nabla_v f$, where $\mathbf{F} = (GM/r^2)\mathbf{r}$. On the right-hand side the collision operator $\mathcal{J}[f]$ describes the effects of thermalizing collisions restoring the distribution function to Maxwellian, in competition with the production of fast atoms, $Q(r, v)$. A simplified local description of hot atom production and thermalization can be obtained from (34),

$$\partial f / \partial t = \mathcal{J}[f] + Q(r, v) \quad (35)$$

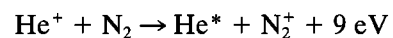
where the system is assumed to be spatially homogeneous and the effects of gravity are neglected. The collision operator is similar in form to (32), but there is also a loss of atoms from a given velocity interval as well as a

gain. The collision operator can be written in the form [Chapman and Cowling, 1964]

$$\mathcal{J}[f] = \int \int [f(\mathbf{v}_1) f_M^{\max}(\mathbf{v}_2) - f(\mathbf{v}) f_M^{\max}(\mathbf{v}')] g \sigma(g, \Omega) d\Omega dv' \quad (36)$$

where it is assumed that the background moderator species is in large excess and at equilibrium so that it is described by a Maxwellian f_M^{\max} . This assumption implies that $\mathcal{J}[f]$ is a linear operator. The velocities of the colliding particles before and after a collision are shown in Figure 7. The first term in the integral represents the gain of particles, whereas the second is the loss of particles from a given interval. At equilibrium, in the absence of $Q(r, v)$, the gain and loss are equal, detailed balance exists, and the distribution function of the escaping species f becomes Maxwellian.

The Boltzmann equation takes into account, in a statistical manner, the cascading or degradation in energy of hot atoms through a series of reversible collisional events. This could be simulated by Monte Carlo methods [Hodges, 1994]. Shizgal and Lindenfeld [1979] determined the solution of such a Boltzmann equation which included the departure from a Maxwellian distribution owing to the loss of energetic particles due to thermal escape. A brief outline for the use of the Boltzmann equation to take into account the competition between production of energetic particles and thermalization with thermal ambient species was given several years later [Shizgal, 1987]. A very similar approach for the thermal escape problem based on solutions of the Boltzmann equation was also reported by Stannes *et al.* [1991]. A Boltzmann equation analysis was also carried out by Lie-Svendensen *et al.* [1992] and Lie-Svendensen and Rees [1996a, b] in their recent study of the collisional production of energetic helium from the reaction



They employed an elastic, hard sphere cross section to model the thermalization due to He-O collisions and suggested that the details of the differential cross were not too important. The results of their calculations indicated that this charge exchange mechanism is potentially important as a loss of He and the resolution of the ⁴He budget problem. The methodology used in these calculations is very similar to that employed previously in the solution of the so-called Milne problem [Lindenfeld and Shizgal, 1983; Barrett *et al.*, 1992; Barakat and Lemaire, 1990].

Similar techniques were used to study the population of nonthermal O(³P) atoms in the thermosphere of the Earth [Lindenfeld and Shizgal, 1979], as well as nonthermal O(¹D) [Schmitt *et al.*, 1981] and hot N(⁴S) atoms [Lie-Svendensen *et al.*, 1991], although hard sphere cross sections were generally employed for thermalizing collisions. A similar study was carried out by Shematovich *et*

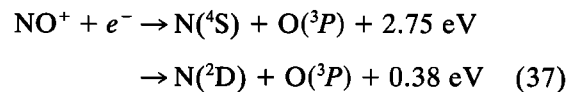
al. [1991], where they claim that there is a sufficient population of hot nitrogen atoms to have a significant role in the odd nitrogen chemistry of the lower atmosphere. *Sharma et al.* [1996] have recently reported a calculation of the energy distribution of fast nitrogen atoms in the nighttime terrestrial atmosphere. Our primary interest in this paper is with regard to processes in the upper thermosphere and exosphere, and there is only a minor overlap with these studies in the lower thermosphere. However, the techniques for the study of similar nonthermal processes are of considerable interest, and there is some potential coupling between the two regions.

These methods based on a Boltzmann equation are rigorous. Other researchers have employed similar techniques that have their origin in radiative transfer theory. Calculations based on the so-called two-stream model were carried out by Nagy and coworkers [Nagy *et al.*, 1981; Nagy and Cravens, 1988] and reviewed recently [Nagy *et al.*, 1990]. The two-stream model splits the distribution function in a plane-parallel atmosphere into two parts; one, $f^+(r, v)$, represents particles moving upward, whereas the other, $f^-(r, v)$, represents particles moving downward. This is a very simplified description of the actual anisotropic velocity distribution function. In the first paper [Nagy *et al.*, 1981] these workers considered the two-stream approximation in addition to a diffusion approach to model the production and thermalization of hot oxygen in the Venus exosphere. The thermalization is with the ambient CO_2 , O, and H and modeled by a hard sphere cross section. Since the energy distribution of the product oxygen atoms from dissociative recombination is not known, this was modeled as a Gaussian with each product atom sharing the available energy. There are additional uncertainties with the model regarding the ion and electron densities and temperatures. Nevertheless, their calculations clearly indicated the existence of an extended oxygen corona on Venus. The Pioneer Venus ultraviolet spectrometer verified, from signatures of the O I resonance triplet near 130.4 nm, the existence of a hot oxygen component above 350 km and extending out to 1500 km. These observations were cautiously confirmed by Venera 11 observations [Bertaux *et al.*, 1981]. Nagy and Cravens [1988] employed more realistic density profiles and a different value of the hard sphere cross section which controls the rate of thermalization, and their revised calculations lowered the estimated densities of hot atoms to give better agreement with the observations.

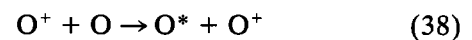
Lammer and Bauer [1991] carried out a Monte Carlo simulation of the oxygen corona on Mars that arises from dissociative recombination (reaction (24)) and estimated the escape flux of atomic oxygen at $6 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$, corresponding to a loss of oxygen atoms at a rate of 0.14 kg s^{-1} . The oxygen energy distribution can be represented by two Maxwellian distributions at 850 K and 7800 K with densities of $2 \times 10^3 \text{ cm}^{-3}$ and $1.5 \times 10^4 \text{ cm}^{-3}$, respectively. The formation of the oxygen corona

of Mars was also considered by Ip [1988, 1990]. His treatment is also a Monte Carlo simulation and not a direct solution of the Boltzmann equation. As mentioned earlier, there are many uncertainties in the dynamical and atmospheric parameters, and these calculations only approximate the actual exosphere. Nevertheless, the existence of an extended oxygen corona on both Venus and Mars is clear. It is far more extended on Mars than on Venus owing to the smaller gravitational field. There is considerable theoretical work to be considered to develop quantitative models.

Shematovich et al. [1994] presented a detailed kinetic theory analysis of the formation of the oxygen geocorona from dissociative recombination of O_2^+ (reaction (24)) as well as from the reaction



They also include the resonant charge exchange process



They begin with a set of Boltzmann-type kinetic equations similar to (34), which include source terms for the production of energetic oxygen atoms as well as the thermalization processes, and considered a stochastic/Monte Carlo method of solution. Since they consider collisions of hot oxygen with thermal oxygen, the collision operator used in their approach is not linear, in contrast to (36). Solutions of the nonlinear Boltzmann equation for the thermal escape of a one-component exosphere were provided by Merryfield and Shizgal [1994]. Marconi *et al.* [1996] carried out a detailed Monte Carlo study of a one-component escaping exosphere. Several years ago, Weinert and Shizgal [1987] considered a simple analytic solution of the nonlinear Boltzmann equation for a one-component planetary atmosphere. These considerations of the nonlinear Boltzmann are important, and the solutions are difficult to obtain.

Shematovich et al. [1994] showed that the oxygen geocorona is formed primarily by energization of the thermal oxygen component with superthermal $\text{O}(^1\text{D})$ and $\text{O}(^1\text{S})$ atoms produced from O_2 photodissociation and dissociative recombination of O_2^+ and NO^+ . At 600 km the hot oxygen has a temperature of 4100 K and a density of 10^4 cm^{-3} . Their solutions were valid through the transition region of the atmosphere in the vicinity of the exobase. The measurements by Yee *et al.* [1980] and Hedin [1989] suggest that at 550 km the temperature of the neutral atmosphere is 4000–5000 K and the densities are of the order 10^5 – 10^6 cm^{-3} . Richards *et al.* [1994] suggested that there are numerous other sources of terrestrial hot oxygen from the quenching of metastable species such as $\text{O}^+(^2\text{D})$, $\text{O}^+(^1\text{D})$, $\text{N}^+(^2\text{D})$, $\text{O}^+(^2\text{P})$, and vibrationally excited N_2 by atomic oxygen.

The theoretical treatment of nonthermal processes in the atmospheres of the terrestrial planets requires cross-section data for binary collisions and temperature and

density profiles (preferably global) including solar cycle variability. In addition, the nature of the nonequilibrium distribution functions from below to well above the exobase are required from solutions of the appropriate transport or Boltzmann equations. Observations are required to provide an important constraint on the theoretical models.

4. SOLAR WIND INDUCED ESCAPE

Mars and Venus have little or no planetary magnetic fields, in contrast to the Earth's moderate field with a magnetic moment of $8.06 \times 10^{25} \text{ G cm}^3$. The interaction of the solar wind with the strong magnetic field of the Earth results in the solar wind being largely deflected around the planet. This results in a large standoff distance of the solar wind of about 10 Earth radii. By contrast, the solar wind interacts directly with the ionospheres of Mars and Venus and perhaps a small intrinsic magnetic field, so that the standoff distance is much smaller and of the order of 1.5 planetary radii. Detailed reviews of this subject can be found in the collection of papers edited by *Luhmann et al.* [1992a, b] and *Gombosi* [1993], as well as in *Space Science Reviews*, 55, 1–498, 1991.

The nature of the interiors of the terrestrial planets and the conditions necessary for a dynamo effect leading to an intrinsic magnetic field are beyond the scope of this paper, and further details can be found elsewhere [*Parkinson*, 1983]. There is a wealth of data for the magnetic field strength in the vicinity of Earth, some for Venus primarily from the Pioneer Venus Mission, and a little for Mars from Mars 2, 3, and 5 and Phobos 2. *Russell* [1978] estimates the magnetic moment of Venus at $6.5 \times 10^{22} \text{ G cm}^3$. The situation for Mars is uncertain and controversial [*Nagy et al.*, 1995]. *Hanson and Mantas* [1988] analyzed the Martian electron temperature profiles obtained from Viking retarding potential analyzer data and concluded that the data do not uniquely establish whether the magnetic field is intrinsic or induced. *Axford* [1991] estimates the magnetic moment of Mars at $0.5 \times 10^{22} \text{ G cm}^3$. *Slavin and Holzer* [1982] estimate the Martian magnetic moment at $2.6 \times 10^{22} \text{ G cm}^3$. *Vaisberg* [1992] has provided a history of the estimates of the intrinsic magnetic moments of Mars which hover around $2 \times 10^{22} \text{ G cm}^3$. *Dolginov and Zhuzgov* [1991] estimate a Martian magnetic moment of $1.22 \times 10^{22} \text{ G cm}^3$. *Lammer and Bauer* [1992] suggest an upper limit at somewhat less than 10^{22} G cm^3 from a simulation of the heavy ion escape from Mars. *Krymskii et al.* [1995] have very recently suggested, from an examination of the observed electron density profiles, that Mars must have an intrinsic magnetic field. A weak intrinsic magnetic field would make the profiles depend on the zenith angle and also on the magnetic latitude and longitude defined by the intrinsic field. *Trotignon et al.* [1996] suggest that from their study of solar wind measurements near Mars with

Phobos 2 data, Mars does not appear to possess an intrinsic magnetic field, and they set the upper limit at $2.2 \times 10^{22} \text{ G cm}^3$. This is a very controversial subject and a definitive conclusion regarding the intrinsic field of Mars may be forthcoming from the data from the upcoming satellite missions.

The interaction of the solar wind plasma with Mars and Venus is substantially different from the interaction with Earth. For Venus and Mars the interaction is primarily with the high-altitude portion of the atmosphere and involves both neutral and charged species. For Earth the interaction is predominantly with the geomagnetic field which deflects the flow around the planet. In all three cases the interaction results in the formation of a stationary bow shock. This region is similar to a typical shock wave front, acting as a boundary or transitional region between supersonic and subsonic flow. In terms of the respective planetary radii the bow shock is located at $10 R_E$ for Earth, whereas it is of the order of 1.2–1.5 planetary radii for Mars [*Luhmann and Brace*, 1991; *Luhmann et al.*, 1992b] and Venus [*Breus*, 1986]. The position of the bow shock depends on many different physical conditions and is highly variable [*Zhang et al.*, 1990]. The situation for Venus is much better understood than for Mars primarily because of Pioneer Venus data. An excellent discussion of the basic physics of the interaction of the solar wind with Venus and Mars has been given by *Luhmann* [1995].

The ionopause is the upper boundary of the thermal ionosphere and occurs where the solar wind dynamic pressure is balanced by the thermal pressure of the ionospheric plasma. The location of the ionopause is highly variable, depending on many factors. At Venus it is between an altitude of about 300 and 400 km most of the time during solar cycle maximum [*Breus*, 1986; *Luhmann*, 1986; *Mahajan and Magr*, 1990; *Brace and Kliore*, 1991; *Luhmann et al.*, 1992b], while for Mars it can be estimated at about 400 km [*Shinagawa and Cravens*, 1988, 1989, 1992; *Lammer and Bauer*, 1992; *Ip*, 1992; *Ip et al.*, 1994]. The thickness of the ionopause for both planets is of the order of several tens of kilometers. There is some evidence that for Mars the thermal ionospheric pressure is at times insufficient to balance the solar wind dynamic pressure, and the ionopause is not clearly defined [*Hanson and Mantas*, 1988; *Luhmann*, 1995]. Between the bow shock and the ionopause is the ionosheath (or magnetosheath).

The solar wind interaction with the atmospheres of Mars and Venus alters the conditions of the atmospheres, which in turn affects the shocked solar wind in the magnetosheath. For example, the ionization of the neutral atmosphere by the solar wind plasma (or solar photons) results in ions that produce currents which deflect the solar wind plasma. The neutrals that have been ionized can be accelerated from an escaping trajectory back into the atmosphere. These accelerated ions of planetary origin can collide and energize neutral particles into escaping trajectories. This process, re-

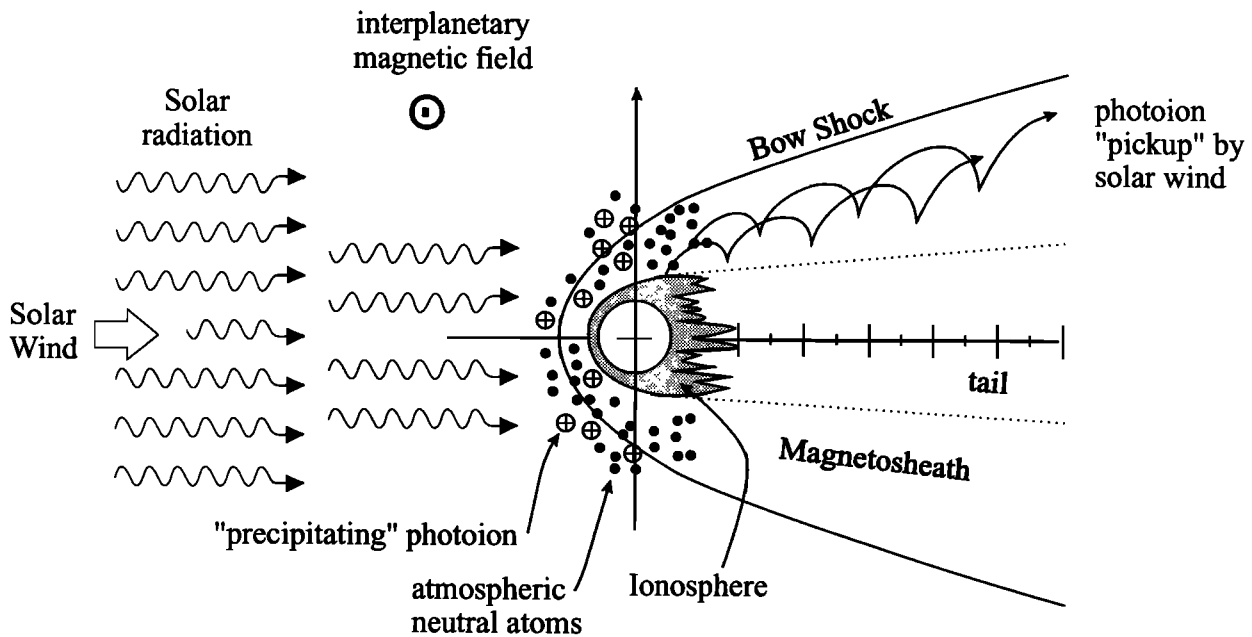


Figure 8. Schematic of the solar wind interaction with Venus and Mars and the solar wind induced escape of ions. Ions produced in the region of solar wind by photoionization and/or charge exchange are either removed by the solar wind or redirected into the lower atmosphere (adapted from *Luhmann and Kozyra* [1991]).

ferred to as knock on, is analogous to the energy transfer processes discussed in section 3 [*Cooper et al.*, 1984]. If the incident energy of an ion is high, there can be a degradation or thermalization due to a succession of charge exchange collisions that cycle through ionization and neutralization.

A theoretical treatment of the solar wind–atmosphere interaction must consider both systems, the solar wind and the atmosphere, simultaneously. The models often used to study this interaction are mainly fluid models of the solar wind [*Tanaka*, 1995; *Murawski and Steinolfson*, 1996], and excellent reviews have been provided recently by *Johnson* [1994], *Luhmann et al.* [1992b], and *Breus* [1986]. *Johnson* [1994] and *Shapiro et al.* [1995] have emphasized kinetic theory aspects of the interaction and other associated physical processes such as sputtering. *Luhmann and Kozyra* [1991] considered the interaction of the solar wind plasma with the exospheres of Venus and Mars with regard to the scavenging of planetary ions and the associated problem of the heating of the ionosphere, leading to anomalous plasma density and temperature profiles. They employed a combination of the hydrodynamic model of *Spreiter and Stahara* [1980] for the solar wind and the exospheric models of *Nagy and Cravens* [1988]. The energy loss of a fast oxygen ion passing through a background of neutral oxygen is simulated with a Monte Carlo scheme. The models of the extended exospheric coronae of the planets, such as the hot oxygen coronae of Mars and Venus, are almost collisionless. These different treatments of these two interacting systems, the solar wind and the exosphere, should be reconsidered. Figure 8, adapted from *Luh-*

mann and Kozyra [1991], is a depiction of the interaction of the solar wind and Venus and shows the ionosphere (or magnetosheath) between the ionopause and the bow shock. Neutral atoms are ionized, execute helical type trajectories with very large Larmor radii, and are swept out of the atmosphere by the solar wind magnetic field.

The main topic of interest in the present paper is the way in which this interaction leads to the loss of atmospheric constituents. This can be significant, since the hydrogen and oxygen coronae of the planets, discussed in section 3, extend to large radial distances and the solar wind plasma extends to fairly low altitudes. In either case the extended hot coronae of these planets extend well beyond the ionopause, and a strong solar wind–ionosphere interaction is to be expected. There can be a significant atmospheric loss as a consequence of this interaction.

The main mechanism for loss of atmospheric constituents appears to be the ionization of the neutral atmosphere by photoionization, by impact with solar wind electrons, or by charge exchange with solar wind ions such as reaction (22). The product ion can then be captured in the solar interplanetary magnetic field and swept away from the planet and/or accelerated in the $\mathbf{v} \times \mathbf{B}$ drift. The accelerated ion can also reenter the atmosphere and transfer its energy to a neutral atom in a subsequent collision. This process has been referred to as sputtering [*Johnson*, 1994], in analogy to a similar laboratory process when a plasma is in contact with a metal surface. As pointed out by *Johnson* [1994], the correct treatment of this nonequilibrium process requires the solution of the Boltzmann equation. The

details of the energy transfer processes require the appropriate set of collision cross sections.

The process by which atmospheric ions become an integral part of the solar wind plasma is referred to as mass loading [Breus, 1986; Breus *et al.*, 1989; Dubinin *et al.*, 1994] in the sense that additional mass has been added to the solar wind. In more quantitative terms it implies that the continuity equation for the hydrodynamic description of the solar wind (equation (11)) must be augmented by a source term to account for the additional mass of planetary origin. This mass-loading effect and the escape of the planetary atmosphere have an important effect on both the exosphere and the solar wind.

Luhmann *et al.* [1992b] and Luhmann [1995] have provided an excellent overview of the interaction of the solar wind with Mars and Venus. The situation for Venus was reviewed by Luhmann [1986], and a discussion of the mass-loading effect was presented by Breus [1986]. Comparisons between available satellite data and theoretical models were provided. There is some discussion by Breus [1986] as to the applicability of magneto-hydrodynamic (MHD) theory to mass loading, that is, the interaction of a fluid-like (though rarefied) plasma of the solar wind and an extended, nearly collisionless, planetary corona. The conclusion was that MHD theory can provide useful models of the solar wind-atmosphere interaction. Ip *et al.* [1994] studied the effect of charge exchange as a loss process for solar wind protons interacting with the exosphere of Mars and demonstrated that this process affects the formation of the planetopause-magnetopause boundary. They mention that a quantitative assessment would require a kinetic simulation of the solar wind-Mars interaction and the collisional loss effect by charge exchange.

The interaction of the solar wind with the Martian exosphere can lead to a significant loss of oxygen. As mentioned previously, this could be an important mechanism for the loss of water if the net loss of oxygen is accompanied by the appropriate stoichiometric loss of hydrogen. The original inventory of water on Mars could be equivalent to several tens of kilometers in depth or more. The oxygen atoms in the Martian exosphere are converted to ions by photoionization, electron impact, or charge exchange. The ions are swept out by the solar wind or reenter the atmosphere where they can sputter neutrals from near the exobase (see Figure 8) [Luhmann and Kozyra, 1991]. Luhmann *et al.* [1992c] and Zhang *et al.* [1993a, b] have estimated the oxygen loss rates from Mars. Typical results for the neutral oxygen escape rate and O^+ pickup are of 8×10^{25} O atoms s^{-1} and 6×10^{24} ions s^{-1} , respectively. These energetic O^+ ions reimpact the exobase and create additional energetic neutral O that is ejected at a rate of 3×10^{23} O atoms s^{-1} . These estimates are very model dependent.

Jakosky *et al.* [1994] have presented a detailed study of the solar wind induced escape from Mars and the way this process can lead to isotopic fractionation. They

reiterate that energetic O^+ formed by ionization of neutral O in the hot corona of Mars can be picked up by the magnetic field lines of the solar wind and that this is a significant loss mechanism. They also add that the loss of ^{36}Ar and ^{38}Ar , ^{20}Ne and ^{22}Ne , and ^{14}N and ^{15}N is even more significant owing to their increased abundance at the exobase. Jakosky *et al.* construct elaborate evolutionary models and consider the fractionation of the isotopes of the inert gases as well as that of ^{16}O , ^{18}O , ^{12}C , and ^{13}C . They find that the solar wind induced escape does not account for any significant fractionation of $^{18}\text{O}/^{16}\text{O}$ or of $^{13}\text{C}/^{12}\text{C}$. Of interest is their conclusion that a period of hydrodynamic escape is not required to reproduce the fractionation of $^{36}\text{Ar}/^{38}\text{Ar}$.

5. EVOLUTIONARY ASPECTS OF NONTHERMAL ESCAPE FOR VENUS AND MARS

Nonthermal processes in planetary exospheres, reviewed in Sections 3 and 4, have an impact on the evolution of planetary atmospheres. Evolutionary processes involve the interplay of numerous phenomena in several different disciplines. The most difficult aspect is the extrapolation of present-day observations to the distant past on geologic timescales. One of several extremely important items is the evolutionary history of the Sun and the variability over time of its EUV output. In this section we review recent discussions of possible scenarios of evolution for the atmospheres and surfaces of Mars and Venus and, in particular, the question of whether water existed in abundance on either planet. We present this subject not as active practitioners in this extremely difficult and controversial area but rather as interested bystanders with research interests that overlap work in the field.

As discussed in the introduction and in section 3, the Pioneer Venus Orbiter determined that Venus has a D/H ratio approximately 100 times that of Earth. This value has been confirmed using Earth-based observation of HDO and H_2O absorption spectra [De Bergh *et al.*, 1991]. If Venus and Earth both developed with similar initial D/H ratios, this would seem to indicate that during early atmospheric evolution, Venus had over 100 times its present amount of water. The mixing ratio of water in the lower Venusian atmosphere (about 10^{-4} by volume) can be used to calculate a rough global water inventory for present day Venus of about 0.0014% of that of Earth [Kasting and Pollack, 1983]. When considered in addition to the D/H ratio, this seems to suggest that Venus had an initial volume of water of only 0.14% of that of Earth. It has been argued that Venus could have had a much lower initial budget of water due to its accretion from desiccated materials in the much warmer region of the solar nebula near the Sun [Lewis, 1970; Lewis and Kreimendahl, 1980]. The gradient of mean planetary densities does provide some evidence that the initial bulk compositions of the terrestrial planets may

not have been uniform [Hunten, 1993]. The view of a wet Venus was also questioned by Grinspoon [1987, 1993], who suggested that Venus may exist in a steady state with regard to water, with volcanic outgassing or impacts of volatile rich bodies (such as comets) providing a water source with an enhanced D/H ratio. He attributes the current D/H ratio to a signature of some catastrophic injection of water into the atmosphere followed by massive fractionating escape (possibly diffusion limited) within the last billion years, rather than to a signature of a primordial ocean. However, most explanations offered to account for the measured D/H ratio seem to imply a higher water content on Venus in the past.

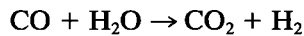
The standard view of Martian atmospheric evolution [Fanale et al., 1992; Squyres et al., 1992; Hunten, 1993] has Mars much as it is today for the last 3 Gyr: a thin atmosphere of predominantly CO₂ with some amount of water incorporated into the regolith as permafrost or frozen at the polar caps but with abundant liquid water before about 3.5 Gyr ago [Jakosky and Jones, 1994]. Recently, there have been suggestions [Kerr, 1993; Hunten, 1993] of cyclic warming over the last few billions of years on Mars to explain observed surface morphology. These theories hypothesize massive outgassing of CO₂ to increase the surface pressure to the point that liquid water is stable and estimate that an equivalent of a planetwide layer of water a few hundred meters deep is released. If at least some of the observed morphology of the Martian surface is relatively recent (<3 Gyr), a significant amount of water must be available for exchange with the surface from subsurface, polar cap, and atmospheric reservoirs, since the amount of water required to form these features could not have escaped from the planet in the time since formation, given the available loss mechanisms [Squyres et al., 1992]. However, there are many other factors which complicate an estimate of the current Martian water reservoir. For example, it has been noted [Kieffer et al., 1992; Kieffer and Zent, 1992] that changes in Martian obliquity strongly affect the amount and distribution of absorbed solar radiation and can subsequently have important effects on the exchange of volatiles between surface and atmospheric reservoirs.

The loss of water from an atmosphere is strongly tied to the breakdown and escape of hydrogenous constituents. The photodissociation of water vapor in the middle or upper atmosphere followed by the escape of hydrogen, if accompanied by the appropriate loss of oxygen, is the suggested principal mechanism for the loss of water. The excess oxygen could be lost from the atmosphere or removed through reactions with gases in the atmosphere or compounds at the planet's surface [Kasting and Pollack, 1983]. The interpretation of measured D/H ratios is based on the assumption that the amount of deuterium in a planetary atmosphere has remained roughly constant from early atmospheric formation. However, current models of atmospheric escape indicate that there is some escape of deuterium, and so the present concen-

tration may not be indicative of the value during formation of the initial atmosphere [Hunten, 1993]. A constant deuterium concentration would result in higher D/H ratios than are currently observed and would increase the implied early volume of water on Venus or Mars. Since the D/H ratio is sensitive to initial deuterium concentrations, processes which may enhance the escape of both deuterium and hydrogen must be closely examined, as discussed in section 3. Hunten [1990] has reviewed published estimates of the globally averaged hydrogen flux from Venus for various nonthermal processes, and current values are at about $(0.2\text{--}2.7) \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$. It may have been 1000 times larger in an early atmosphere much richer in hydrogen [Kasting and Pollack, 1983]. Deuterium escape via the analogous reaction (23) is thought to be approximately one tenth as efficient [Kasting and Pollack, 1983]. McElroy et al. [1982b] estimated the escape flux of hydrogen from Venus from dissociative recombination of O₂⁺ and subsequent energy transfer to hydrogen (processes (24)–(26)) at $8 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$. The hydrogen escape flux due to charge exchange with hot protons (reaction (21)) is approximately $1.2 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ [Kumar et al., 1983]. The combined effect of these loss processes is only sufficient to remove approximately 40 cm of water planetwide [Hunten et al., 1989; Atreya et al., 1989]. On Mars, estimates of the hydrogen escape flux are in the range of $(1\text{--}2) \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ [Barth et al., 1972; Anderson, 1974].

Kasting and Pollack [1983] mention that the escape of hydrogen is only one aspect of the problem of loss of water. Oxygen must also be removed at a rate consistent with the stoichiometry of water. This is particularly difficult on Venus where the escape energy of such massive constituents is high. McElroy et al. [1982a] estimated the average escape flux of oxygen due to ionization of thermal and nonthermal oxygen atoms above the Venusian plasmopause and subsequent pickup by the solar wind at $6 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$. This is approximately half the hydrogen escape rate and implies that the hydrogen and oxygen loss is equivalent to the loss of water. This loss rate, however, would account for only the loss of a fraction of an Earth equivalent ocean of water. The model of massive hydrogen loss by hydrodynamic escape during early atmosphere formation such as employed by Kasting and Pollack [1983] to remove water does not address the removal of the oxygen that is left behind. It has been suggested that the excess oxygen could react with iron in crustal rocks or early magmas [Watson et al., 1981; Kasting and Pollack, 1983]. The rate of surface rejuvenation and the level of geologic activity required for such a process have been questioned [Kasting and Pollack, 1983; Richardson et al., 1984]. Recent radar imaging results from Venera and Magellan spacecraft appear to indicate widespread and relatively recent geologic and volcanic activity on Venus [Hunten, 1993], although it is unclear whether these processes have been sufficiently vigorous over geologic timescales to absorb the required excess oxygen.

Other mechanisms not requiring sinks similar to those of the crustal incorporation model have been suggested to augment the removal of water. *Richardson et al.* [1984] investigated the reaction



which links the removal of oxygen to the availability of carbon monoxide. However, it is necessary to postulate C/H ratios of the order of 5 times that of Earth in order to create a sufficient atmospheric CO abundance. *Bauer* [1983] and *Hunten* [1993] both mention the possibility of a solar T Tauri phase, which could have enhanced hydrodynamic escape of heavier species through increased EUV output in addition to increasing direct mass loss by photoionization of neutrals and subsequent incorporation into the much more active solar wind (see section 4). The removal of oxygen from Mars is more straightforward than for Venus because of the much lower escape energy. As we can see from comparisons of the required escape energy in Table 1, both thermal oxygen and hot oxygen generated by the charge exchange reaction given by process (24) can escape directly from the upper atmosphere of Mars. *McElroy* [1972], *Lammer and Bauer* [1991], and *Fox* [1993a] estimated the escape flux of oxygen from Mars at $(6-7) \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$, $6 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$, and $3 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$, respectively. The latter two estimates are significantly less than half the hydrogen escape flux. Other mechanisms for the removal of oxygen through sputtering and the interaction with the solar wind have also been proposed [*Luhmann and Kozyra*, 1991; *Zhang et al.*, 1993a, b; *Johnson*, 1994; *Kass and Yung*, 1995; *Fox*, 1993a]. On Venus, exospheric oxygen is largely gravitationally bound and thus contributes to nonthermal escape mainly through momentum transfer reactions such as (25) and (26). Loss of oxygen from Mars also occurs through the solar wind interaction with the planet's ionosphere. The thicker atmosphere of Venus and the correspondingly larger standoff distance of the bow shock make direct removal of oxygen less important. As can be seen from Table 1, even for an early Earth and Venus, at nearly their present masses the relatively high escape velocities may have made this process inefficient. Mars, however, would have remained vulnerable to this process for a much longer period [*Hunten*, 1993].

For an early Venus with a much higher water vapor content in the upper atmosphere, photodissociation by EUV radiation would have created atomic hydrogen in much greater amounts than at present. For this dense corona of hydrogen, escape may have been hydrodynamic rather than kinetic in nature [*Watson et al.*, 1981]. The hydrodynamic escape of hydrogen could have dragged more massive constituents, such as xenon, argon, and others, with it. This would mean, for example, that the deuterium enrichment on Venus would reflect only enhanced hydrogen loss after hydrodynamic escape fluxes fell below the level required to remove deuterium

[*Kasting and Pollack*, 1983]. The hydrodynamic formulation of the escape problem was described in section 2.2. This hydrodynamic drag-induced escape has important consequences for isotopic fractionations observed in the noble gases on Venus, Earth, and Mars.

The various theories to explain both Martian and Venusian atmospheric evolution are strongly influenced by the efficiency at which water loss processes have operated over the evolution of their respective atmospheres. Many of the current limits on the history and abundance of Martian water are implied from D/H measurements from Earth and of SNC meteorites [*Owen et al.*, 1988; *Pepin*, 1991, 1992, 1994] and also from analysis of images of surface morphology from past missions to the planet, most notably the Viking missions [*Pollack et al.*, 1987]. For Venus the strikingly large D/H ratio recorded by the Pioneer Venus Orbiter (and confirmed by Earth-based observations) is the primary constraint on the modeling of past water abundances. Images and data from upcoming Mars missions will help to resolve many of the current uncertainties in geologic interpretation and atmospheric modeling which make it difficult to comment with certainty on the origins of the observed features of Mars [*Kerr*, 1993]. The improved constraints on some of the model parameters may also aid the interpretation of atmospheric evolution on Venus.

The noble gases are important indicators of atmospheric evolutionary history. With the exception of helium, the noble gases are too heavy to have escaped thermally from the terrestrial atmospheres over a time-scale comparable with the age of the solar system. They are also chemically inert and do not react with atmospheric or crustal constituents and are thus expected to have remained in the planetary atmospheres following accretion [*Hunten*, 1993]. It is thought that fractionation of the noble gases must thus be the result of drag-induced escape during massive hydrodynamic hydrogen outflow during early planetary history [*Kasting and Pollack*, 1983; *Zahnle et al.*, 1990].

The rapid hydrodynamic escape of molecular hydrogen from a dense primordial atmosphere could have resulted in a mass dependent fractionation. Such a process could explain the mass dependent depletion of the noble gases observed in the Martian atmosphere. Enhanced solar UV fluxes from a young Sun would have provided the energetics for this expansion. The methodology developed by *Kasting and Pollack* [1983], *Zahnle and Kasting* [1986], and *Zahnle et al.* [1990] is based on the solution of the hydrodynamic equations analogous to those used for the solar wind expansion. A more analytic approach was developed by *Hunten et al.* [1987] and reviewed by *Hunten* [1990]. The fractionation occurs because of the competition between the downward force on an atom (or molecule) and the upward drag force which depends on the diffusion parameter b (see section 2.3) which is independent of mass. *Hunten et al.* [1987] showed that at some crossover mass m_c the two forces are equal. Their final result is that the inventory of

component 2 at time t relative to the original abundance at time t_0 , N_2/N_2^0 , is dependent on the mass m_2 and given by

$$\ln \left(\frac{N_2}{N_2^0} \right) = - \frac{(m_2 - m_1)}{(m_c - m_1)} \left[\frac{F_1^0}{N_1} (t_2 - t_0) \right] \quad (39)$$

where F_1^0 is the flux at some reference level r_0 . Using (39), *Hunten et al.* [1987] studied the mass fractionation of the isotopes of xenon as a result of large hydrodynamic escape fluxes, or blowoff, of hydrogen. The result of their study showed a linear relationship between relative abundance and mass of each isotope. Similar studies of hydrodynamic escape induced fractionation for other noble gases have been carried out by *Zahnle and Kasting* [1986], *Zahnle et al.* [1990], and *Pepin* [1991, 1992, 1994]. An alternative method for causing fractionation of the noble gases based on escape from planetesimals has been presented by *Donahue* [1986] but does not give the same level of agreement with observed planetary noble gas isotope ratios as hydrodynamic blowoff models [*Pepin*, 1991; *Hunten*, 1993].

At present, there are still many uncertain parameters in the hydrodynamic models used to predict isotopic fractionation of the noble gases for Venus, Earth, and Mars. These include the strength and time dependence of the solar EUV output of the young Sun, the history and speed of planetary accretion, the acquisition of initial noble gas reservoirs, the strength and timing of volatile outgassing, the geochemical behavior of xenon in planetary interiors, and the temperature profiles of the atmospheric constituents. As pointed out by *Pepin* [1991] and *Hunten* [1993], because of these and other uncertainties the hydrodynamic fractionation scenarios are not unique. Information from future planetary missions should help in this regard.

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