particles is about an order of magnitude greater than the rate of H_2O absorption. The production rate is about 30 cm^{-3} sec^{-1}, and the lifetime is about 300 seconds.

The implications for particle composition of the rates of growth, the observed particle charge, and the upper limits for impurity species will be discussed elsewhere (*8*). We list here some of the conclusions. The maximum amounts of gaseous or particulate impurities contained initially in the added gases are not sufficient to provide a significant fraction of the total mass of the particles. Any particulate species originating from the walls during the gas-filling operation would, through coagulation and sedimentation, be reduced to a concentration too low to contribute significantly to the total particle mass. A gaseous impurity supplied continuously from the walls is unable to supply a significant mass to the particles by direct addition, even if such a species were to stick to the particles at every collision. If such an undetected impurity is important, it must be activated at almost every collision with a newly formed H_2O photolysis product and then stick at nearly every collision with a particle.

In conclusion, our results show that necessary conditions for the formation of the particles are the presence of H_2O vapor, UV light, and enough buffer gas to overcome wall effects. We do not yet have enough information to conclusively prove that these are sufficient conditions for particle formation. Explanations for our observations that involve superreactive undetected impurities seem to be unlikely—but then so does the logical alternative. This alternative, the simplest interpretation of our observations, is that the absorption of UV light by H_2O vapor leads to the formation of a low-density nongaseous substance that resembles neither the liquid nor the solid phase of ordinary H_2O.

If such a process does occur, it has, in addition to its obvious chemical interest, possible implications for planetary atmospheres where H_2O vapor is exposed to the sun's UV radiation. One might conjecture that the particulate substance we have described could be a constituent of Venusian clouds. On Mars the presence of particulate fragments with more than four or five atoms each could provide intermediates that circumvent the three-body rate limitations which currently plague explanations for the stability of the Martian atmosphere (*9*). In Earth's atmosphere direct production of particles by H_2O absorption would be limited to altitudes above 80 km. If the presence of $O(^1D)$ and H_2O constitute a sufficient condition for particle production, it could occur in the stratosphere where $O(^1D)$ is produced in O_3 photolysis. When such particles fall to lower altitudes, they could conceivably act as nucleation sites for raindrop formation.

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Mars: Has Nitrogen Escaped?

Abstract. *If eddy mixing is about as effective on Mars as it is on Earth, then there seems to be less nitrogen present on Mars than we would expect if terrestrial-type outgassing were the source. However, in this event a nonthermal escape mechanism involving the predissociation of exospheric nitrogen can be invoked to explain the low nitrogen concentration.*

One of the more interesting results from Mariner 6 and Mariner 7 was the apparent failure of the ultraviolet spectrometer to detect molecular nitrogen. Dalgarno and McElroy (*1*) concluded that the ultraviolet data "are consistent with a mixing ratio of N_2 in the martian atmosphere as large as 5 percent, if eddy mixing is extremely efficient." This is about the amount expected if outgassing is the source. However, they go on, "If the eddy mixing coefficient is similar to that for the earth, the limit is reduced by a factor of about 10." In this event there would be a serious conflict with our notions about the origin of the martian atmosphere. I suggest here that, in this latter case, nitrogen may well have been outgassed to the extent of the order of 5 percent but may subsequently have escaped from the planet, and thus that we need not abandon our ideas about its origin on this account.

Ordinary thermal escape is quite ineffective in removing N or N_2 from Mars. One possible nonthermal mechanism is the absorption of solar far-ultraviolet radiation by ground-state exospheric N_2 to give N_2^*, followed by predissociation of the excited molecules into atoms having sufficient kinetic energy and proper direction to escape from the planet (1.731 ev for N and upward). I consider here only the energy range of incident photons from about 12.5 ev (992 Å) to the first ionization limit, 15.58 ev (796 Å). Higher energy photons may be quite important but there is not as much information on the fraction predissociating (dissociative recombination may also contribute to the escape rate).

The photon's momentum can be disregarded, because the speed change for N_2 is considerably less than 1 m/sec.

Table 1. Calculated amount of nitrogen lost if outgassing occurred early in martian history.

Effective absorption cross section of N_2, 796 to 822 Å (15.07 to 15.58 ev) (*4*) (considering the path length dependence):	3×10^{-17} cm^2
Solar flux at 1 astronomical unit (*5*)*:	7×10^8 photon cm^{-2} sec^{-1}
Time-averaged flux at martian exobase:	$\frac{0.5}{(1.5237)^2} \times 7 \times 10^8 = 1.5 \times 10^8$ photon cm^{-2} sec^{-1}
Loss rate, *L*†:	$\frac{1}{2} \times 1.8 \times 10^6 \times 10\ \rho$ atom cm^{-2} sec^{-1}
Fractional loss rate‡:	$L/2 \times 2.5 \times 10^{23}\ \rho\ cm^{-2} = 0.18 \times 10^{-16}$ sec^{-1}
Fraction lost in 1.4×10^{17} seconds:	$1 - e^{-2.52} \approx 92$ percent

* This value is lower by a factor of 3 than Hinteregger's earlier values. † Where ρ is the N_2 mixing ratio of the atmosphere as a whole. ‡ On the assumption that the surface pressure has always been 7 mbar $\approx 2.5 \times 10^{23}$ CO_2 molecules per square centimeter.

The photon's excess energy, if the N_2 predissociates, will appear as excitation energy of the product atoms or kinetic energy of the product atoms, or both. Hudson and Carter (*2*) have reported from line-broadening observed in laboratory absorption studies that most of the excited states of N_2 in this energy range seem to be strongly predissociated.

The dissociation products are either $^4S^0$ and $^2D^0$ or $^4S^0$ and $^4S^0$ (*3*). I shall consider here the former, energetically more difficult case, as it seems to be preferred. I assume first a model in which most of the outgassing occurred early in martian history, and subsequently I shall consider the case of constant outgassing throughout geological time. I assume that the N_2 mixing ratio, ρ, is enhanced at the exobase by a factor of 10, which would be the case if the eddy diffusion coefficient on Mars were the same as it is on Earth (*1*). I adopt an atom-molecule collision cross section of 50 Å^2 and double the exospheric depth to allow for the strong forward-directedness of the differential cross section (small-angle scattering robs the collision partners of negligible energy) to obtain an effective exospheric thickness of $4 \times 10^{14}\ \rho$ N_2 molecules per square centimeter.

The energy required for escape after dissociation is 12.13 ev + 3.46 ev = 15.59 ev, which is just above the ionization threshold. Since I consider here only features below the ionization threshold, it would seem that no escape could result if $^2D^0$ is produced in the photodissociation. However, if we take account of the Maxwell-Boltzmann motions of the N_2 molecules in the atmosphere, a different picture emerges. I assume an exospheric temperature of 500°K. At any given instant half of the exospheric N_2 molecules will be moving upward and half will be moving downward. I consider only those moving upward. Their root-mean-square upward speed is $\sqrt{kT/\mu}$ = 385 m/sec, where k is the Boltzmann constant, T is the absolute temperature, and μ is the molecular mass. For these molecules, we can, on the average, neglect their upward motion and reduce the escape speed to about 4500 m/sec (4885 m/sec − 385 m/sec). The escape energy is then 1.469 ev. Photons with energy greater than 12.13 ev + (2 × 1.469) ev = 15.07 ev can then cause the escape of N atoms. The amount of nitrogen lost is calculated as shown in Table 1. This fraction of nitrogen lost would be even larger if (i) absorption above the ionization threshold were considered, (ii) $^4S^0 + {}^4S^0$ was produced in significant quantities, (iii) the eddy diffusion coefficient is smaller on Mars than on Earth (not considered likely), (iv) the exobase were ever hot, or (v) the ultraviolet solar flux is or ever was greater than the value adopted in Table 1.

I now consider the case of uniform, constant outgassing over geologic time. The fractional loss rate is (loss rate of N at time t divided by twice the N_2 column density at time t)

$$\boxed{\frac{\tfrac{1}{2} \times 1.8 \times 10^{6} \times 10\,\rho\ \mathrm{cm^{-2}\,sec^{-1}}}{(2 \times 2.5 \times 10^{23}\rho\ \mathrm{cm^{-2}}) \times [t/(1.4 \times 10^{17}\ \mathrm{sec})]}} = \frac{2.52}{t}$$

The total fraction lost is

$$1 - \frac{1}{\tau}\int_{0}^{\tau} e^{-\int_{t'}^{\tau} \frac{2.52\,dt}{t}}\,dt' = 72\%$$

where $\tau = 1.4 \times 10^{17}$ seconds.

In this latter model approximately three-fourths of the nitrogen would have escaped. In the former model less than one-tenth of the nitrogen would remain. In light of these considerations, the low concentration of martian nitrogen need not cause us to reject our notions about its origin.

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Ice Nucleation by Coprecipitated Silver Iodide and Silver Bromide

Abstract. *The ability of silver iodide to cause freezing of supercooled water is improved if up to 30 percent of the iodine atoms in the crystal are replaced with bromine atoms.*

One of several explanations offered for the effectiveness of AgI in initiating the freezing of supercooled water involves its crystal structure, which is similar to that of ice (*1*). A theory of nucleation catalysis based on the elastic distortion that results because the lattice constant of AgI is 1.5 percent larger than that of ice accounts for the 2.5°C of supercooling that is required to cause water to freeze in the presence of AgI and leads to the prediction that a substance having a smaller lattice misfit would be an even better nucleus (*2*).

By coprecipitating AgBr with AgI we have formed metastable solid solutions in which Br atoms are substituted for as many as 30 mole percent of the I atoms in the AgI crystal structure.

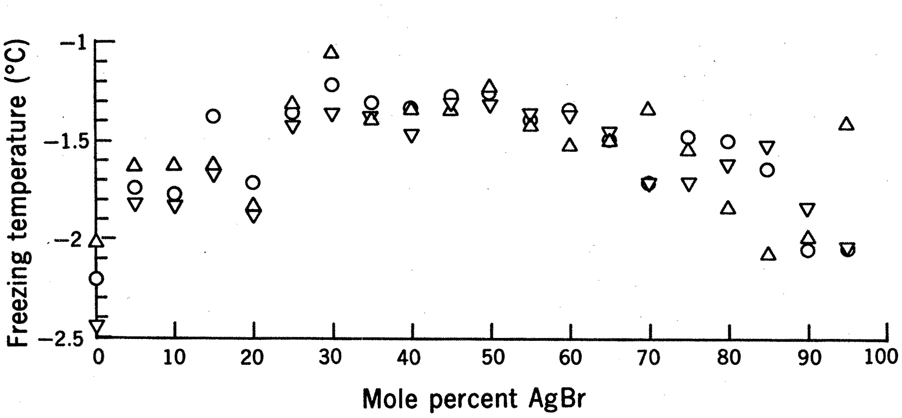

Fig. 1. Freezing temperatures of water samples as a function of the composition of the AgI-AgBr nuclei.