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 Å² 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 × 10^{14} ρ 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)

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

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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29 July 1971

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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.

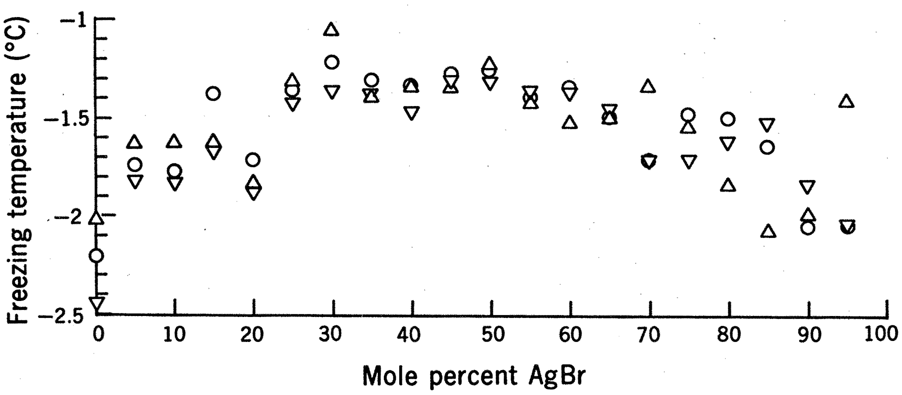

Fig. 1. Freezing temperatures of water samples as a function of the composition of the AgI-AgBr nuclei.

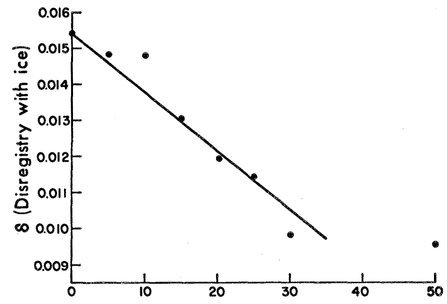

Fig. 2. Disregistry of the silver halide precipitates with respect to ice as a function of composition.

X-ray diffraction measurements show that precipitates can be made having a unit cell that is up to 0.5 percent smaller than that of pure AgI (*3*). These substances, which can be prepared having any desired lattice constant over a limited range, provide a means for studying the effect of lattice disregistry on heterogeneous nucleation.

The technique for producing the silver halide precipitates is described elsewhere (*3*). To determine their relative effectiveness as nucleants, we seal small samples of the precipitates in glass tubes containing water and observe at what temperature they freeze when they are immersed in a vigorously stirred bath whose temperature, measured with Beckmann thermometer to an accuracy of 0.01°C, is lowered at a rate of 0.01°C per minute.

The freezing temperatures determined in three experiments for the 20 water samples containing silver halide precipitates whose compositions range in 5 percent increments from pure AgI to 95 percent AgBr are shown in Fig. 1. The sample containing pure AgBr freezes at −8°C, a value inconveniently large to be shown on this scale. It is evident that, as the fraction of I replaced by Br increases up to about 30 percent, supercooling is reduced by almost a factor of 2. There is little change in the temperature of nucleation as the amount of Br is further increased to 50 percent, but above this value supercooling increases gradually until at 95 percent AgBr it is about the same as for pure AgI. For compositions from 95 to 100 percent AgBr there is an abrupt increase of almost a factor of 4 in the supercooling necessary to cause freezing.

The decrease in the supercooling necessary to produce freezing evident as the concentration of AgBr increases to about 30 percent can be attributed to the gradual decrease in the lattice constant shown by x-ray diffraction to be taking place in this composition range (*3*). In the samples having a composition from 30 percent to about 60 percent AgBr, x-ray analysis shows the presence of the solid solution of AgBr in AgI whose lattice constant most closely approaches that of ice. It seems probable that this phase is responsible for nucleation over this range. For compositions from 60 to 95 percent AgBr, the nucleation effectiveness, although decreasing, is still superior to that of pure AgI, even though x-ray diffraction shows no trace of the AgI structure. Conceivably, the AgBr structures evident may be serving as the nuclei causing the freezing, but this explanation appears unlikely in view of the very large supercooling observed in the presence of 100 percent AgBr. More probably, nucleation in the range from 60 to 95 percent AgBr is still being produced by traces of the AgI structure, which may be present in concentrations less than the few percent detectable with our x-ray techniques. The low ability of 100 percent AgBr to cause nucleation is not surprising, since its lattice constant is 9 percent smaller than that of ice.

The measurements of nucleation temperature in the range from 0 to 30 percent AgBr can be compared with the quantitative predictions of coherent nucleation theory (*2*), that the amount of supercooling necessary for nucleation should vary with the square of the disregistry between the crystal lattices defined as

$$\delta = |\Delta a/a_0|$$

where $\Delta \alpha$ is the amount by which the dimension of the catalyst unit cell exceeds α_0, the dimension of the ice unit cell. Figure 2 shows the disregistry of the precipitates as a function of composition up to 30 percent AgBr, calculated from their lattice constants and that of ice (*3, 4*). Figure 3 is a plot of the smallest observed supercooling with precipitates in the range from 0 to 30 percent AgBr as a function of values for the disregistry smoothed according to the straight line in Fig. 2. It can be seen in Fig. 3 that the supercooling required to cause freezing appears to vary approximately as the square of the disregistry, as predicted by theory. That the dashed line predicted by Turnbull and Vonnegut (*2*) lies above the observed values can be attributed, at least in part, to their neglect of the elastic deformation of the silver halide lattice and perhaps to an overestimate of the elastic modulus of ice.

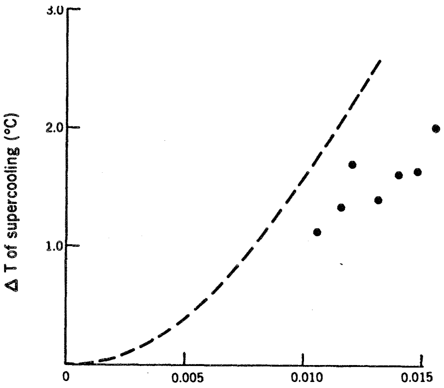

Fig. 3. Supercooling of water as a function of nuclei disregistry. The dashed curve is predicted from the theory of coherent nucleation (*2*).

The improvement in the ice-nucleating property of AgI produced when Br atoms are substituted for some of the I atoms in its lattice appears to confirm theoretical predictions indicating that lattice registry may be a factor in the heterogeneous nucleation of crystalline solids. We recognize, however, that in altering the lattice constant of the nucleating material, we have also changed other physical and chemical properties of its surface that undoubtedly have an effect on nucleation. Further experiments in which lattice constants are varied by the substitution of different atoms in the crystal may shed light on the relative importance of these other factors.

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