DIFFUSION KINETICS OF SOLID METHANE AND NITROGEN: IMPLICATIONS FOR TRITON; R. L. KIRK, Branch of Astrogeology, U.S.G.S., Flagstaff, AZ 86001

Introduction The presence of methane on the surface of Triton has been known from Earth-based spectral studies for a decade [1] and that of nitrogen for roughly half as long [2]. The recent Voyager 2 flyby [3] answered some questions about the disposition of these species on Triton (yes, we see the surface; no, there are no lakes of liquid nitrogen; but yes, the volatiles appear to be seasonally active) but left others as yet unanswered: how is the observed N2 band depth achieved in the solid phase? How thick a nitrogen-methane layer is on the surface? What role do these substances play in creating the cryovolcanic features observed by Voyager? The answers to these questions all involve, in part, the kinetics of self-diffusion in the cryogenic ices, for diffusion is the mechanism of both grain growth (thermal metamorphism) and subsolidus creep. In this abstract I attempt to make the best possible estimates of the diffusion kinetics of solid CH4 and N2 based on published information, and to apply these estimates to try and answer or at least illuminate the above questions about Triton.

Self-Diffusion Rates The temperature dependent rate of self-diffusion in solid CH4 has been measured using nuclear magnetic resonance spectroscopy [4]. The diffusion coefficient at the melting point (90.08 K) is \( D_{\text{eq}} \approx 1.8 \times 10^{-12} \text{ m}^2 \text{s}^{-1} \), and the activation energy \( \Delta H^* \approx 20.8k_{\text{B}} \text{m} \text{s}^{-1} \). Corresponding experiments have unfortunately not been performed for N2, but the diffusion of other gases in the solid phase and at one temperature in the beta phase [5]. The authors of that study assert that, given the similarity in molecular radius between Sn, SnO, and N2, the mechanism and rate of the observed diffusion should be similar to that for self-diffusion. I therefore tie my estimate of the self-diffusion coefficient for nitrogen to the beta phase measurements of [5]. To estimate the temperature dependence of the diffusion rate, I appeal to the analogy with the noble gas solids, which have similar properties to nitrogen, and which have been well studied. Argon, krypton, and xenon all exhibit thermally activated self-diffusion with \( \Delta H^* \approx 1.9\Delta H_{\text{bulk}} \) [6], where \( \Delta H_{\text{bulk}} \) is the latent heat of sublimation; this is close to the theoretical prediction for a vacancy diffusion mechanism. Adopting the same relation for nitrogen, I obtain the estimates \( D_{\text{eq}} \approx 1.8 \times 10^{-12} \text{ m}^2 \text{s}^{-1} \) and \( \Delta H^* \approx 24.9k_{\text{B}} \text{m} \text{s}^{-1} \), where \( T_{\text{eq}} \) is 63.29 K.

Granite Metamorphism Zent et al. [7] have published estimates of CH4 and N2 grain growth rates on Triton that are based on a direct analogy with measurements for water ice at terrestrial temperatures. Specifically, they assume that \( \Delta H^*/\Delta H_{\text{bulk}} \) and the grain growth rate \( K = \left( dL/dt \right) /L \) (where \( L \) is the grain size) extrapolated to infinite temperature are the same for H2O. I assert, however, that the behavior of H2O is a poor source of analogies for that of the cryogenic ices, and that the predictions of [7] are questionable variously by Asumo and Higuchi [8]. In the case of the observed diffusivity is about 40% higher. The pressure-dependence of K and differences conflict with the data of Gow and Stephenson [9] cited by Zent et al. [7]: the observed rates at \( -5 \) to \( -15^\circ C \) are two orders of magnitude larger, and the activation energy is about 40% higher. The pressure-dependence of K and differences between natural and artificial ice reported in [8] are also difficult to interpret. A theoretical model for grain growth [10], which is in good agreement with observation for metals, predicts growth rates for ice about an order of magnitude smaller than those observed by Gow or Stephenson [9] and with a mechanism based on self-diffusion measurements [11] that is significantly larger. None of the observed activation energies for grain growth or diffusion correspond to a vacancy diffusion mechanism such as is expected to operate in nitrogen. I believe that more reliable estimates of grain growth in CH4 and N2 can be made using the physically based theory [10]. Where the needed material constants for these substances are not known, other Van der Waals crystals such as the noble gases are a more appropriate source of analogies than is water ice.

The theoretical model of grain growth [10] involves grain boundary migration driven by surface tension and mediated by diffusive transport of material. The growth rate is given by \( K = \left( \pi/16 \right) M G \), where \( G \) is the surface tension of the crystal and the “intrinsic grain boundary mobility” \( M \) = \( D_{\text{eq}}/28kT \). In the latter relation, \( D \) is the molecular volume of the crystal, \( \delta \) is an estimate of the half-width of the boundary, usually taken to be equal to the lattice spacing, \( k \) is Boltzmann’s constant, and \( T \) is temperature. The remaining quantity, \( D_{\text{eq}} \), is an estimate of the rate of diffusion across the boundary, for which I will substitute the bulk self-diffusion coefficients \( D \) calculated above. The remaining uncertainty is then the value of \( \gamma \), of which I am not aware of any measurements in cryogenic ices. Because \( \gamma \) is a measure of the energy per unit surface area of the crystal, I posit the scaling \( \gamma \propto \Delta H_{\text{bulk}}/\Delta H^* \) and scale the values for CH4 and N2 to the known value for H2O [12]. Using a reference temperature of 40 K, I obtain \( K \approx 0.30 \) for CH4 and 0.53 for N2.

The above calculations predict grain growth on Triton, over a period of 100 Earth years and at the global average temperature of 37 K, to only 7.3 mm for CH4 and 4.8 mm for N2. The corresponding sizes at the 65 K melting temperature of nitrogen are only 220 \( \mu \)m and 2.6 cm. The initial grain size is assumed to be negligibly small in these calculations. As a check on the predicted growth rate for CH4, I calculate a grain size of 1.2 \( \mu \)m after 10 minutes at 77 K. This is consistent with observations of changes on a timescale of minutes in the spectral features of line methane frost kept at the temperature of liquid nitrogen [V. H. Brown, personal communication].

My estimates of grain sizes attained after one season’s annealing on Triton are substantially lower than those of Zent et al. [7], who predicted \( \sim 10 \) \( \mu \)m grain diameters for CH4 and \( \sim 1 \) \( \mu \)m diameters for N2. The values I obtain for nitrogen are also too small even at 63 K to account for the observed spectral feature at 2.15 \( \mu \)m. Cruijenhank et al. [2] measured an absorption coefficient of 0.15 m\(^{-1}\) in liquid nitrogen and concluded that a path length through condensed nitrogen on the order of meters was required to account for the 13% contrast they observed in the spectral band. To relate this estimated path length to a grain diameter, I performed simple Monte Carlo simulations of radiative transfer in a solid nitrogen layer. I was able to reproduce the spectral contrast of 13% [2] and the albedo outside the band of 0.7 [2] by assuming a wavelength-dependent absorption coefficient of 0.15 m\(^{-1}\) in addition to the wavelength dependent absorption, and a grain diameter of 25 cm. The estimated grain growth rate would have to be increased by a factor of 3 \( \times 10^9 \) to account for such large grains at 37 K, and by 100 even at 63 K. Although the estimates are admittedly uncertain, such increases seem unlikely. The normalized diffusivity at the melting point \( D(T_{\text{eq}})\Gamma^3/8 \) is already unusually large compared to most materials [13]. Furthermore, although \( \Delta H^*/\Delta H_{\text{bulk}} \) was chosen to be the same as for the noble gases, the resulting value of \( \Delta H^*/\Delta H_{\text{bulk}} \) is substantially larger than for those materials [6]. Thus, if anything, the diffusion rate (and hence grain growth rate) at the melting point is likely to be less than estimated above. The depth of the observed N2 spectral band is thus difficult to account for. One conceivable mechanism for obtaining the required grain size in seasonal nitrogen deposits would be for these deposits to form not as a fine frost but epilithically on underlying material that had annealed over a much longer period. Even over a billion years, however, sustained temperatures of \( \sim 43 \) K would be required to reach a grain diameter of 25 cm in the substrate. Direct observations of grain growth in N2 are clearly desirable to help resolve this problem. They are within the realm of feasibility even for the growth rates estimated here: the predicted grain size after 10 days at the melting point is \( \sim 0.4 \) mm (the corresponding prediction from [7] is of the order of 10 cm).

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Solid-State Viscosities: The self-diffusion rates calculated here may also be used to estimate the viscosities of the cryogenic layers on Triton. Diffusion of molecules through the grains and along the grain boundaries in response to a stress gradient leads respectively to the deformation mechanisms known as Nabarro-Herring creep [14] and Coble creep [15]. These mechanisms are linear, while the viscosity 

\[ \eta = kT^2/\rho L^2 \]

in these equations \( k \) is a numerical correction factor for finite strain equal to roughly 0.4 [16] and \( D_0 \) is the diffusivity along grain boundaries. It is commonly assumed that the values of \( D_0 \) extrapolated to infinite temperature are equal, and that the activation energy for boundary diffusion is \( \sim 0.6 \) times that for bulk diffusion [17]. With these assumptions, we have for CH\(_4\) \( \eta_{NH} (T_m) = 1.45 \times 10^{11} \) Pas, \( \eta_c (T_m) = 9.57 \times 10^{12} \) Pas, and \( \Delta H^\circ_0 = 12.5 \). The corresponding values for N\(_2\) are \( \eta_{NH} (T_m) = 5.6 \times 10^{10} \) Pas, \( \eta_c (T_m) = 7.3 \times 10^{11} \) Pas, and \( \Delta H^\circ_0 = 14.9 \). I have used a nominal temperature of 40 K and grain diameter of 1 mm in the preexponential factor in these formulas. The transition between Nabarro-Herring and Coble creep occurs at 37 K at a grain size of 2.5 mm in methane and 9 cm in nitrogen. Nabarro-Herring creep being favored at the higher temperatures and larger grain sizes.

Global Volatile Layer Thicknesses: We can use the estimated viscosities from the last section to constrain the thicknesses of widespread surface layers of CH\(_4\) and N\(_2\) that may be present on Triton. I have calculated viscous relaxation timescales for a number of models having a finite layer in which viscosity varies exponentially with depth down to a rigid lower boundary [18]. From these I calculated the degree of relaxation of features of various horizontal sizes after a nominal time of 150 m, and require that features be less than about 0.6 km in extent before significant relaxation. The exponentially varying viscosity is an approximation to the temperature-dependent viscosity given above, with a thermal gradient due to radiogenic heating. The most uncertain in these calculations is the appropriate value of the grain size to use. Grain growth by annealing can in some cases determine the grain size. If the initial grain size is sufficiently small, the grain size after time will be determined by annealing, as calculated above. The temperature dependence of \( K \) and \( \eta_{NH} \) cancel, leading to a viscosity that is independent of depth but increases linearly with time. In the Coble case, the temperature dependence of \( K \) dominates, so the viscosity actually increases with depth. Creep in a N\(_2\) layer is essentially always by the Nabarro-Herring mechanism, because no matter how small the initial grain size is, there is always an increase in viscosity even at the surface after 10\(^6\) a. The limit on the thickness of the nitrogen layer in this situation is \( \sim 100 \) m. Methane, in contrast, is in the Coble regime. If \( d < 3 \times 10^4 \) m initially so that the layer is everywhere annealed, the limiting thickness is only \( \sim 300 \) m. For \( d > 2 \) mm even the base is unannealed and the limiting thickness is \( \sim 100 \) m. Increasing the grain size further will lead only to logarithmic increases in the permissible layer thickness.

Cryovolcane: Features: Determination of the chemistry, physics, and timing of the several distinct styles of cryovolcanism on Triton is an underraking to occupy many years for years to come. My purpose here is to address one very limited aspect of this problem: what do rheological considerations tell us about the likelihood that solid methane or nitrogen were involved in any of the types of cryovolcanism? The viscous relaxation results of the previous section can be applied directly to the caldera-filling flows and the layered eruptions to their east [3]. Measurements of relief in these areas using two-dimensional photomontage [R. L. Kirk, in preparation] gives typical values on the order of 200 m. If this is the approximate thickness of the erupted material, the observed separation of reflectance on the fronts rules out both N\(_2\) and CH\(_4\) compositions for the flows.

The case of the ridge-like linear features is quite different. Postulating that these forms are formed by erosion from linear vents followed by spreading to either side that ceased as the flows cooled, I use a model similar to glacial flow models [19] to describe their widening and lowering with time. Setting the time required to attain the present height \( H \) and half width \( L \) equal to the cooling time \( T^2/\rho L^2 \), I obtain an estimate of the required viscosity at the initial elevated temperature: \( \eta \geq 10^9 \text{Pas} \). Using \( L = 10 \) km and \( H = 200 \) m, the best based on photometric measurements, I find \( \eta \geq 5 \times 10^{13} \text{Pas} \) for CH\(_4\) \((1.5 \times 10^{-9} \text{m}^2 \text{s}^{-1})\) and \( \eta \geq 3 \times 10^{13} \text{Pas} \) for N\(_2\) \((1.1 \times 10^{-9} \text{m}^2 \text{s}^{-1})\). At the melting temperatures of the materials, these viscosities correspond to grain sizes of 6 mm and 17 mm respectively, which are not implausible. An equally important consideration is the degree of further spreading of the features over longer time periods at the ambient temperature. Using the viscosity appropriate to material annealed at the base of the flow for 10\(^5\) a, I calculate spreading times of 8 \( \times 10^{15} \) a for methane and 2 \( \times 10^{11} \) a for nitrogen. Thus neither candidate material can be ruled out on rheologic grounds alone. It is worthwhile to point out in this context that, although the linear features on Triton have been compared to flows on Ariel, for which the viscosity was calculated previously to be appropriate to the composition of NH\(_4\)BO\(_3\) [22], the latter typically have an aspect ratio \( H/L \) ten times as large and a "viscosity product" \( H^2/L^2 \) that is up to 100 times larger. The linear features on Triton may therefore be quite different in composition and origin.


The author would like to take this opportunity to retract the statement in his Ph.D. thesis (1987) to the effect that once we have seen Triton we will understand Ganymede.