PECULIARITIES OF HEAT TRANSFER IN POROUS SOLID NITROGEN

R. S. Mikhal'chenko, V. F. Getmanets, and V. T. Arkhipov

UDC 536.242:536.483:546.17

An experimental study was made concerning the peculiarities of heat transfer in porous solid nitrogen. It has been established that the rate of heat transfer in this medium is basically governed by the rate of mass transfer.

In laboratory practice gases are solidified most often by evacuating vapors of cryogenic liquids to below the triple-point pressure [1, 2]. The process conditions under which liquefied gases solidify during the evacuation will determine the intrinsic porosity of the solid [3]. A porosity above 20% and a capillary structure [4] should indicate a pronounced influence of mass transfer processes on the heat transfer in a solidified gas. Many studies concerning the sublimation of ice and naphthaline under vacuum have dealt with the external heat transfer problem [5-7]. In this study the authors attempted to explain the peculiarities of heat and mass transfer in porous solidified gases under transient heating—cooling conditions.

The experiments were performed on an apparatus shown in [4]. The test procedure was as follows. A Dewar flask made of glass was filled 225-230 mm high with liquid nitrogen at the triple-point temperature (about 63°K). Then, without a change in the geometrical layout of the suction system, the vapor was pumped out to produce solid nitrogen and to cool it below the triple point.

After some time, depending on the initial suction rate, a dynamic equilibrium between both the sublimation and the vapor suction processes was reached inside the flask at temperatures within the 62-47°K range. The steady-state temperature of solid nitrogen was maintained for 10-240 min. The thermal influx to the solid nitrogen was determined from the rate of vapor suction under stable thermal conditions: 1.0-1.5 W. In some of the tests a power of 0.5-2.0 W was supplied to a horizontal heater in the lower part of the flask. Then, in order to study the rate and the mechanism of the temperature rise in solid nitrogen, in relation to the mode of heat supply, we discontinued the suction and performed one of the following operations at a time in the flask with solid nitrogen: a) gaseous nitrogen or hydrogen was injected at a temperature of 300°K (until the pressure had risen to 94-760 mm Hg), b) liquid nitrogen was injected at a temperature of 77°K until the solid nitrogen had been covered with a liquid layer 15-20 mm thick, c) the heater in the lower part was turned on, and d) the specimen in the flask was heated by thermal influxes from outside.

During the tests we continuously recorded temperature changes in the solid nitrogen at the points where thermocouples $T_1 - T_5$ had been installed (accurately within ±0.05°K in the case of differential thermocouples), pressure changes above the solid nitrogen (within an accuracy of ±0.05 mm Hg), and volumes of vapor pumped out of the flask. Thermocouples T_1 and T_5 had been placed respectively 7 and 216 mm above the heater in the lower part.

In Fig. 1 is shown the temperature trend of solid nitrogen during freezing (range A), during cooling (range B), during equilibrium with the heater off (ranges C, E), during heater energization to a 1 W power level (range D), and during heating (range F). The following basic process peculiarities are evident on the diagram.

Physical Engineering Institute of Low Temperatures, Academy of Sciences of the Ukrainian SSR, Kharkov. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 23, No. 3, pp. 393-400, September, 1972. Original article submitted November 16, 1971.

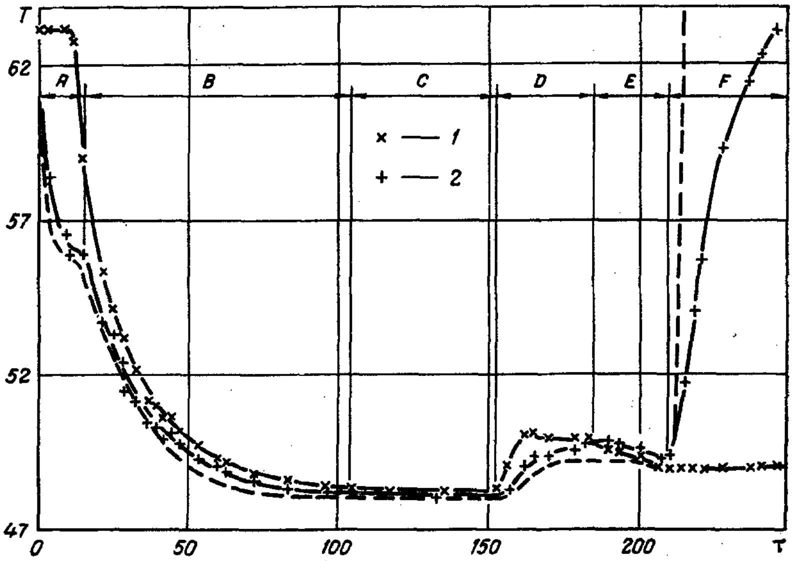

Fig. 1. Temperature-time characteristic (T, °K and τ, min) of solid nitrogen: temperature T_1 at the bottom of solid nitrogen (1), temperature T_5 at the top of solid nitrogen (2), temperature corresponding to saturated-vapor pressure in the flask (solid line). Freezing range A, supercooling range B, steady-state range C, heater turned-on range D (Q = 2.4 W), heated turned-off range E, injection of gaseous nitrogen F (at T = 300°K).

After solidification has been completed, the cooling of solid nitrogen (at a vapor suction rate within the 0.2–1.0 kg/h · dm^3 range) is almost linear and rather fast, but then slows down quasiexponentially. During this period the temperature drop across the height of the solid phase is almost negligible of the order of 0.5°K; it is much larger during the preceding stage.

Under steady-state thermal conditions (range C) the temperature at the test points is, within measurement accuracy, constant and almost the same as the temperature calculated from the saturated-vapor pressure.

Energizing the heater in the lower part (range D) produces some pressure rise in the flask and some temperature rise in the solid nitrogen. Gradually the temperature throughout the volume of solidified gas approaches the temperature corresponding to the pressure in the flask.

It is noticeable that the variation of the suction rate with time follows a trend similar to the temperature curve.

The heating processes with different modes of heat supply are characterized by specific peculiarities. In Fig. 2 is shown the variation of temperature with time at the upper section (T_1) and at the lower section (T_5) of solid nitrogen under the various modes of heat supply in this experiment.

The fastest temperature rise is achieved by injecting gaseous nitrogen into the flask at a temperature close to the temperature of the solid phase (curve 1). Cold gas and simultaneously precipitating nitrogen snow were obtained by throttling the liquid nitrogen from 1 atm abs down to the flask pressure. According to the diagram, the temperature and the pressure in the upper layer of solid nitrogen quickly reached the triple-point level during throttling. The temperature in the lower part of solid nitrogen followed the temperature in the upper part, but was lagging behind it. At the instant when a liquid layer appeared above the solid nitrogen, a temperature drop of 0.5–0.2°K had been established across the thickness of that layer. According to Fig. 2, the further heating of solid nitrogen proceeded at a much slower rate.

Heating with the heater in the lower part (curve 2) or by thermal influxes from outside (curve 4) proceeded linearly with time and with a small temperature gradient along the height of the solid layer, the direction of this gradient being dependent on the location of the heat source. The heating rate of solid nitrogen was in this case determined entirely by the quantity of heat supplied to the flask.

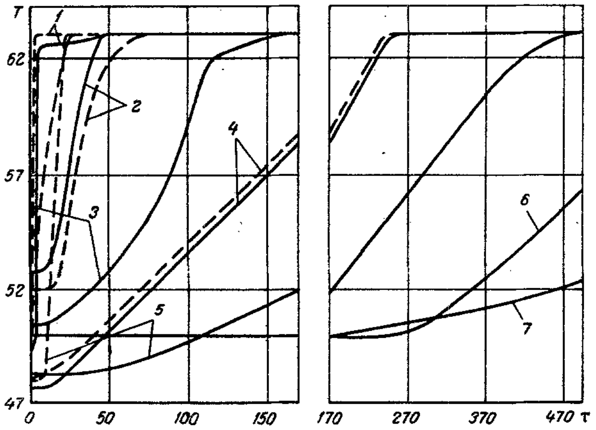

Fig. 2. Heating rate of solid nitrogen at various modes of heat supply (T, °K and τ, min): injection of liquid nitrogen at T ≈ 77°K into the flask (1), energization of the heater with a 1 W power (2), injection of gaseous nitrogen at T = 300°K (3), heat influxes from outside (4), injection of gaseous hydrogen at T = 300°K (5), variation of the bottom temperature T_1 according to Eq. (2) with T_5 = const. (6), variation of temperature T_1 according to Eq. (3) (7), temperature T_1 of solid nitrogen at the 225 mm depth (solid line), temperature corresponding to the saturated-vapor pressure in the flask (dashed line).

When warm gaseous nitrogen (curve 3) or hydrogen (curve 5) were supplied, the upper layer of solid nitrogen heated up quickly to the triple point and on its surface appeared a layer of liquid. The remaining mass of solid nitrogen, however, heated up slowly.

The thermal conductivity of gaseous hydrogen is much higher than that of nitrogen. Nevertheless, heating in a hydrogen atmosphere proceeded much slower.

In order to analyze the results, it is necessary first to estimate the porosity of solid nitrogen. Assuming zero thermal flux from outside and assuming that the volume of the solid phase is equal to the volume of the original liquid, we have the following relation for the porosity:

$$P = 1 - \frac{\rho_L}{\rho_S} \cdot \frac{r}{r_S + \int\limits_{T_3}^{T} C_s(T)\,dT}. \qquad (1)$$

The integral $\int_{T_3}^{T} C_S(T)dT$ here represents the quantity of heat dissipated during the cooling of the solid phase. In deriving this equation we have disregarded the erosion of droplets and crystals, which, according to the experiment, is entirely valid at low suction rates (below 0.2 $\mathrm{kg/h \cdot dm^3}$).

According to Eq. (1), the porosity should be 0.27 at a cooling temperature of 48.2°K (see Fig. 2), which agrees closely with the value obtained on the basis of this test.

Depending on the temperature of solid nitrogen, at the end of suction (62-47°K) during the heating test its porosity varied from 0.2 to 0.3. On the basis of these data, we will try to establish the essential factors affecting the heat transfer in the given substance.

It is well known that the heat transfer in porous media occurs by radiation, by convection, and by conduction through the matrix as well as through the filler material. In our case one must also consider the heat transfer coupled to the mass flow and the overcondensation of gas.

The first two modes of heat transfer may be disregarded on account of the low temperature of the medium and the small size of pores.

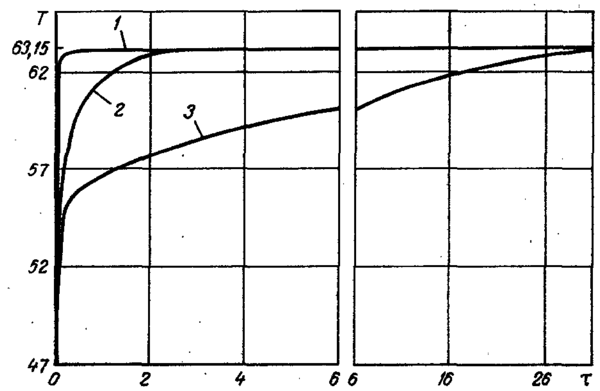

Fig. 3. Effect of the porosity of solid nitrogen on its heating rate, when liquid nitrogen is throttled into the flask: porosity P = 20 ± 1% (1), 5 ± 1.5% (2), 2.5 ± 1.5% (3).

The effective thermal conductivity of a porous structure in the form of parallel channels oriented in the direction of heat flow is [8]

$$\lambda_{\text{eff}}=\lambda_S(1-P)+P\lambda_G \tag{2}$$

Inasmuch as the gaseous phase occupies not more than 30% of the total volume and its thermal conductivity is, even in the case of hydrogen as the filler gas, by one order of magnitude lower than that of the solid phase, therefore, according to formula (2), the heat transfer through the gas is negligible.

In order to evaluate how the thermal conductivity of solid nitrogen affects its heating rate, we will consider the heat transfer through a layer of solid nitrogen under the various conditions.

As the bottom surface of solid nitrogen was made adiabatic, the boundary condition here can be stated as

$$\left.\frac{\partial T}{\partial x}\right|_{x=220\,\text{mm}}=0.$$

Since the lateral surface of the cylindrical flask containing solid nitrogen was also made adiabatic, hence the problem of a cylinder can be reduced to the problem of one-dimensional heat transfer through an infinitely large plate:

$$a\frac{\partial T}{\partial \tau}=\frac{\partial^2 T}{\partial x^2}.$$

The specific heat of the gas may be disregarded in these calculations, because the mass of gas is much smaller than the mass of solid nitrogen. We, therefore, consider the entire heat supply to be used for heating the solid phase. For the purpose of calculations, the thickness of solid nitrogen will be assumed 220 mm and its initial temperature T_0 = 50°K.

In the case of solid nitrogen heated by thermal influxes from outside, the latter are transmitted almost entirely by radiation from the flask flange and, consequently, the boundary condition at the top surface of the plate is

$$Q=\text{const}=1.3\ \text{w}.$$

The temperature of a body heated under these conditions is determined according to the equation [9]:

$$T(x,\tau)=T_0+\frac{q}{\lambda_S}\left[\frac{a\tau}{R}-\frac{(R-x)^2}{6R}\right.$$

$$\left.+R\sum_{n=1}^{\infty}\frac{2}{\mu_n^2}\cos\mu_n\frac{x}{R}\exp(-\mu_n^2\,\text{Fo})\right]. \tag{3}$$

When gaseous nitrogen or hydrogen or when liquid nitrogen was injected into the flask containing solid nitrogen, on the surface of the solid phase very soon appeared a layer of liquid at the triple-point temperature (curves 1-3 in Fig. 2). The temperature at the solid-liquid interphase boundary remained constant from then on, i.e.,

$$T(0, \tau) = \text{const} = T_3 .$$

The solution to this problem is [9]:

$$T(x, \tau) = T_3 - (T_3 - T_0)$$

$$\times \sum_{n=1}^{\infty} (-1)^{n+1} \frac{2}{\mu_n} \cos \mu_n \frac{x}{R} \exp(-\mu_n^2 \mathrm{Fo}).$$

The temperature of solid nitrogen at the bottom surface (x = 220 mm) was calculated, as a function of time, on a digital computer according to Eqs. (3) and (4). The results are shown in Fig. 2 (curves 6 and 7). On the basis of a comparison between these curves and the corresponding test curves 1-5 (Fig. 2), one may conclude that heat conduction through the matrix plays no significant role in the heat transfer through the layer of solid nitrogen. The calculations were based on the following values: $\lambda_T = 0.3$ W/m $\cdot$°C, $c_S = 1.57$ J/g$\cdot$°C, $\rho_0 = 0.695$ g/cm^3, $T_0 = 50$°K, and $T_3 = 63.15$°K.

The discussed results indicate that the heat transfer through porous solidified gases is determined basically by mass transfer processes and is effected in the following manner. The heat supplied to solid nitrogen is absorbed around the source, owing to the sublimation of part of the solid phase. As a result of vapor generation near the heat source, the pressure here rises. For this reason, the vapor flows toward the lower-pressure and thus lower-temperature region.

During desublimation, the vapor releases the heat of phase transformation causing a rise in the local temperature. It must be assumed that in this case the local temperature determines also the local saturation pressure and vice versa.

The absence of large temperature gradients during the heating of solid nitrogen by thermal influxes from outside or with the heater in the lower part indicates that the gas permeability of the matrix is high. This is related to the condition that many capillaries are formed along the suction path in the nitrogen during solidification.

The excellent gas permeability of the structure explains why solid nitrogen heats up and cools down so fast during suction. The rate of thermal processes and the temperature distribution across the thickness of the solid layer are in all cases determined by the mass rate of gas flow. From this standpoint, the absence of a steady-state temperature gradient along the layer height in our case (range C in Fig. 1) is explained by the absence of a mass flow through solid nitrogen. After the heater in the lower part was turned on, gas began to flow and a temperature gradient appeared accordingly.

The slower heating during injection of gaseous nitrogen at a 300°K temperature is explained as follows. The inrush of warm gas makes for a higher rate of heat supply to the top layer of solid nitrogen, where the gas cools down. This layer of solid nitrogen heats up fast and, after its temperature has reached the triple-point, there forms a liquid layer on top of it. Violet ejection of vapor from the bottom surface of the liquid into the vacuum space underneath results in the solidification of some layer of that liquid. The latter covers the access to the capillaries and thus impedes the passage to the lower part of the solid mass.

From this instant on, the heat transfer rate decreases (curve 3 in Fig. 2) and is determined by the rate of sublimation under vacuum at the bottom surface of the solid phase covering the capillaries. The rate of mass transfer is in this case determined according to the formula [10, 11]

$$\dot{m} = \rho_0 \sqrt{\frac{k \cdot T_3 \cdot N_A}{2\pi M}} \exp\left(-\frac{r_0}{kT_3}\right) F. \tag{5}$$

The mass flow rate is found from the heating rate of the solid phase:

$$\dot{m} = \frac{Q}{F r_s}, \tag{6}$$

with the cross section area F of the flask in our case equal to 62.8 cm^2.

When heating was effected by warm gaseous nitrogen (curve 3 in Fig. 2), the magnitude of the thermal influxes was $Q \approx 5.8$ W. The total surface area of sublimation can be estimated with the aid of expressions (5) and (6). Calculations show that this area amounted to 3-4% of the flask cross section area F.

Although the porosity of solid nitrogen exceeds 20%, a sublimation area of 3-4% is entirely feasible, since the capillaries evidently freeze at the areas of maximum resistance to gas flow, i.e., where they are narrowest.

When a pressure much below the triple-point level is maintained within the volume of solidifying gas, then the sublimating molecules move away from the solid surface. While vacuum is gradually lost during the heating process, however, part of the sublimating molecules returns to the solid surface as a result of collisions. This requires that the sublimation factor h

$$h = \left(1 - \frac{p}{p_3}\right) f$$

be introduced into Eq. (5) [10,11].

As the triple point is approached, the value of h decreases to zero. This explains why the heating rate is lowest under the liquid layer when the triple point is approached (curves 1, 3, 5 in Fig. 2).

When warm gaseous hydrogen was injected, the heating process followed a similar trend as in the preceding case. The heating rate under the liquid layer decreases appreciably (curve 5 in Fig. 2), however, because in this case the sublimation rate of nitrogen and the flow of gaseous nitrogen are governed by diffusion of its molecules through gaseous hydrogen.

Thus, in all cases of heat transfer through porous solid nitrogen the process rate is determined by the rate of mass transfer through the gaseous phase.

From this standpoint, the heat transfer rate ought to depend on the porosity of solid nitrogen in a highly nonlinear manner. In order to clarify this, we have studied the behavior of solid nitrogen with 20 ± 1%, 5 ± 1.5%, and 2.5 ± 1.5% porosities (corresponding to a 63°K temperature) during heating by throttling in a flask containing liquid nitrogen. According to Fig. 3, the heating rate decreases by almost two orders of magnitude as the porosity changes from 20 to 2.5%. Nevertheless, according to a comparison between curve 6 in Fig. 2 and curve 3 in Fig. 3, even with a 2.5-4.0% porosity the heat transfer is governed by the rate of mass transfer.

NOTATION

P	is the porosity;
ρ_L	is the density of liquid nitrogen at the triple-point temperature;
ρ_S	is the density of monolithic solid nitrogen;
r	is the heat of evaporation at the triple-point temperature;
r_S	is the heat of sublimation;
T_3	is the triple-point temperature;
T	is the temperature at any instant of time;
x	is the height coordinate in the solidifying gas layer;
Q	is the thermal flux;
τ	is the time;
T_0	is the initial temperature of solid nitrogen;
$\mu_n = (2n - 1)\pi/2$	are characteristic numbers;
R	is the height of solid nitrogen;
$Fo = a\tau/R^2$	is the Fourier number;
a	is the thermal diffusivity;
ρ_0	is the density of solid nitrogen obtained during suction;
$\bar{\rho} = \rho_0/\rho_S$	is the relative density of solid nitrogen;
$\dot{m}$	is the mass flow rate;
M	is the molecular weight;
k	is the Boltzmann constant;
N_A	is the Avogadro's number;
r_0	is the heat of sublimation per molecule;
F	is the surface area;
p_3	is the triple-point pressure;
p	is the pressure at any instant of time;
f	is the fraction of molecules returning after collision;

λ_{eff} is the effective thermal conductivity;
λ_S is the thermal conductivity of solid phase;
λ_G is the thermal conductivity of gaseous phase;
c_S is the specific heat of solid nitrogen at the saturation line;
q is the thermal flux density.

LITERATURE CITED

1. B. G. Lazarev, Yu. A. Milenko, and K. G. Breslavets, Dokl. Akad. Nauk SSSR, 178, No. 1 (1968).
2. A. Rouse-Ince, Low-Temperature Experimental Technique [Russian translation], Izd. Mir (1966).
3. A. F. Fowle, Advances in Cryogenic Engineering, 11 (1966).
4. V. F. Getmanets, R. S. Mikhal'chenko, and V. T. Arkhipov, Inzh. Fiz. Zh., 22, No. 4 (1972).
5. D. P. Lebedev, Abstr. Cand. Dissert., Moscow (1968).
6. A. A. Gukhman and A. Z. Volynets, Inzh. Fiz. Zh., 5, No. 5 (1968).
7. A. A. Gukhman and E. A. Ermakova, Zh. Tekh. Fiz., 23, No. 8 (1953).
8. G. N. Dul'nev and Z. V. Sigalova, Inzh. Fiz. Zh., 13, No. 5 (1967).
9. A. V. Lykov, Theory of Heat Conduction [in Russian], Izd. Vysshaya Shkola, Moscow (1967).
10. K. P. Shumskii, Vacuum Apparatus and Instruments for the Design of Chemical Apparatus [in Russian], Mashgiz, Moscow (1963).
11. K. P. Shumskii et al., Principles of Vacuum Sublimators Design [in Russian], Izd. Mashinostroenie, Moscow (1967).