

becomes possible to form carbonate in the presence of water and silicate minerals, and this provides a way to build up a storehouse of CO_2 in a planet's interior, which can be outgassed later. The following exercise shows that it would require exceedingly high temperatures to directly dissociate stable chemical constituents.

Exercise 8.3 Using the relation $\Delta E = h\nu$ convert the photodissociation wavelengths in Table 8.3 into energies. Find the temperatures for which the thermal energy kT is equal to the dissociation energy threshold for each of the species.

Hence, it is not likely that dissociation of H_2O in a post-impact cloud or planetary atmosphere with a temperature of a few thousand kelvin would provide enough oxygen to oxidize carbon into CO_2 . However, at temperatures of a few thousand kelvin, the reaction



can proceed swiftly. The CO can then be gradually oxidized into CO_2 using photolytically produced OH. The *water gas shift reaction*



can accomplish the same thing thermally. These reactions are in fact the same ones used industrially in coal gasification. In order to produce a large inventory of CO_2 the necessary reactants must be brought together and held at a high temperature for a sufficiently long time. The range of possible outcomes of this process during atmospheric formation has not been much explored, and is a fruitful area for further inquiry.

Another familiar industrial process, however, could intervene and prevent the formation of CO_2 . In the *Fischer-Tropsch process*, metallic catalysts including iron, cobalt, nickel, or ruthenium catalyze the production of hydrocarbons from the CO-H_2 mixture. If this happens, it would form organic carbon or methane at the expense of CO_2 , with attendant consequences for the subsequent fate of the planet's evolving atmosphere.

8.7 ESCAPE OF AN ATMOSPHERE TO SPACE

Atmospheric escape calculations play a role in determining how a planet got to be the way we see it today, and what kind of atmosphere it might have had in its past; escape calculations can also indicate how long a planet can maintain a habitable climate, and can inform investigations into the mechanisms needed to maintain an atmosphere in a given state. For example, does there need to be a source of N_2 outgassing to maintain Titan's largely N_2 atmosphere? The answer to that hinges primarily on how rapidly a small, cold body like Titan can lose a relatively heavy gas like N_2 . Similar questions apply to maintenance of CH_4 on Titan, since the processes which turn CH_4 into ethane and other compounds which accumulate on the surface liberate H_2 , which must escape to space or accumulate in the atmosphere. Likewise, if Venus ever had an ocean comparable to Earth's, and went into a runaway state, both the hydrogen and oxygen in the water must have been lost somehow, since there is very little water in Venus' atmosphere today. Could the hydrogen escape to space at a sufficient rate? The oxygen? The escape of water to space is what makes a runaway greenhouse essentially irreversible, so it enters into the habitability question for Venus and other planets subject to a runaway greenhouse. One picture of the climate of Early Mars posits a warm, wet climate supported in part by the greenhouse effect associated with a CO_2

have to look at hydrogen-dominated exospheres, and find means other than thermal escape to pump the hydrogen into space.

Hydrogen, in the form of H_2 , is one of the substances commonly outgassed from volcanoes on Earth and probably on other geologically active planets. In Earth's present highly oxygenated atmosphere, this hydrogen rapidly oxidizes into water, so there is little opportunity for free hydrogen to accumulate. On the anoxic Early Earth, however, the accumulation of hydrogen would be limited by the rate of escape to space. For a cold N_2 -dominated exosphere, the exobase density of atomic hydrogen is $6.7 \cdot 10^{15}/m^3$ if the molar concentration is 10%. Using the Jeans escape coefficient from Table 8.5, the hydrogen escape flux would be a mere $\Phi = 3.32 \cdot 10^9/m^2s$. It has been estimated that the volcanic outgassing rate of H_2 on the Early Earth could have been on the order of 10^{15} molecules per second per square meter of Earth's surface, which is many orders of magnitude in excess of the Jeans escape flux. Thus, if Jeans escape were the only escape mechanism for hydrogen, hydrogen would accumulate to very high concentrations on the Early Earth. In reality, it would only accumulate to the point where the exosphere became hydrogen-dominated, whereupon other, more efficient escape mechanisms would take over. Still, we have learned from this exercise that hydrogen has the potential to build up to high values on an anoxic planet, that a cold exobase plays an important role in allowing this to happen, and that the exosphere is likely to have been hydrogen-dominated.

Another case of interest is hydrogen loss from Titan. In this case, the hydrogen is supplied by decomposition of CH_4 in the atmosphere, and the loss is important because the atmospheric chemistry would change quite a bit if hydrogen stuck around in the atmosphere. Let's suppose a 10% atomic hydrogen concentration at an N_2 -dominated exobase on Titan. From Table 8.5, we see that the Jeans escape coefficient for atomic hydrogen is very large in the Titan case, owing to the low gravity. The exobase particle density is about $1.3 \cdot 10^{14}/m^3$ based on the table, whence the assumed hydrogen density is $1.3 \cdot 10^{13}/m^3$ and the escape flux is $\Phi = 6 \cdot 10^{16}/m^2s$. Assuming a CH_4 molar concentration of 30% over a layer 15 km deep in Titan's lower atmosphere, there are $1.3 \cdot 10^{30}$ hydrogen atoms per square meter of Titan's surface, stored in the form of CH_4 . The calculated Jeans escape rate would be sufficient to remove this entire inventory in under a million years. The precise rate of hydrogen loss depends on the rate of decomposition of methane and the rate of delivery of hydrogen to the exobase, but it seems quite likely that Jeans escape can get rid of the hydrogen resulting from methane decomposition.

Before taking on more complicated and effective means of escape, there is one more basic concept we need to take on: diffusion and gravitational segregation of atmospheric species. Let's track the position of a molecule of species A moving with typical speed v , and colliding with background molecules from time to time. The typical distance the molecule moves between collisions is the mean free path ℓ computed earlier. If we idealize the collisions as causing a randomization of the particle's direction, then the particle will undergo a random walk. For particles undergoing random motions of this sort, the flux is proportional to the gradient of particle concentration; the process is called *diffusion*, and the proportionality constant is the *diffusion coefficient*, which we shall call D . It is closely related to the heat diffusion coefficient we have introduced in previous chapters. In addition, molecules or atoms in a gravitational field will accelerate downward under the action of gravity until the drag force due to collisions with the rest of the gas equals the gravitational force. This equilibration happens quickly, so that the particles attain a *terminal fall velocity* w_f . The terminal velocity is proportional to the local acceleration of gravity, and leads to a downward particle flux which is the product of the fall speed with the particle density.

The diffusion coefficient has units of length squared over time, and by dimensional analysis must be proportional to the product of mean free path ℓ with the typical thermal velocity $\sqrt{kT/m}$ where m is the particle mass of the species we are tracking. Since ℓ is inversely proportional to the total particle density n , the diffusion coefficient increases in inverse proportion to n . For this reason, it is often expressed in terms of a *binary diffusion parameter* b , via the expression $b \equiv Dn$. For any given pair of species, b is a function of temperature alone. For ideal hard-sphere collisions between particles with masses m_1 and m_2 and radii r_1 and r_2 , the binary collision parameter is given by the expression

$$b = \frac{3\sqrt{2}\pi}{64} \frac{v}{\chi} \quad (8.38)$$

where χ is the collision cross-section area based on radius $(r_1 + r_2)/2$ and $v \equiv \sqrt{kT/\bar{m}}$ is the thermal velocity based on the harmonic mean of the masses, $\bar{m} = m_1 m_2 / (m_1 + m_2)$. For an ideal hard-sphere gas the binary parameter, and hence the diffusion coefficient, increases with the square root of temperature. For actual gases, however, the effective collision diameter goes down somewhat with temperature, leading to other empirical temperature scaling laws, generally with temperature exponents in the range of 0.7 to 1. As with collision radius, atomic hydrogen is an exception, having a temperature scaling exponent between 1.6 and 1.7 for collisions with most species. The magnitude of the binary parameter for atomic hydrogen is also greater than one would expect from hard-sphere theory, since the effective collision radius is that of atomic hydrogen even when it is colliding with a substantially larger particle. Thus, atomic hydrogen has anomalously large diffusion, which increases anomalously strongly with temperature. The diffusion coefficient of atomic hydrogen is even larger than one would expect solely on the basis of its low mass and hence large thermal velocity.

Next, we remark that the fall speed scales with the velocity acquired by the particle through gravitational acceleration in the time between collisions. Thus w_f scales with $g\ell/\sqrt{kT/m}$. The ratio D/w_f thus is proportional to $(kT/m)/g = R_A T/g$, where R_A is the gas constant for the species A . This is just the isothermal scale height H_A that the species would have in isolation. In fact a more detailed calculation shows that for an isothermal ideal gas, the ratio D/w_f is not just proportional to H_A , but is actually exactly equal to it. (As a short cut to this result, we may argue that it is implied by the requirement that the scale height be equal to the usual hydrostatic result when the species A dominates the atmospheric composition.) In the following, we will keep things simple by restricting attention to the isothermal case, which will be sufficient for our purposes.

Let n_A be the particle density of species A , which may be one of many constituents of the gas. Putting together the flux due to diffusion and the gravitational settling, the net flux of the species (upward positive) is

$$F_A = -\overset{\text{fall}}{w_f n_A} - D \overset{\text{diffuse up}}{\frac{dn_A}{dr}}. \quad (8.39)$$

Equilibrium is defined by a state of zero flux. In that case, the particle density is governed by the equation

$$\frac{dn_A}{dr} = -\frac{1}{H_A} n_A, \quad H_A \equiv \frac{w_f}{D} = \frac{R_A T}{g(r)} = \frac{kT}{m_A g(r)} \quad (8.40)$$

where m_A is the mass of a molecule of species A . Thus, the particle density decays exponentially with scale height H_A . Note that this is identical in form to the particle density given by hydrostatic balance, except that the equation we have just derived applies to the particle density of each species separately, and not just to the particle density of all species together.

In fact, in equilibrium each species acts as if it were in hydrostatic equilibrium separately, and has the same hydrostatic scale height as if the other gases were not there at all. Since we are assuming thermodynamic equilibrium, all species are characterized by the same temperature, and of course all species are subject to the same gravitational acceleration. Thus, the scale height varies inversely with the molecular weight of the species. Since the density of light species decays less sharply with altitude than the density of heavier species, the atmosphere will tend to sort itself out in the vertical according to molecular weight. Light constituents will congregate near the top of the atmosphere like escaped helium balloons at the top of a circus tent.

This can only happen, however, if the mixing is dominated by molecular diffusion. In the lower atmosphere, mixing is overwhelmingly due to turbulent fluid motions, which treat all species equally and keep the mixing ratios uniform, in the absence of strong sinks or sources by chemistry or phase change. Since the molecular diffusivity is inversely proportional to total particle density, it will increase roughly exponentially with altitude, and will therefore come to dominate turbulent mixing at sufficiently high altitudes. The altitude where diffusive segregation begins to set in is called the *homopause* (sometimes *turbopause*) and the lower part of the atmosphere where mixing ratios of non-reactive substances are uniform is called the *homosphere*. It is very difficult to get an *a priori* estimate of turbulent mixing rates - indeed at one time it was expected that the Earth's stratosphere would be diffusively segregated. More often than not, observations of atmospheric composition provide the most reliable estimate of the degree of turbulent mixing. For the present Earth, the homopause is near 100 km, at which point the observed particle density is $n_h(\text{Earth}) = 1.2 \cdot 10^{19}/\text{m}^3$. ←

Above the homopause, then, atmospheric constituents segregate in the vertical according to molecular weight. The region above the homopause is also typically (though not necessarily) where atmospheric molecules begin to be exposed to ultraviolet photons sufficiently energetic to break up even the more stable components into lighter constituents, which also will stratify according to molecular weight. For Earth the scale height for N_2 is 9.1 km, for CO_2 5.8 km, for O_2 8.0 km, for atomic oxygen 15.9 km, for H_2 127.3 km, and for atomic hydrogen 254.5 km, all based on a temperature of 300 K. Numbers for Venus are similar. The first implication of these numbers is that the scale height for hydrogen is so large that even a small concentration of hydrogen at the homopause can cause the atmosphere to become hydrogen-dominated a small distance above the homopause. For example, if an N_2/H_2 atmosphere contains 1% molar concentration of H_2 at the homopause, then 50 km up the concentration has risen to 63% and 70 km up it is 93%. If the H_2 is converted to atomic hydrogen above the homopause, the segregation is even more effective. Similarly, if we take an Earthlike atmosphere that is 80% N_2 and 20% O_2 at the homopause, and then convert the O_2 into atomic oxygen, we wind up with 33% atomic oxygen near the homopause. By 20 km up, the concentration reaches 56%, and at 40 km it is 76% and thoroughly dominates the atmospheric composition. Finally, if we take an Early Earth CO_2/N_2 atmosphere consisting of 10% CO_2 at the homopause, then the CO_2 concentration falls to 0.5% at 50 km up, whereby we expect the outer atmosphere to be N_2 -dominated. It is possible that the dissociation of CO_2 into CO and O could lead to an exobase dominated by atomic oxygen, but the fact that this does not happen on Venus today suggests strongly that the dissociation is too weak for this to happen, or the recombination of the two species is too efficient.⁴

⁴ Venus at present does have a region above the exobase which is dominated by atomic oxygen, but this layer is too tenuous to affect the exobase height. The question of the circumstances in which oxygen can build up to a hot Earth-type exobase is a delicate and difficult one, which hinges on

Given an estimate of the turbulent diffusivity D_{turb} , the homopause density can be estimated directly from the scaling of the diffusion coefficient. Specifically, since $D \approx \ell(kT/m)^{1/2}$ then setting $D = D_{turb}$ and using the expression for the mean free path ℓ implies

$$n_h \approx \frac{1}{\chi D_{turb}} \left(\frac{kT}{2m} \right)^{1/2}. \quad (8.41)$$

In cases where no observations bearing on D_{turb} are available, assuming D_{turb} to be the same as for Earth is probably as good an assumption as any. In that case, the homopause density is related to Earth's value by the formula

$$n_h \approx \frac{\chi(\text{Earth})}{\chi} \left(\frac{T}{T(\text{Earth})} \frac{m(\text{Earth})}{m} \right)^{1/2} n_h(\text{Earth}). \quad (8.42)$$

Given the weak variation of the factors multiplying $n_h(\text{Earth})$ in typical cases, a good rule of thumb for use in making crude estimates of escape fluxes is simply to assume the homopause density to be the same as Earth's, though of course where observations are available it is better to use the observed value. For most escape calculations, it is not necessary to know the homopause altitude, though it can be estimated from the lower-atmosphere scale height if it is desired. The homopause altitude only becomes important when it is high enough that gravity is significantly attenuated relative to surface gravity.

The homopause density provides the essential point of reference for most atmospheric escape problems involving multicomponent atmospheres. Since most of the atmospheric mass is in the troposphere, in order to understand how long it takes to lose some part of an atmosphere, we need to relate the escape flux to the tropospheric composition, which in turn requires us to relate the composition of the exobase to the tropospheric composition. This proceeds via the intermediary of determining the homopause composition. To take the simplest case first, consider gases that do not undergo condensation or significant chemical sinks or sources within the lower atmosphere – for example O_2 and N_2 on Earth. These will be well mixed throughout the homosphere, so if there is about 20% molar O_2 in the troposphere, there will be about 20% molar O_2 at the homopause. To get the O_2 particle density, we multiply this ratio by the homopause density, which we know how to determine. This then gives the supply of O_2 molecules, which dissociate above the homopause into atomic oxygen, allowing us to determine the atomic oxygen concentration at the exobase using the scale height for atomic oxygen alone to extrapolate from the homopause to the exobase. (A more precise calculation would require modeling of dissociation and reaction rates above the homopause.) Things would work similarly for other gases that are non-reactive/non-condensing in the lower atmosphere.

For condensing gases, such as water vapor mixed with air on Earth, CH_4 mixed with N_2 on Titan, or water vapor mixed with CO_2 on Early Venus, there is an additional step on the way to determining the composition of the homopause. Condensable gases do not have uniform concentrations in the homosphere, because of the limitations imposed by Clausius–Clapeyron. Let's take water vapor on Earth as an example. Water vapor makes

details of atmospheric chemistry and atmospheric composition. An early water-rich Venus atmosphere would have another source of oxygen through dissociation of water vapor, which could conceivably lead to an oxygen-dominated exobase. Calculations performed to date do not seem to bear out this possibility, but the situation has not been thoroughly explored and there is plenty of room for surprises.

up a few percent of the lower atmosphere at present, but most water vapor entering the stratosphere must make it through the cold tropical tropopause. The temperature there is around 200 K, and the corresponding water vapor mixing ratio, by Clausius-Clapeyron, is $1.6 \cdot 10^{-5}$, given a tropopause pressure of 100 mb. Though there are slight additional water vapor sources in the stratosphere from oxidation of methane, the tropopause concentration is a good estimate of the water vapor concentration that will be found at the homopause. The tropopause acts as a *cold trap*, dehumidifying the upper atmosphere and strongly limiting the opportunity for water vapor to escape or for hydrogen to build up in Earth's upper atmosphere through decomposition of water vapor.

The cold trap temperature is defined as the lowest temperature encountered below the homopause, and to determine it precisely, one must carry out a full radiative-convective calculation of the atmospheric structure. On an adiabat, temperature would go down indefinitely with height until absolute zero were reached; it is the interruption of temperature decay by the takeover of radiative equilibrium in the stratosphere that usually determines the cold trap temperature. In the absence of a full radiative-convective equilibrium calculation, the skin temperature of the planet often provides an adequate crude estimate of the cold trap temperature. Once the cold trap temperature is known, the maximum possible partial pressure of the condensable at the cold trap is given by Clausius-Clapeyron. However, it is the molar concentration of the condensable we need, since this is the quantity that is preserved as air is mixed up toward the homopause without further condensation. To determine the molar concentration we need the partial pressure of the non-condensable gas at the cold trap. This is obtained using the tools provided in Chapter 2. One computes the adiabat starting from a specified surface pressure, surface temperature, and surface condensable concentration - following the dry adiabat with constant condensable condensation until the atmosphere becomes saturated, and following the moist adiabat thereafter until the cold trap temperature is reached. The usual procedure for computing the moist adiabat then yields the necessary molar concentration. All other things being equal, as more non-condensable is added to the atmosphere, the cold trap concentration goes down owing to greater dilution of the condensable substance. The precise functional form of the dilution depends on the thermodynamic constants of the condensable and non-condensable substances under consideration.

As an example, let's look at the cold trap water vapor concentration that would be encountered during a dry runaway greenhouse in a $\text{CO}_2\text{-H}_2\text{O}$ system. Recall that in a dry runaway the surface gets so hot that the entire ocean is evaporated into the atmosphere, and there is no liquid water at the surface; in this case, the shutoff of silicate weathering should allow any outgassed CO_2 to accumulate in the atmosphere, resulting in atmospheres consisting of CO_2 and water vapor in proportions determined by the abundance of these substances in the planetary composition (less whatever water may have already escaped). Results for various sizes of oceans and various CO_2 abundances are given in Table 8.6, based on a cold trap temperature of 200 K. The saturation vapor pressure and the adiabat were computed using the ideal gas equation of state and the idealized exponential form of Clausius-Clapeyron; these are not quantitatively accurate for the pressures and temperature under consideration, but they suffice to delineate the general behavior of the cold trap concentration. We see that, for any given inventory of water, the cold trap concentration approaches unity (pure steam) when there is little CO_2 present, but that the cold trap concentration falls to very small values as the CO_2 inventory approaches values similar to that of Venus, or the CO_2 equivalent of Earth's crustal carbonates. Also, for any fixed partial pressure of CO_2 at the surface, the cold trap concentration increases as the water inventory

	Partial pressure CO ₂					
	0 bar	1 bar	10 bar	30 bar	60 bar	90 bar
H ₂ O inventory 25 bar	1	0.83	0.23	0.016	$3.3 \cdot 10^{-4}$	$5.7 \cdot 10^{-5}$
50 bar	1	0.90	0.42	0.11	0.0090	$9.3 \cdot 10^{-4}$
100 bar	1	0.95	0.61	0.28	0.092	0.024

The column headers give the partial pressure of CO₂ at the surface. For each row, the mass of the water vapor inventory (which has come from evaporation of an ocean) is held fixed at the indicated amount. The water vapor inventory is expressed as the pressure that would be exerted by the ocean if the water were condensed out into a liquid layer. For a planet with $g = 10 \text{ m/s}^2$, a 100 bar ocean corresponds to a mass of 10^6 kg/m^2 , or a depth of about 1 km. The 25 bar and 50 bar cases were computed with a surface temperature of 540 K, while the 100 bar case was computed at 570 K so as to allow for a more massive water content without bringing the surface too close to saturation. Note that, as discussed in Chapter 2, the equivalent pressure of ocean differs somewhat from the partial pressure of water at the surface, since the mixing ratio of water is not uniform above the altitude where condensation first occurs.

Table 8.6 Table of water vapor molar concentrations at a 200 K cold trap, for a CO₂-water atmosphere.

increases. Still, for a 90 bar ocean (about half the mass of Earth's), and with a 90 bar inventory of CO₂, the cold trap concentration is only 2.4%. Thus, unless the CO₂ inventory on a planet is very low or the water inventory is very high, the cold trap is likely to impose a significant barrier to water loss during a dry runaway scenario. Even if the water inventory is initially high, as water is lost the cold trap becomes a progressively more severe impediment, making it hard to lose the last 90 bars worth of ocean, and even harder to lose the last 50 bars.

For a single-component condensing atmosphere such as a water-vapor-dominated runaway atmosphere on Venus or a condensing CO₂ atmosphere on Mars, one no longer has to consider the cold trap issue, however. If there is only a single atmospheric component, then perforce knowing the total homopause density tells us the particle density of the atmospheric substance, regardless of how much condensation it has undergone in the troposphere.

Besides condensation traps, there can be chemical reactions which affect the homopause concentration. Notably, H₂ has little chance to escape in the modern oxygenated Earth, because it oxidizes to the heavier, condensable H₂O before it has a chance to reach the homopause.

Now let's revisit the problem of hydrogen loss from Early Earth, a runaway-state Venus, and Titan. We will assume a mixture of hydrogen with some other gas in a known proportion at the homopause, and then use the scale heights of the two gases to compute the changing composition as the exobase is approached. This allows us to say when hydrogen dominates the exobase, and what the resulting exobase height is. An important complication is the anomalously small collision cross-section of atomic hydrogen, and we must remember to take this into account when computing the mean free path for hydrogen-dominated exospheres.

For the anoxic Earth, we wish to determine how high the homopause concentration has to be in order for the escape flux to equal the volcanic outgassing. We simplify the problem by assuming H₂ to be well mixed below the homopause, but to dissociate into atomic hydrogen

just above the homopause. Thus, if we know the homopause concentration of atomic hydrogen, the well-mixed tropospheric H_2 density is half this value. Start by assuming the atomic hydrogen density at the homopause to be 20%, and the balance of the atmosphere to be N_2 . Using the scale heights for the two gases, when we compute the exobase position taking into account the varying composition with height, we find that the exobase is completely hydrogen-dominated, and that the exobase has moved out to an altitude of 1853 km (based on an exobase temperature of 300 K). The escape flux from this extended pure hydrogen exobase is $\Phi = 10^{12}/\text{m}^2\text{s}$, which is still three orders of magnitude below the estimated volcanic outgassing rate of H_2 . Unless some more effective escape mechanism intervenes, hydrogen should build up to extremely high concentrations in the lower atmosphere.

For Venus, we assume an all water-vapor lower atmosphere. We take the homopause density to be $1.2 \cdot 10^{19}/\text{m}^3$ and assume that one-half of the water vapor there breaks up into atomic hydrogen and oxygen. To avoid dealing with a three-component atmosphere, we'll somewhat arbitrarily ignore the resulting oxygen (perhaps it recombines into O_2 which has such a small scale height that not much of it reaches the exobase) and compute the exobase from a homopause composition consisting of one-third water vapor and two-thirds atomic hydrogen; in addition, we'll assume a 300 K exobase temperature. The exobase is again found to be hydrogen-dominated, and at the relatively high altitude of 3050 km above the surface. The escape flux is $\Phi = 1.1 \cdot 10^{14}/\text{m}^2\text{s}$, which would remove the hydrogen in one bar of water vapor in 200 million years. This is significant, but in 2 billion years one could only remove 10 bars of ocean. By this means one could get rid of an ocean only about a tenth the mass of Earth's, though one could get rid of more if one could justify using a higher exobase temperature. Assuming that the water vapor at the homopause dissociates completely into atomic oxygen and atomic hydrogen changes these numbers very little, since the exobase is still hydrogen-dominated.

It should be remarked that it is hard enough to get rid of an ocean's worth of hydrogen on a runaway Venus, but getting rid of an ocean's worth of oxygen by escape to space is completely out of bounds and none of the other escape mechanisms we will consider come close to closing the gap. The only hope of getting rid of the oxygen resulting from runaway followed by hydrogen escape is to react the oxygen with crustal rocks. Even this is problematic, since a great volume of crustal rock must be made available in order to take up the oxygen from an appreciable ocean. Whether this is indeed possible is one of the outstanding Big Questions. There is no data that absolutely forces us to assume that Venus indeed started with an ocean, so it remains possible that Venus was quite dry from the very beginning.

In our earlier calculation of hydrogen loss from Titan we found that a 10% hydrogen concentration at the exobase was sufficient to sustain a large thermal escape rate. How low does the homopause concentration have to be in order to keep the exobase N_2 -dominated? To answer this, we again make use of the scale heights of the two gases to compute the exobase composition simultaneously with the exobase height. In this case, we find that with a 300 K exobase, the homopause mixing ratio of hydrogen must be 10^{-6} or less in order to keep Titan's exobase N_2 -dominated. With that homopause concentration, the escape flux is $\Phi = 8.8 \cdot 10^{15}/\text{m}^2\text{s}$, which is somewhat less than our previous estimate (mainly because of the different means of estimating the exobase density). The main conclusion to be drawn from this exercise is that it only takes a tiny hydrogen concentration at the homopause to sustain the large escape rates we computed earlier. If the hydrogen concentration is increased to the point that the exosphere begins to become hydrogen dominated, then the exobase in fact moves out to infinity, because of the large scale height and low gravity. In that regime, hydrogen is likely to escape hydrodynamically (Section 8.7.4) rather than thermally.

8.7.2 Diffusion-limited escape

The efficiency of escape of material that reaches the exobase is not necessarily the controlling factor determining atmospheric mass loss. For mass to escape from the exobase, it must first be delivered to the exobase, and in many circumstances the rate of transport of mass to the exobase is the limiting factor. When a minor constituent of an atmosphere is escaping, it must first diffuse through the dominant component on its way to the exobase, and even if the escape from the exobase is very effective, mass cannot escape faster than the rate with which it can diffuse up to the exobase. In such cases we can put an upper bound on the rate of escape without knowing much about the precise means of escape from the exobase. This upper bound is the rate of *diffusion-limited escape*. It has the virtue that it can be computed in a very simple and straightforward fashion.

We consider the diffusion in a gravitational field of a substance A with number density $n_A(r)$ through a background gas with density $n(r)$ satisfying $dn/dz = -n/H$, where H is the scale height of the background gas. The equilibrium distribution of A was determined earlier by setting the flux to zero, but now we will determine its distribution assuming a constant non-zero flux. If we let b be the binary diffusion parameter for substance A in the background gas, then Eq. (8.39) for the flux can be re-written

$$(8.38) \quad F_A = -\frac{1}{H_A} \frac{b}{n} \cdot n_A - \frac{b}{n} \frac{dn_A}{dr} = -b \frac{n_{A,e}}{n} \frac{d}{dr} \frac{n_A}{n_{A,e}} \quad (8.43)$$

where $n_{A,e}$ is the equilibrium distribution of substance A , which satisfies $dn_{A,e}/dr = -n_{A,e}/H_A$. As expected, the flux vanishes when $n_A = n_{A,e}$.

For the density distribution to be time-independent, the net flux through a spherical shell, $4\pi r^2 F_A(r)$, must be independent of r . We'll normalize this constant flux to the surface area, writing $\Phi = (r/r_s)^2 F_A$ as we did for the Jeans flux. For a given constant Φ , Eq. (8.43) defines a first order differential equation for n_A . The upper boundary condition for this equation is applied at the exobase, and states that the flux delivered to the exobase must equal the escape flux from the exobase. The escape flux can be written $w_* n_A(r_{ex})$, where w_* is the escape flux coefficient associated with Jeans escape or some other mechanism. Thus, the upper boundary condition can be written $(r_{ex}/r_s)^2 w_* n_A(r_{ex}) = \Phi$. This determines $n_A(r_{ex})$ in terms of Φ , and we must then solve the equation to get $n_A(r)$ and adjust Φ so that the lower boundary condition on n_A at the homopause is satisfied. Now, when w_* becomes very large, molecules are removed essentially instantaneously when they reach the exobase. In this case $n_A(r_{ex}) \rightarrow 0$ and we can take a shortcut to determine the limiting flux.

For simplicity we'll assume that the layer is isothermal, so that b is constant. Multiply Eq. (8.43) by $n/n_{A,e}$ and integrate from the homopause to the exobase to yield

$$\Phi \cdot \int_{r_h}^{r_{ex}} \frac{r_s^2}{r^2} \frac{n}{n_{A,e}} dr = b \cdot \frac{n_A(r_h)}{n_{A,e}(r_h)}, \quad (8.44)$$

which makes use of the assumption $n_A(r_{ex}) \approx 0$. The integral involves only known quantities, so this equation defines the limiting flux in terms of the homopause density of the escaping substance. Let's suppose that the exobase has low altitude in comparison with the radius of the planet. In this case, gravity is nearly constant and $n/n_{A,e}$ varies like $\exp(-(1/H - 1/H_A)z)$ where z is the altitude. The ratio decays exponentially if the scale height of the background gas is less than the scale height of minor constituent, i.e. if the minor constituent is lighter than the background gas. If, moreover, the layer between homopause and exobase is thick enough that the ratio decays to zero at the exobase, then the integral is simply $n/n_{A,e}$ at the

homopause divided by $(1/H - 1/H_A)$. Therefore, under these assumptions, which are quite widely applicable, the diffusion-limited escape flux takes on the simple form

$$\Phi = b \frac{n_A(r_h)}{n(r_h)} \cdot \left(\frac{1}{H} - \frac{1}{H_A} \right) = D n_A(r_h) \cdot \left(\frac{1}{H} - \frac{1}{H_A} \right) \quad (8.45)$$

where D is the diffusivity at the homopause. The escape of the minor constituent cannot exceed this flux no matter how effective the escape mechanism may be.

Exercise 8.5 Derive an expression for the diffusion limited flux in the case when the diffusing constituent has greater molecular weight than the background gas. How does the limiting flux depend on the layer depth in this case?

As a first simple example of diffusion-limited escape, let's take a look at the escape of hydrogen from an anoxic Early Earth. Suppose that H_2 diffuses through pure N_2 above the homopause. At 300 K, the binary parameter for this pair of species is $2 \cdot 10^{21}/\text{ms}$. Then, noting that n_{H_2}/n is the molar concentration η_{H_2} of hydrogen at the homopause and that the scale height for H_2 is much greater than the scale height for N_2 , Eq. (8.45) implies that $\Phi \approx (2 \cdot 10^{21}/H_{N_2})\eta_{H_2} = 2.2 \cdot 10^{17}\eta_{H_2}/\text{m}^2\text{s}$. We'll assume that H_2 has nearly uniform concentration below the homopause, as is reasonable in the absence of oxygen. With this assumption, we can directly determine how high the concentration has to go in order to lose the volcanic hydrogen source, assuming the loss to be diffusion limited. Thus, $\eta_{H_2} = 10^{15}/2.2 \cdot 10^{17} = 0.0045$. Therefore, while Jeans escape would allow H_2 to build up to very high concentrations in the troposphere, diffusion-limited escape of H_2 could hold the concentration to well under a percent. Of course, for the diffusion limit to be reached, we would need a much more efficient means than Jeans escape of removing H_2 once it reaches the outer atmosphere. If the H_2 were to dissociate into atomic hydrogen near the homopause, the diffusion-limited escape flux would be much greater and the equilibrium diffusion-limited concentration would be much lower, since the binary coefficient for atomic hydrogen diffusing through N_2 is $10^{24}/\text{ms}$ at 300 K.

Exercise 8.6 Suppose that an N_2/H_2 atmosphere has some initial hydrogen concentration which is escaping at the diffusion-limited rate, but which is not being replenished by volcanic outgassing or any other source. Compute the exponential decay time of the hydrogen in the atmosphere assuming (a) H_2 diffuses through N_2 above the homopause, or (b) H_2 dissociates and diffuses as H through N_2 above the homopause.

As a second example, let's consider diffusion-limited water escape for a dry runaway state on a planet like Venus. For the dry runaway, we assume that the entire ocean is evaporated into the atmosphere as water vapor, and that in the absence of liquid water a dense CO_2 atmosphere accumulates because of weak or absent silicate weathering. In this case, water may escape in the form of H_2O diffusing through CO_2 . The binary parameter for this pair is $8.4 \cdot 10^{20}/\text{ms}$ at 300 K based on the hard sphere approximation with 140 pm radii. Plugging in the appropriate scale heights for Venus, Eq. (8.45) implies that $\Phi \approx 7.8 \cdot 10^{16}\eta_{H_2O}/\text{m}^2\text{s}$, where η_{H_2O} is the water vapor concentration at the homopause. For the present application, we are interested in how long it takes to lose the hydrogen in an ocean, assuming it diffuses upwards as water vapor which then dissociates at high altitudes. We have seen earlier that η_{H_2O} is determined by the cold trap concentration in a dry runaway, which can range from minuscule values of a few parts per million to values approaching unity as wet runaway conditions are approached. As a point of reference, let's

atmosphere with a surface pressure of around 2 bars. How much of such an atmosphere could be lost to space in the available time? How much would have to be lost into chemical reaction with surface rocks instead? Is it possible that a body as small as Mars could remain habitable for billions of years, or does escape to space inevitably doom such a planet to the long chill? The contrast between Mars and Titan is stark. We expect atmospheres to be in some sense bound by gravity, but why is it then that Titan, with far weaker gravity than Mars, retains a 1.5 bar atmosphere while Mars retains practically none? One feels it must have something to do with the lower temperature of Titan, but that notion begs to be quantified. Even for Earth, escape mechanisms are important: before the rise of atmospheric oxygen, there is the possibility that large amounts of hydrogen could accumulate in the atmosphere, if it does not escape rapidly to space. This is important because hydrogen and carbon dioxide can serve as feedstocks for synthesis of many prebiotic organic molecules.

Atmospheric escape may also play a critical role in determining the habitable zones around M-dwarf stars. These stars have low luminosity, and therefore a planet needs to be in a close orbit in order to be warm enough to be in the habitable zone as conventionally defined with respect to liquid surface water. However, M-dwarfs episodically have much higher EUV output relative to net energy output than G stars, so such a planet would be blasted by so much high energy radiation that it would risk eroding even higher-molecular-weight components of the atmosphere, such as N_2 or CO_2 .

8.7.1 Basic concepts

The problem of permanently removing a molecule from a planet's atmosphere is much the same as the problem of sending a rocket from Earth to Mars: one must impart enough velocity to the object, and in the right direction, to allow the object to overcome the potential energy at the bottom of the gravitational well, and still have enough kinetic energy left over to allow the object to continue moving away. This leads to the central concept of *escape velocity*, which is the minimum velocity an object needs in order to escape to infinity, provided no drag forces intervene. The escape velocity is obtained by equating initial kinetic energy to the gravitational potential energy. Let m be the mass of the object, v its speed, and r its initial distance from the center of the planet. Let M_P be the mass of the planet and G be the universal gravitational constant. Then, equating kinetic to potential energy we find that $\frac{1}{2}mv^2 = GM_Pm/r$, so $v = \sqrt{2GM_P/r} = \sqrt{2gr}$ where g is the acceleration of gravity at distance r from the planet's center. In many situations of interest, the altitude from which the molecules escape is sufficiently close to the ground that g is only slightly less than the surface gravity. Important exceptions include small bodies with a massive atmosphere, such as Titan, or such as the Moon would be if it were given a massive atmosphere. In this section, we will use g to represent the actual radially varying acceleration $g(r)$, and will use the symbol g_s when we need to refer specifically to the surface gravity. The acceleration at distance r is then $g(r) = g_s(r_s/r)^2$, where r_s is the radius of the planet's surface.

In order to allow a molecule to escape, enough energy must be delivered to the molecule to accelerate it to the escape velocity. The study of atmospheric escape amounts to the study of the various ways in which the necessary energy can be imparted. Since the kinetic energy of a molecule with mass m is $\frac{1}{2}mv^2$, light molecules like H_2 will escape more easily than heavier molecules like N_2 , given an equal delivery of energy. Dissociation of a molecule like CO_2 or H_2 into lighter individual components also aids escape. Using the formula for escape velocity, we can define the *escape energy* of a molecule with mass m as mgr . For escape of N_2

from altitudes not too far from the Earth's surface, this energy is $2.9 \cdot 10^{-18}$ J, or 2.9 attoJ.³ For H₂ the escape energy is only 0.2 attoJ.

In the end, like so many things in planetary climate, atmospheric escape is all about energy. There are four principal sources of energy that could potentially feed atmospheric escape:

- The general thermal energy of the atmospheric gas, which ultimately comes either from absorbed solar radiation or from heat leaking out of the interior of the planet.
- Direct absorption of solar energy in the outer portion of the planet's atmosphere, which may energize particles to escape velocity either directly or through indirect pathways, or which may manifest itself in a hydrodynamic escaping current of gas. The solar radiation responsible for these mechanisms is typically in the extreme ultraviolet (EUV) portion of the solar spectrum because there is so little mass in the regions involved that absorption is weak, whence there is a premium on absorbing individual photons which have a great deal of energy.
- Collisions with the energetic particles (usually protons) of the stellar wind which streams outward from the atmosphere of the planet's star.
- Kinetic energy imparted to the atmosphere by the impact of large objects.

For a portion of the atmosphere where collisions are frequent enough to maintain thermodynamic equilibrium, each degree of freedom gets an energy of $\frac{1}{2}kT$ on average. Some molecules will have more energy than this, and some will have less, but if the mean energy is considerably less than the escape energy, only a very small proportion of molecules will have sufficient energy to escape. For $T = 300$ K, the typical energy is only 0.002 attoJ. At this temperature only a small fraction of H₂ molecules would have sufficient energy to escape from Earth, and the escape rate becomes only moderately higher if the temperature of the escaping gas is raised to 1000 K. Heavier molecules like N₂ could hardly escape from a planet with Earth's or Venus' gravity at all, if the only source of energy were thermal motions. Even on a light body like Titan, the escape energy for N₂ is still 0.16 attoJ based on surface gravity, so escape will not be easy. Escape due to the energy associated with the thermal motions of particles in thermodynamic equilibrium is called *thermal escape*, or sometimes *Rayleigh-Jeans escape*. The ratio of escape energy to kT , namely $\lambda_c \equiv mgr/kT$, is an important parameter in the theory of thermal escape. In this formula, r is the radius of the atmospheric shell from which particles escape, g is the acceleration of gravity at that radius, and T is the typical temperature there.

For a particle to escape, it is not enough to have reached escape velocity. It must also have a reasonable chance of escaping the gravitational well of the planet without suffering many collisions, since each collision will divert the particle from its outward path and rob it of some of its velocity. If the particle undergoes many collisions, it will undergo a random walk, leading to slow diffusion of the substance rather than rapid outward streaming. The portion of the atmosphere where particle collisions are so infrequent that a particle with sufficient energy has a good chance of escaping without collision is called the *exosphere*. In order to define the exosphere quantitatively, we first introduce the notion of *mean free path*, which is the mean distance traveled by a molecule between collisions. The mean free path depends on the total number density of particles, n , and the effective cross-section area of the molecules, χ . For simplicity, we'll assume for the moment that all the molecules

³ One frequently sees the unit *electron volt* used for measuring small quantities of energy in a context like this. 1 eV = 0.16 attoJ.

in the gas are identical. Two molecules are considered to collide if their centers approach within a distance of $2\sqrt{\chi/\pi}$. To estimate the mean free path, construct an imaginary cylinder with axis aligned with the direction of travel of the particle we are tracking, and having a radius $\sqrt{\chi/\pi}$. A collision is inevitable if this cylinder contains a particle from the rest of the gas, which becomes likely when $nV = 1$, where V is the volume of the cylinder. Writing $V = \ell\pi a^2 = \ell\chi$ we find that the mean free path is $\ell \approx 1/n\chi$. This estimate would be precise if the particles being collided with were stationary. In reality, the distance moved by the test particle before collision is affected by the fact that some of the other particles are moving toward the test particle, while others are moving away from it; a more precise calculation making use of the actual distribution of particle velocities in thermodynamic equilibrium yields the slightly modified result

$$\ell = \frac{1}{n\chi\sqrt{2}} \quad (8.33)$$

when all the particles have the same mass. When the background particles are very massive compared with the particle we are tracking, then they can be regarded as essentially stationary and the $\sqrt{2}$ factor in the denominator can be dropped; for most of the uses to which we will put the mean free path, this effect is of little importance.

The effective particle collision cross-section depends on the pair of molecules which are colliding, and is also a weak function of the energy of the collision, since molecules are not hard spheres but rather can be penetrated when the collision energy is large enough. Still, the effective collision radius does not differ greatly between one molecule and another. The collision radius can be inferred from measured diffusion rates, and a few typical values are given in Table 8.4. For the most part, the effective collision radius is between 100 and 200 picometers (pm). An important exception is atomic hydrogen (H), which has an effective radius on the order of a mere 10 picometers. Curiously, the effective binary collision radius remains this small even when H is colliding with a much larger molecule. Evidently, the H atoms are like little bullets, which punch right through the outer electron clouds of the bigger molecules. This effect gives atomic hydrogen an anomalously large mean free path for a given density, which has a number of important consequences. Data for atomic oxygen (O) is hard to come by, but neon is believed to be an analog and should have a similar collision radius. Air at the Earth's surface with a temperature of 300 K has a particle density of $2.4 \cdot 10^{25}/\text{m}^3$. Based on a collision radius of 125 pm the mean free path is about 0.6 μm . Adopting a scale height of 8 km, the particle density at an altitude of 100 km falls to $9.0 \cdot 10^{19}/\text{m}^3$ and the mean free path increases to 16 cm – about the width of a hand.

The mean free path increases exponentially with altitude, because the particle density in a gravitationally bound atmosphere decreases exponentially with altitude, at a rate given by the density scale height (RT/g for the isothermal case). The exosphere is said to begin where the mean free path becomes sufficiently large that further collisions before escape are unlikely; this critical altitude is called the *exobase*. Commonly, it is defined as the altitude where the mean free path becomes equal to the scale height, since the exponential increase of mean free path with height means that if a particle doesn't collide with another within the first scale height, it is basically home free and unlikely to find another to collide with. When the exobase is not too far above the ground in comparison to the planet's radius, g can be approximated by the surface gravity and one can immediately estimate the exobase altitude in terms of the temperature of the exosphere and the scale height for the dominant constituent of the exosphere. In applying this procedure, one must keep in mind that the temperature of the exosphere could be quite different from the temperature of the lower

Table 8.4 Effective collision radius for various binary collisions, computed from diffusion data.

	100 K	300 K	1000 K
H-H ₂	11.08	6.02	3.09
H-air	12.26	6.34	3.08
H-CO ₂	13.63	7.46	3.85
H ₂ -air	144.50	125.96	108.36
H ₂ -CO ₂	157.24	137.06	117.91
H ₂ -N ₂	146.65	123.01	101.46
H ₂ O-air	194.71	142.21	100.78
CH ₄ -N ₂	177.57	154.87	133.31
Ne-N ₂	139.88	122.40	105.74
Ar-air	166.62	145.32	125.09

The radius is given for three different temperatures, in units of picometers. (1 pm = 10⁻¹² m). The collision cross-section for collision radius a is $\chi = \pi a^2$.

atmosphere, and the composition could differ greatly from the bulk composition of the atmosphere. We will have more to say about both these aspects of the exosphere a bit later. For the most part, one is interested in the exobase particle density, since that is what will determine the flux of particles to space. When one at least knows that the exobase is low enough that $g \approx g_s$, the exobase density is immediately given by the requirement that $\ell = H$, which implies that the exobase particle density is

$$n_{ex} = \frac{g_s}{\chi R T_{ex} \sqrt{2}} = \frac{mg_s}{\chi k T_{ex} \sqrt{2}} \quad (8.34)$$

where T_{ex} is the exobase temperature, m is the actual mass (in kilograms) of the molecule which makes up most of the exosphere and k is the Boltzmann thermodynamic constant.

For the more general case, one must extend the hydrostatic relation to account for the decay of gravity with altitude. This case is important for light constituents like H or H₂, which have a large scale height because low molecular weight implies large gas constant R . The exosphere can also be very extended even for heavier molecules, for small bodies with low surface gravity, such as Titan. Allowing for the inverse-square reduction of gravity with distance r from the center of the body, the equation of hydrostatic balance becomes

$$\partial_r p = -\rho g_s \frac{r_s^2}{r^2}. \quad (8.35)$$

As in the treatment of the hydrostatic relation in Chapter 2, the equation is closed by using the ideal gas law, $p = \rho RT$, where R is the gas constant for the mixture making up the uppermost part of the atmosphere. In escape problems it is often more convenient to deal with particle number density rather than mass density. The particle density $n(r)$ is obtained by dividing ρ by the mass of a molecule, m . If the upper atmosphere is isothermal with temperature T_0 , then the solution expressed as number density is:

$$n(r) = n(r_0) \exp \left(\frac{r_s}{H_s} \left(\frac{r_s}{r} - \frac{r_s}{r_0} \right) \right), \quad H_s \equiv \frac{RT_0}{g_s} \quad (8.36)$$

where r_0 is some reference distance, generally presumed to be in the upper atmosphere. From this equation, it follows that the local scale height at radius r is $H(r) = (r/r_s)^2 H_s$.

Because distances are large, the formula neglects space with there. To tially end time. The ing densit exobase. S there is a increases which the constituen radius of temperatu for heavie Even for T of 100 K. Titan had would be preclude a terrestrial is best def

Exercise 8

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Because of the attenuation of gravity, the density no longer asymptotes to zero at large distances from the planet. The limiting value is $n_\infty = n(r_0) \exp -(r_s/H_s)(r_s/r_0)$. Since this formula neglects all gravity but that of the planet, it is not surprising that one can fill infinite space with a finite density and have it stay put, since there is essentially zero gravity out there. To do so would require infinite mass, though, which means that if the planet is initially endowed with a finite-mass atmosphere, it will all leak away to space, given sufficient time. The estimate of that time scale is the objective of this section. In reality, the limiting density is not achieved, because the atmosphere is truncated by particle loss from the exobase. Still, it is important that there is a non-zero limiting density, since this implies that there is a non-zero limiting mean free path. Combined with the fact that the scale height increases with r , this can remove the exobase to infinity, meaning that there is no altitude at which the atmosphere can be considered collisionless. This situation will not arise for heavy constituents on reasonably massive bodies, since n_∞ is exceedingly small. Using a collision radius of 125 pm, the limiting mean free path is over 10^{167} m for O on Earth, based on a temperature of 300 K. This is well in excess of the size of the Universe. The limiting value for heavier constituents is even greater, and considerations for Venus turn out similarly. Even for Titan, the limiting mean free path for N_2 is about 10^{44} m based on a temperature of 100 K. The situation for the light species H and H_2 is more ambiguous. For example, if Titan had a pure H_2 atmosphere with a temperature of 100 K, the limiting mean free path would be only 850 m even if the surface pressure were a mere 0.1 Pa. This would certainly preclude a collisionless exosphere. Since H and H_2 typically appear in the atmospheres of terrestrial-type bodies as minor constituents mixed in with a heavier gas, further discussion is best deferred until after we have considered inhomogeneous atmospheres.

Exercise 8.4 Show that Eq. (8.36) reduces to the conventional hydrostatic relation derived in Chapter 2 when $r = r_s + z$ with $z/r_s \ll 1$, r_s being the radius of the planet.

To determine the exobase height, we need a model of the atmospheric structure which gives us the total number density $n(r)$ as a function of position. This can be challenging to do precisely, since $n(r)$ depends on the temperature and composition profile of the atmosphere; often, exobase heights for present-day Solar System planets are calculated from measured rather than theoretical density profiles. The other factor involved is the scale height at the exobase, which depends on the exosphere composition, position (through gravity) and temperature. Higher temperature increases the scale height and hence tends to move the exobase further out. The temperature of the exosphere is determined by a balance between heating by absorption of solar radiation (mainly ultraviolet), heating by absorption of outgoing thermal infrared from deeper in the atmosphere, and cooling by emission of infrared radiation. In some cases, there can be energy gain from collision with solar wind particles, and there can also be energy loss by outward streaming of mass in *hydrodynamic escape* (see Section 8.7.4). The radiative transfer in the exosphere is simplified by the fact that the atmosphere is optically thin, but is complicated by the fact that it is so tenuous that local thermodynamic equilibrium (and hence Kirchhoff's law) is not accurate. Still, when the exosphere is made of a good infrared emitter, the temperature tends to be on the order of a skin temperature, augmented a bit by solar absorption. Thus, the CO_2 -dominated exobase of Venus has temperature between 200 K and 300 K, and that of Mars is somewhat higher. The Earth's exosphere is unusually hot, since it is dominated by atomic oxygen which comes from photodissociation of the large O_2 concentration of the lower atmosphere. Atomic oxygen is a good ultraviolet absorber, but

Planet	p_s (bar)	T_0	T_{ex}	z_{ex} (km)	t_{loss} (Gyr)	$w_{J,H}$ (m/s)
Earth, N ₂	1.0	300	300	221	$7 \cdot 10^{286}$	$4.97 \cdot 10^{-7}$
Earth, O	0.2	300	1000	401	$4 \cdot 10^{42}$	7.94
Venus, CO ₂	90.0	500	300	304	$> 10^{300}$	$1.7 \cdot 10^{-5}$
Venus, H ₂ O	1.0	400	300	542	$7 \cdot 10^{147}$	$3.458 \cdot 10^{-5}$
Mars, CO ₂	2.0	250	300	352	$3 \cdot 10^{81}$	36.41
Mars, O	1.0	250	1000	1312	4000	808.13
Titan, N ₂	1.5	100	200	774	$3 \cdot 10^{15}$	268.83
Titan, N	1.5	100	200	2454	5000	365.18
Moon, N ₂	1.0	260	300	6145	4	613.54

The planet and the atmospheric composition are given in the leftmost column. In the other columns, p_s is the surface pressure in bars, T_0 is the effective mean temperature of the atmosphere below the exobase, T_{ex} is the exobase temperature, z_{ex} is the altitude of the exobase above the surface (in kilometers), t_{loss} is the time needed to lose the atmosphere by thermal escape (in billions of years), and $w_{J,H}$ is the Jeans escape coefficient for atomic hydrogen (in m/s). The hydrogen escape coefficient assumes that hydrogen is a minor constituent at the exobase. The mean free path was computed using a fixed molecular collision radius of 125 pm in all cases.

Table 8.5 Characteristics of the exosphere and loss rates for various hypothetical single-component atmospheres.

radiates infrared poorly, leading to high temperatures. Exosphere temperatures for N₂ or N-dominated exospheres are a delicate matter, since N₂ neither absorbs nor emits well, and slight contamination by infrared emitters or good solar absorbers can make a big difference. Titan's N₂-dominated exosphere has an observed temperature of about 200 K.

Once the parameters of the outer atmosphere are settled, the exobase position is determined by solving $\ell(r)/H(r) = 1$ by iteration, where $H(r)$ is the scale height at position r and the mean free path $\ell(r)$ is inversely proportional to $n(r)$. To get some numbers on the table for discussion, let's adopt a simple model atmosphere in which $n(r)$ is computed based on Eq. (8.36) with a uniform equivalent lower atmosphere temperature T_0 all the way down to the planet's surface, where the surface pressure p_s is specified. The exobase temperature is specified separately. Exobase altitudes for some hypothetical single-component atmospheres are given in Table 8.5. The atomic oxygen case for Earth is meant to serve as a crude representation of the oxygen-dominated exosphere of Earth. In this approximation, the atmospheric structure is computed as if all the Earth's oxygen were in the form of O, and ignores the fact that the O₂ is only converted to O at altitudes above 100 km as well as ignoring the effect of other gases on the vertical structure. We'll be able to do better later when we take up mixed atmospheres, but it is interesting to note that the exobase height of 400 km in this approximation is not too far from the true exobase height (500 km) computed on the basis of the observed O density in Earth's upper atmosphere. The N₂ case may be thought of as approximating an Early Earth situation in which there is little O₂ available to feed an oxygen-dominated exosphere. The two Venus cases represent approximations to the present state of Venus, and a hypothetical past near-runaway state with a pure steam atmosphere. The first Mars case assumes a dense CO₂ atmosphere such as might have prevailed on Early Mars, while the second is an approximate to the situation where the exosphere is dominated by atomic oxygen arising from photodissociation of CO₂. The first Titan case approximates the present, while the second gives some indication of what would happen if the N₂ were to dissociate into atomic nitrogen (a somewhat implausible situation, but one which is included to allow us later to put a generous bound on nitrogen loss from Titan).

Finally, the N_2 lunar atmosphere gives us an indication of what an atmosphere on Earth's Moon might have looked like if it had retained or gained an atmosphere after formation. The lower atmosphere temperature approximates the temperature the Moon would have with little or no greenhouse gas in its atmosphere.

Relative to the planetary radius, the estimated exobases are all fairly close to the ground with the exception of the atomic oxygen case on Mars, the N_2 case on Titan, the atomic nitrogen case on Titan, and the N_2 case on the Moon. In the first two cases, the altitude of the exobase is on the order of a third of the planetary radius, but in the latter two cases the exobase extends far out into space. The effect is particularly pronounced in the lunar N_2 case. Note that the exobase extends much farther out than in the Titan N_2 case, even though the Moon has somewhat higher surface gravity than Titan. This happens because we have assumed a greater atmospheric temperature for the lunar case, consistent with its closer proximity to the Sun. This remark underscores the importance of lower atmospheric temperature in determining the characteristics of atmospheric escape: perfectly apart from the exospheric temperature, a hotter lower atmosphere has a larger scale height, and therefore can extend further out to where the gravity is lower and the atmosphere can escape more easily. This is not much of an issue for bodies as massive as Earth or Venus but for smaller bodies it can be quite a significant effect.

Let's take stock of what we know so far. To determine the rate of escape of a constituent, we need to know the height of the exobase, the number density of that constituent at the exobase, and the proportion of particles whose energy exceeds the escape energy computed at the exobase. The definition of the exobase involves the temperature at the exobase, through the definition of scale height, so we must know a temperature for the exobase as well. This temperature might or might not also serve to characterize the distribution of particle velocity, depending on circumstances. Note that the concept of "exobase" is itself a severe idealization. The picture this calls to mind is of a distinct surface separating lower altitudes where collisions are frequent enough to maintain thermal equilibrium and higher altitudes where particles undergo ballistic trajectories without collision. This would be nearly the case for evaporation of a liquid into a vacuum, since there is a near-discontinuity in density in that situation. For gases, the transition is gradual, and it would be better to talk in terms of an "exobase region" involving a continuous profile of collision frequency and some escape to space from each layer - more toward the top, less toward the bottom. Modern calculations of atmospheric escape do indeed employ this level of sophistication, but the refinement alters estimates based on the ideal picture only by a factor of two or so. We'll see soon that this is not a serious threat to our main conclusions.

To proceed further, we need a probability distribution for molecular energy. The simplest case is one in which the molecules near the exobase can be regarded as being in thermodynamic equilibrium. This leads to what is called *Rayleigh-Jeans* or *thermal* escape. It is by far the simplest theory of atmospheric escape, but it is also the most useless; its main utility is to show that thermal escape is not a significant means of removing atmospheric constituents with the possible exception of light species such as He or molecular hydrogen (and even those only to a limited extent and in limited circumstances). The calculation proceeds as follows. For a gas in thermodynamic equilibrium at temperature T , the probability of a molecule with mass m having speed v is proportional to $\exp(-\frac{1}{2}mv^2/kT)$. This is the *Maxwell-Boltzmann distribution*. Note that if the gas is a mixture of molecules with various m , this formula still applies for the velocity distribution of each species separately, with the corresponding m used in the formula. The Maxwell-Boltzmann distribution has the important property that the proportion of molecules with energy much greater

than kT becomes exponentially small. To determine the escape flux, one must integrate the Maxwell-Boltzmann distribution to determine the proportion of particles that have enough energy to escape, taking into account also the fact that particles are moving isotropically in all directions and that it is only the part of energy associated with radially outward motion that contributes to escape. If $n_{ex,m}$ is the number density at the exobase of a species whose molecules have mass m , then the flux of particles to space is $w_{J,m}n_{ex,m}$, where

$$w_{J,m} = \frac{1}{2\sqrt{\pi}}(1 + \lambda_c(m))e^{-\lambda_c(m)}\sqrt{\left(\frac{2kT_{ex}}{m}\right)}, \quad (8.37)$$

in which $\lambda_c(m) = mg(r_{ex})r_{ex}/kT$ is the escape parameter defined previously. The Jeans flux coefficient $w_{J,m}$ has the dimensions of a velocity, and consists of the typical thermal velocity at the exobase reduced by an exponential factor that accounts for the proportion of molecules whose energy exceeds the escape energy. The total escape flux from the planet, expressed as molecules per second, is $4\pi r_{ex}^2 w_{J,m} n_{ex,m}$. For calculations of the lifetime of an atmospheric constituent, it is convenient to introduce the escape flux per unit surface area of the planet, for which we will use the notation Φ . Thus, $\Phi = w_{J,m} n_{ex,m} (r_{ex}/r_s)^2$.

The penultimate column of Table 8.5 gives the characteristic loss time of the dominant constituent of the hypothetical atmosphere by Jeans escape. This loss time is obtained by dividing the Jeans loss rate for the dominant constituent into the total number of particles in the atmosphere. With the exception of the lunar N_2 case, all the loss times are far too long to allow significant loss over the lifetime of the Solar System. For that matter, most of the loss times are well in excess of the lifetime of the Universe, and not even the extreme assumption of total decomposition of the atmosphere into lighter atomic constituents changes this conclusion. For the most part, the main constituents of terrestrial-type atmospheres cannot escape to any significant degree by thermal means. In particular, it is impossible to lose a primordial Venusian ocean by Jeans escape of H_2O . Even if we split off the O, the Earth atomic oxygen case says that it would be impossible to lose any significant quantity of the oxygen in the water by Jeans escape. The one case in which thermal escape is of interest for a heavy constituent is the warm lunar case. This case may seem somewhat fanciful but it is of considerable relevance to the question of habitable moons, such as might belong to extrasolar gas giants which orbit their primaries at Earthlike distances. Jeans escape is a real threat to the atmospheres of small moons if they are warm enough to support liquid water.

To get a feeling for the magnitude of the thermal escape of atomic hydrogen in the regime where H is a minor constituent of the exosphere, let's suppose that the molar concentration of H is 10% at the exobase. Later we'll learn how to relate the exobase concentration to the composition of the lower atmosphere. Let's take first the Earth case with an O-dominated exosphere. Using the assumptions of Table 8.5 the total number density at the exobase, obtained by plugging the exobase position and gas constants into Eq. (8.36), is $2.4 \cdot 10^{14}/m^3$, whence the H number density is $2.4 \cdot 10^{13}/m^3$. Multiplying this by the Jeans escape coefficient from the table and normalizing to surface area, we find an H escape flux $\Phi = 2.15 \cdot 10^{14}/m^2s$. If the H ultimately came from decomposition of sea water, then each two atoms of H that escape account for the loss of one water molecule and the generation of one atom of oxygen. Converting this to mass, we find that in four billion years you could lose about 365 000 kg of water from each square meter of the Earth's surface, equal to a depth of about 365 m. You could not come close to losing an ocean on Earth or Venus this way, even with a hot exosphere; with a colder exosphere such as on Venus or the Early Earth, the loss rate would dwindle to practically nothing. If we want to get rid of a primordial Venusian ocean, we'll