Radioactively Induced Sublimation in Solid Tritium

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A horizontal cylindrical cavity bounded by isothermal walls was partially filled with liquid tritium which was then frozen by reduction of the temperature to 1.0 K below the triple point. Visual observations revealed that the solid subsequently redistributed itself into a layer of uniform thickness covering the complete interior of the cavity. The time constant for this effect depends on the age (or ^{3}He content) of the tritium and not on the initial filling fraction. Time constants of 14.9, 92, 219, and 234 min were measured for tritium 0.04, 7, 16, and 17 days old, respectively.

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Radioactive isotopes are classic examples of materials which exhibit internal self-heating. Tritium decays to ^{3}He, emitting a β particle and an antineutrino. Because the β's are reabsorbed within approximately 10 μm, condensed tritium samples have a nearly uniform self-heating rate $\dot{q}$ and a quadratically increasing temperature profile in the direction away from the containing boundary. The interior surface of a thick layer of tritium can thus be warmer than the interior surface of a nearby, thinner layer, as long as the exterior surfaces of these layers are equal in temperature or are radiating with equal emissivities to an infinite thermal sink. Being warmer, the interior surface of the thicker layer has a higher vapor pressure than the interior of the thinner layer, and a preferential sublimation-condensation effect can occur, tending to make the layers uniform in thickness. This effect, dubbed the "β heating effect," was first proposed by Martin, Simms, and Musinski[1] as a method of preparing the "ideal" inertial-confinement fusion target, namely a uniform spherical shell of DT.

Martin and Simms[2] have constructed a one-dimensional model of the β heating effect which predicts that layer-thickness equilibration proceeds exponentially in time with a minimum time constant $\tau_{\min} \equiv H_s/\dot{q}$, where H_s is the heat of sublimation of the solid. For pure T_2 at 19.6 K, $\tau_{\min} = 14.4$ min, representing the rate constant for the hypothetical case where there is no impedance to the flow of vapor in the cavity. Without repeating the arguments used in Ref. 2, we can easily derive the above expression for one-dimensional slabs of material bounded by semi-infinite isothermal plane surfaces. Imagine a layer of radioactively heated solid completely filling a finite space between two such semi-infinite surfaces, both at the same temperature. At steady-state conditions, the solid will have a parabolic temperature profile with a maximum at the exact center. Take a thin sliver of the solid starting at a distance δ from the center and expand it many times its original width, turning the solid into vapor and simultaneously creating a space between two layers of solid of unequal thickness, as shown in Fig. 1. We now assume that the impedance to the flow of vapor is so small that the process of sublimation and condensation can transport heat just as effectively as did the original solid sliver. In other words, the temperature drop across the vapor space is identical to the drop which was present in the original solid sliver. The temperature profile in each of the two opposing solid layers now will be identical to the original parabolic profile which existed in these sections before the split occurred. The heat flux transported in the vapor phase by the sublimation-condensation process is equal to $\rho H_s \dot{\delta}$, where ρ is the molar density and $\dot{\delta}$ is the time rate of change of the "excess thickness" δ. We assume that the temperatures are at quasi steady state, i.e., all the heat generated internally is eventually deposited to the isothermal boundaries. Referring to Fig. 1, we note that no heat can flow past the point of the temperature maximum in the thicker layer, and therefore the heat being generated to the right of this maximum (in a solid layer of thickness

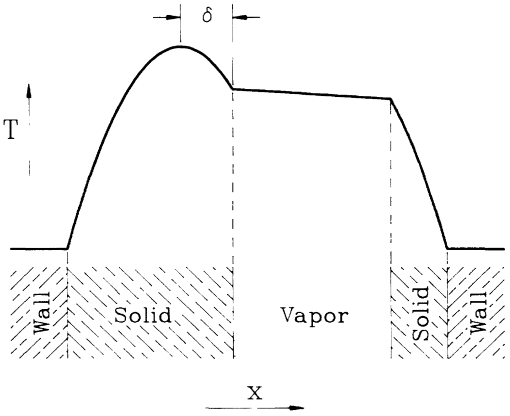

FIG. 1. One-dimensional slab model of the β heating effect. The temperature profiles in the solid, self-heated layers are parabolic. Sublimation-condensation across the vapor space results in the gradual erosion of the excess layer thickness δ. Heat balance at the solid-vapor boundary leads to the limiting rate constant $\tau_{\min} = H_s/\dot{q}$, where H_s is the heat of sublimation and $\dot{q}$ is the self-heating rate.

δ) must be transferred through the vapor phase to the thinner layer and thence to the right-hand boundary. This amount of heat flux is therefore equal to $\rho\delta\dot{q}$. Hence

$$\delta\dot{q} = \dot{\delta}H_s, \tag{1}$$

which has the simple solution

$$\delta = \delta_0 e^{-t/\tau_{\min}}, \tag{2}$$

where $\tau_{\min} = H_s/\dot{q}$ and δ_0 is the excess thickness at zero time.

In the case of tritium, the presence of stagnant noncondensable ^{3}He gas, introduced into the vapor space during the initial condensation, impedes vapor transport, which now must take place by diffusive flow. The parameter H_s decreases weakly with temperature and hence equilibration rates should fall off only slightly at lower temperatures, as long as there is sufficient vapor present to effectively transport the necessary heat.

To investigate the β heating effect experimentally, we chose to work in a cylindrical geometry, which permits better optical clarity than a spherical geometry. Also, isothermal conditions could be easily achieved by use of massive copper cylinder walls and sapphire end windows. We designed a cylindrical cavity of height equal to diameter $D = 5.74$ mm, the volume being small enough to be filled with a relatively low inventory of T$_2$, yet large enough to permit direct visualization of the layer equilibration process. The axis of the cylinder was aligned horizontally so that the observed process would have to work against gravity. The cylinder was mounted inside of a secondary containment vessel of similar cylindrical construction, i.e., massive metal walls and sapphire end windows. During the experiments, the space between the two cylinders was filled with ^{4}He exchange gas. With use of a separate ^{4}He exchange gas supply, the double-cylinder assembly was thermally coupled to a cryostat of our own design cooled by a closed-cycle helium refrigerator. The cryostat was thermally regulated by a thermometer-heater pair, while a separate calibrated thermometer, imbedded in the copper wall of the sample cylinder, measured the slightly higher temperature of the perimeter of the T$_2$ sample.

The sample cylinder was illuminated with low-level incandescent light and was viewed on the opposite side by an autocollimator coupled to a video camera and a VCR recorder. Analyses of sample history were made from measurements taken on photographs of the video screen.

To test the effects of the illumination on frozen hydrogens, we performed a preliminary experiment with pure deuterium. The sample cell was filled about $\frac{1}{3}$ full with liquid D$_2$ and then cooled to 18.2 K, where the D$_2$ froze. We maintained this temperature for 24 h, but observed no changes in the shape of either the bulk solid D$_2$ or the crystals on the sapphire windows. We conclude that the sample cell was highly isothermal and that the illumination levels were too low to induce any migration of the frozen D$_2$.

Our gas-handling system incorporated a bed of Pd powder which allowed us to remove the majority of the ^{3}He gas prior to condensing the T$_2$ into the optical cylinder. The T$_2$ could be also stored in a separate tank where it would "age" or accumulate ^{3}He naturally. Two separate experiments were performed on "fresh" T$_2$. Two experimental runs were conducted on 7-day-old material, followed by one each on 16- and 17-day-old T$_2$.

All the experiments reported here were begun under identical thermal conditions. Typical of all our experiments is the sample history shown in Fig. 2 for 7-day-old T$_2$. The cell was partially filled with liquid T$_2$ at 21.0 K, i.e., just above the triple point temperature[3] of 20.62 K. As shown in Fig. 2(a), the liquid meniscus is quite broad, causing an opaque band in the forward transmitted light. After filling, the sample cell was cooled by 1.4 K. The liquid froze from the outside and roughly assumed the shape of the original meniscus. The fill tube, located on the bottom of the sample cell, froze first and blocked the T$_2$ in the cell from the outside, creating a condition of constant volume. Because solid T$_2$ is considerably more dense than the liquid, void regions developed in the freezing solid as seen in the photograph in Fig. 2(b), taken just moments after freezing. Rather large solid crystals are evident in the thin layers of solid frozen on the upper halves of the sapphire windows (note that we are observing both front and back windows simultaneously). The bulk solid, formed along the bottom perimeter of the sample cell, is perfectly clear. Several small specks of dust lying along the bottom surface, which accumulated when the cell was first filled with liquid, could still be seen through the frozen solid. As evidence by the broad, irregularly shaped opaque band, the solid which has formed near the original liquid surface has many inclusions and/or grain boundaries. This band clears noticeably in the first hour after freezing as the β heating phenomenon erodes the shape of the original meniscus.

After 2 h, as seen in Fig. 2(c), the solid has formed a thick ring around the entire perimeter of the cell. The opaque band has disappeared, leaving traces of the chaotic freezing patterns that occurred near the original liquid surface. 4 h after first freezing, as seen in Fig. 2(d), the solid layer appears nearly perfectly uniform, but our more detailed analysis outlined below shows that the excess thickness δ is still nearly 40 μm. The solid thickness on the sapphire windows is also nearly uniform, as deduced from the thin, circular dark band just inside the clear, bulk solid ring. This band shows that the interior solid surface is slightly curved near the sharp corner where the sapphire windows meet the cylinder walls, as would be expected if the solid surface matches that of an isotherm slightly above the fixed boundary temperature. The windows still show remnants of the chaotic freezing behavior, probably in the form of a higher density of crystalline defects or grain boundaries.

In the experiment on 17-day-old material, we followed the subsequent changes in the sample appearance for a total of 307 h. The "5 o'clock shadow" never cleared completely, but was gradually replaced by a set of larger and larger single-crystal grains, some of which (after 10 days time) eventually spanned the entire window diameter. After approximately 5 h, the outer clear layer of bulk solid began to cloud up slightly due to the appearance of defects or cracks. At the end of this long run, the bulk solid layer was nearly opaque, while the crystal grains seen on the sapphire faces had more sharply pronounced boundaries. We conclude that polycrystalline samples of solid T_2 are broken or fractured by the accumulation of ^{3}He gas liberated *in situ,* but that single-crystal samples are not affected. However, there was no evidence to suggest that the solid layer thickness was rendered less uniform by the accumulation of ^{3}He gas in the solid sample.

Each run was analyzed by measurement of $\delta(t)$ directly on the photographs. Following Eq. (2), we plotted $\ln\delta(t)$ vs t and performed a linear least-squares fit of the data. Data and straight-line fits for the four experiments on aged T_2 are shown in Fig. 3. Because of the opaque band, the equilibrium thickness could not be determined unambiguously. Thus, there is an uncertainty in the absolute δ values on the order of ± 15 μm. At very early times, the error in δ can be as large as 100 μm due to the irregular shape of the solid boundary. These errors are shown in Fig. 3 for just one of our runs.

Different filling fractions were used in the two "fresh" T_2 experiments, resulting in equilibrium solid layer thicknesses d of 880 and 465 μm. The corresponding τ values taken from linear fits of the data were 14.6 and 15.2 min, respectively, which are equal within the experimental uncertainties. The average of 14.9 is surprisingly close to the value of 14.4 predicted by our simple model. For the two experiments performed on 7-day-old T_2 we measured d values of 360 and 320 μm. The corresponding τ values were 91.1 and 92.7 min, respectively, which

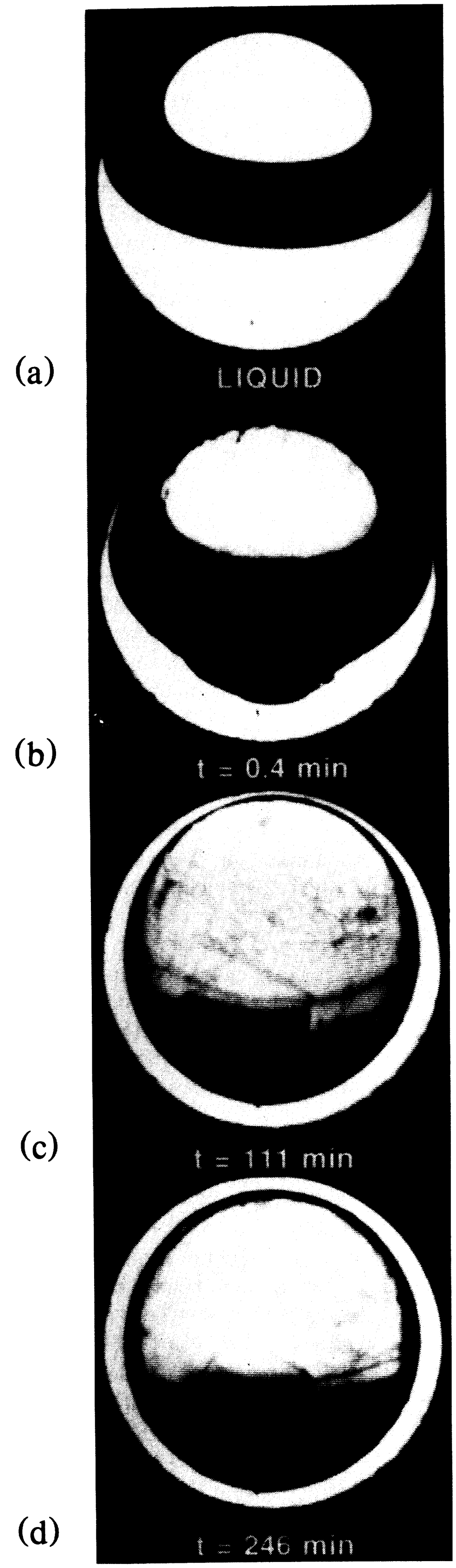

FIG. 2. Photographs of the 5.74-mm-diam sample cell partially filled with pure tritium. (a) The cell at 21.0 K just prior to freezing. (b) Just after freezing at 19.6 K. Large void regions form as the sample freezes at constant volume. Bulk solid has already formed high up on the cell walls. Large crystals are evident on the sapphire windows in the upper, thin layered regions. (c) Nearly 2 h after freezing, the solid has formed a clear layer covering the entire interior surface. (d) 4 h after first freezing, the solid layer is nearly uniform. The broad meniscus seen in (a) and (b) has been reduced to a narrow circular band, showing that the solid on the sapphire windows is equally thick with minimal rounding in the sharp corner regions. The void inclusions and other defects formed in the bulk during the rapid freeze have not yet completely healed, giving rise to the "beard" on the sapphire faces.

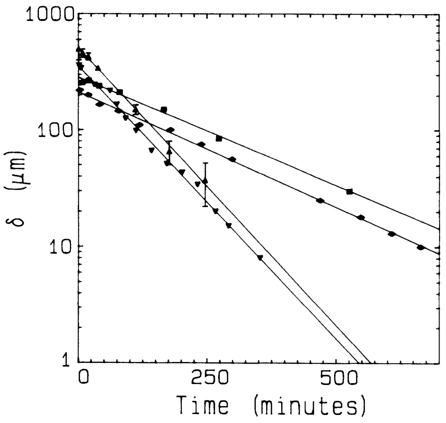

FIG. 3. Excess thickness vs time for four separate experiments. In each experiment, the initial filling fraction was slightly different, resulting in different equilibrium layer thicknesses d and different initial values of excess thickness δ. The least-squares fit of each data set is shown as a solid line. Two separate experiments, represented by triangles, were performed on the same day, just 7 days after the tritium was purified, yielding nearly identical rate constants τ of 92 ± 1 min. The lozenges represent data taken on 16-day-old tritium, where $\tau = 219$ min, while the squares were measured 1 day later, with $\tau = 234$ min.

also are equal within experimental error. For the two experiments performed on 16- and 17-day-old material, the d values were 180 and 250 μm, with τ values of 219.3 and 233.6 min, respectively. As predicted by Eq. (2), our limited data set shows that the rate constant is independent of layer thickness, for samples of equal ^{3}He content.

The effect of ^{3}He content, or age of the T_2, on the equilibrium rate is roughly linear. The expression $\tau = 14.4 + 12.8a$, where a is age in days and τ is rate constant in minutes, fits our data quite well, suggesting that our "fresh" T_2 samples are equivalent to about 1-h-old material. This is quite reasonable, when we consider the time taken to condense the T_2 into the optical cylinder and assume that the Pd bed releases a trace of ^{3}He when the T_2 is desorbed.

Having demonstrated that radioactively induced sublimation is easily observable in solid tritium, we may speculate that the same effect must be present in all other radioactive solids. For most such materials, the vapor pressure above the solid is very low and hence the equilibration rates may be only of geological importance. For instance, we suggest that this same physical phenomenon is responsible for the lithophilic property of natural uranium. Radioactive dating methods may have to be reanalyzed, with the realization that the materials have a tendency to disperse. And the long-term consequences of a "core melt-down" may have to be reassessed.

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[2] A. J. Martin and R. J. Simms, in Proceedings of the Thirty-Fourth National Symposium of the American Vacuum Society, 2–6 November 1987, Anaheim, California (to be published).

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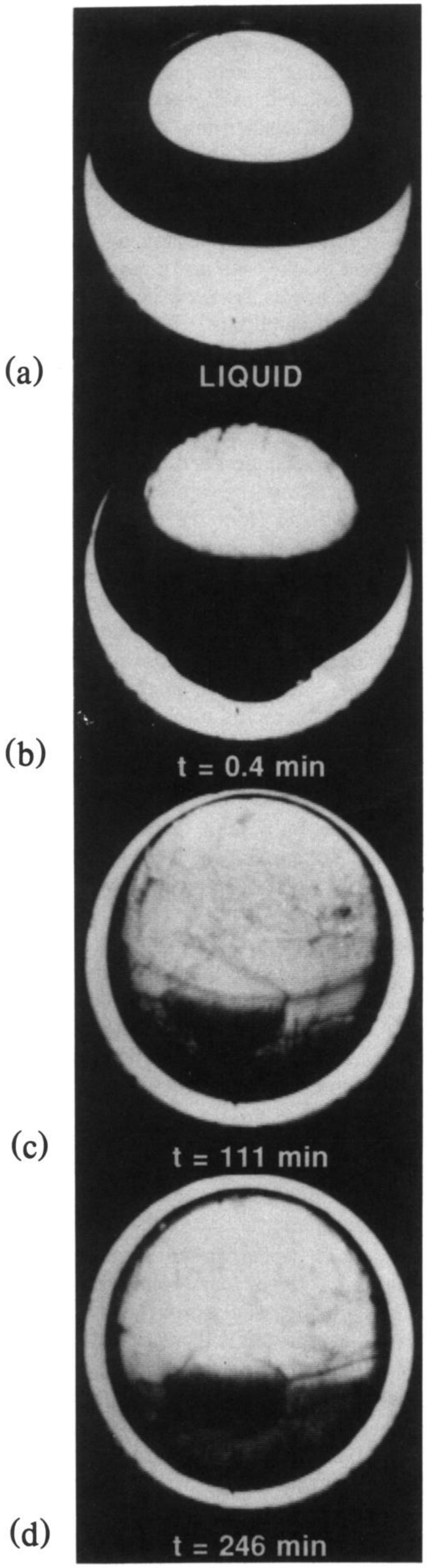

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