FREEZING OF CRYOGENIC LIQUIDS DURING EVACUATION

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An experimental study has been made concerning the mechanism by which liquid nitrogen freezes during evacuation. The density of frozen gases produced by the evacuation method is estimated.

Frozen gases are now used more and more for widening the temperature range of low-temperature research [1-3]. The simplest method of producing them is by pumping a cryogenic liquid down to a pressure below its triple-point level. This method was used on a laboratory scale already in the last century [4]. Nevertheless the mechanism by which liquefied gases freeze during such an evacuation has remained almost completely unexplored. A few studies were concerned with the freezing of water under vacuum [5, 6]. The freezing characteristics of cryogenic liquids, however, may entail some specific features arising from the significant difference between their physical properties and those of water (different trends in the change of specific volume during phase transformation, very different heats of sublimation and triple-point pressures, etc.).

The object of this experimental study was to examine the freezing of liquid nitrogen during evacuation. Some of the tests were performed also with liquid hydrogen.

The test apparatus is shown schematically in Fig. 1. The freezing gases were collected in a Dewar glass flask 1 with a 3 liter capacity, inside a protective vessel 2 with liquid nitrogen. Vertical slots had been provided in the vessels for visual inspection. A vertical graduation scale on vessels 1 indicated the upper level of the liquid or the solid phase.

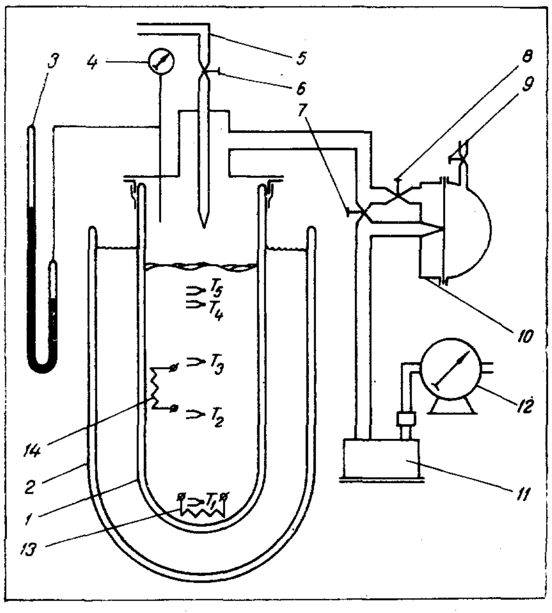

Fig. 1. Schematic diagram of the test apparatus.

Vessel 1 was evacuated by means of a vacuum pump 11 with a 6 liter/sec capacity. The evacuation rate was regulated and maintained by means of valves 7-9 and a membrane-type manostat 10. The flow rate of vapors pumped out of vessel 1 was measured with a drum-type gas meter 12.

The pressure in the vessel was measured with a spring vacuum manometer cathetometer 4 and a U-shaped mercury manometer 3 from which readings were taken with the aid of a cathetometer.

Liquid nitrogen was supplied through a thermally insulated transfer tubing 5 with a regulating valve 6.

Two heaters were installed inside vessel 1 opposite the sighting slot. One of the heaters (13) was placed in the lower part and the other heater (14) 150 mm high. Furthermore, differential copper–constantan thermocouples T_1–T_5 were mounted on tension-wire straps

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in vessel 1 at 7, 83, 143, 205, and 216 mm, respectively, above the lower heater. In order to improve the accuracy of measurements, one wire of each thermocouple ran horizontally for 10-15 mm from the wall and all the way to the exit from the vessel all leads were pasted onto a copper plate inside the solid nitrogen.

The test procedure was as follows. Liquid nitrogen at the temperature of 77°K was poured through the transfer tubing 5 into vessel 1 up to a 225-230 mm level. The temperature was then lowered to the triple-point level (~63°K) by evacuation. Evacuation of vessel 1 was effected through the manostat tubing 10. A constant vapor pressure was established in vessel 1, close to the triple-point level (~94 mm Hg). The thermal power supplied to vessel 1, about 1.0-1.5 W, was determined from the flow rate of evacuated vapor. When manostat 9 was turned off, evacuation continued through the bypass tubing. The upper level of the liquid was read on the scale. With the initial position of valve 7 fixed, the pressure in vessel 1 dropped below the triple-point level. During the freezing of liquid nitrogen, we measured periodically the temperature at the T_1-T_5 points (with a ±0.03°K precision), the pressure in vessel 1 (with a ±0.05 mm Hg precision), the volume of evacuated vapor, and the position of the crystallization front. Evacuation was discontinued after completion of the freezing process. A small portion of hot gaseous nitrogen was poured into vessel 1 for melting and leveling the upper surface of the solid phase. The height of this upper surface was then read on the scale. By means of the heater, the solid nitrogen was warmed up to the triple-point temperature and melted. After that, the level of the resulting liquid at triple-point temperature was also determined.

In some tests the layer of solid nitrogen forming over the sighting slot was quickly removed with the aid of the heater. In this way, it was possible to examine the inner structure of the solid phase.

Kinetics of the Process and Results of the Experiment. The freezing of gases during evacuation of the liquid proceeds in three stages: 1) cooling of the cryogenic liquid down to its triple-point temperature, 2) freezing the liquid phase at its triple-point temperature, and 3) cooling the frozen part below the triple-point temperature.

As part of the liquid boils, the remaining mass is made to cool down to its triple-point temperature. When this temperature is reached, there appears a solid film on the liquid surface. This film of solid nitrogen consists of crystals with a distinct macroscopic hexagonal symmetry and 10 mm long edges. It is to be noted that, unlike in the case of freezing water [5, 6], no subcooling of the liquid below its triple-point temperature takes place here before freezing.

The thickness of the solid phase increases further by way of dendrite formation, mainly along the junction of the original crystals. The growth of the intercrystalline boundaries inhibits evaporation from the liquid surface and, consequently, the pressure above the solid layer drops. Increasing pressure on the solid layer from below deforms it and breaks it away from the liquid surface, but the latter is then immediately covered with a new solid layer. This process may repeat many times. It is stimulated by a high evacuation rate in vessel 1 or by appreciable vapor formation as a result of heat applied to the liquid. The formation of several solid layers reduces the evacuation rate from the liquid surface and impedes their further breakaway. No repetitive breakaway will be observed, if the evacuation rate is made low at the beginning of the freezing process.

After layers have ceased to break away, the solid phase builds up from below. Adhesion of this layer to the vessel walls will then impede any movement of frozen gas. The upper level of the solid phase does evidently drop, as a result of sublimation during the freezing period.

As the thickness of frozen gas builds up, the crystallization front ceases to be flat and becomes bell shaped. The faster progression of the front at the vessel walls is, apparently, related to the presence of crystallization nuclei. Evacuation through the slot in the vessel wall may also have an effect. Owing to the shape of the crystallization front, the phase transformation at the wall occurs at a constant supply of liquid. For this reason, no pores are seen here.

The gas which freezes at the center of the vessel has a friable structure containing many macropores. Under the arched crystallization front there appear vapor bubbles – such bubbles do not appear during the crystallization of water [6]. The boundaries between bubbles and the liquid become covered with a solid film. After some time, the vapor escapes upward while pressing the films against the solid layer. At the crystallization front there form new vapor bubbles, etc. As a result of this process, the solid mass becomes a porous body perforated by a network of vertical capillaries.

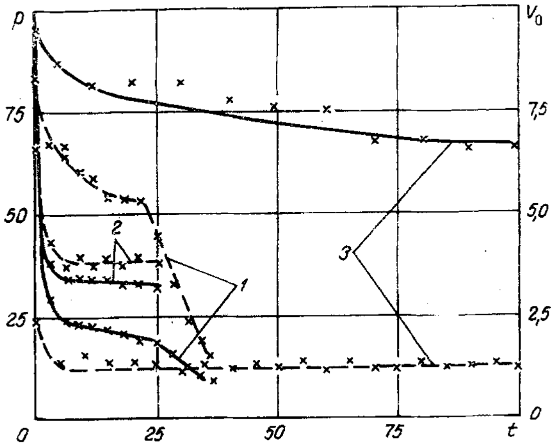

Fig. 2

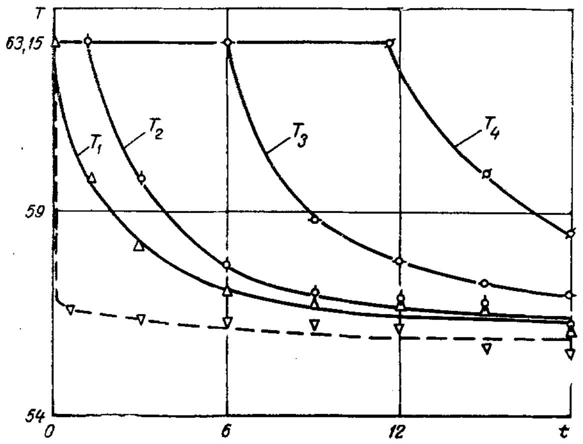

Fig. 3

Fig. 2. Vapor pressure (solid curve) and evacuation rate (dashed curve) as functions of time during the freezing process (p, mm Hg; V_0, nliter/min; t, min). Initial evacuation rate: 1) 8.5 nliter/min; 2) 6.5 nliter/min; 3) 2.5 nliter/min.

Fig. 3. Temperature (°K) as a function of time for a series of points in the solid phase. The dashed line corresponds to the saturated-vapor pressure above the frozen gas.

During freezing, as can be seen in Fig. 2, the rate V_0 at which vapor is evacuated from vessel 1 varies insignificantly (except during the initial period). With time, the reduction of pressure above the solid phase becomes insignificant too.

It is to be noted that at evacuation rates V_0 in the 100-500 nliter/h range, as in our tests, the rate at which the frozen gas layer builds up increases approximately as a linear function of time. It is difficult to locate the crystallization front accurately, however, because of its complex shape.

The graphs in Fig. 3 represent the temperature of solid nitrogen at points T_1-T_4, as a function of time. It is evident here that a passage of the crystallization front is associated with a sharp temperature jump, i.e., immediately after freezing there occurs a cooling of the just-formed solid phase down to the temperature of the frozen gas layer above. Later on the temperature of the solid phase drops slowly.

The temperature of the upper layer approaches the temperature which corresponds to the saturated-vapor pressure in vessel 1. First the temperature drop across the thickness of the frozen gas increases further only slightly. The main temperature drop is noted within the zone near the crystallization front. Later on, even though the total temperature drop increases with time, the temperature drop near the crystallization front decreases gradually.

As the crystallization process ends, the evacuation rate drops sharply (Fig. 2), with the pressure and the temperature also beginning to decrease fast (Figs. 2 and 3).

The density of solid nitrogen in these tests was within 75-80% of the crystal density (at the triple-point temperature) given in [7].

Mechanism of Crystallization. The freezing rate of liquefied gas is determined by the feasibility of carrying the heat of phase transformation away from the crystallization front. This can be effected in two ways: by heat conduction along the solid phase subcooled below the triple-point temperature or by evaporation of the liquid at the interphase boundary and escape of the vapor through capillaries in the solid phase.

As can be seen in Fig. 3, the temperature drop across the thickness of the solid phase may, to the first approximation, be assumed constant and equal to $\Delta T = T_{3p} - T_1$. As the crystallization front deepens, therefore, the amount of heat carried away by conduction along the solid phase must decrease continually. As a result, the rate at which the crystallization front progresses must decrease considerably with time.

This rate can possibly be constant, provided that the conductive heat transfer is effected through a narrow zone along the solid–liquid interface. From the condition of heat balance we obtain for the thickness of the interphase zone during crystallization:

TABLE 1. Relative Density, at the Triple Point, of Gases Frozen by the Evacuation Method and Fractions of the Liquid Evaporated in the Process

Substance	N_2	p-H_2	NH_3	Ne	CO	Ar	CH_4	O_2
x	0,11	0,12	0,19	0,16	0,11	0,16	0,1	0,054
$\bar{\rho}$	0,81	0,79	0,75	0,73	0,81	0,73	0,75	0,90

$$h_i \leqslant \frac{\varkappa \Delta T}{\rho_L \lambda \frac{dh}{dt}} .$$

Inserting the experimentally determined values for the temperature drop ΔT and for the velocity of the crystallization front dh/dt, we find that the thickness of the interphase zone does not exceed 0.3 mm.

The interphase zone moves deeper into the liquid and leaves above it a layer of frozen gas at a below the triple-point temperature; this layer being cooled by the sublimation of some of its part. For this reason, there are many capillaries formed within the solid phase in the direction of the evacuation and this ensures excellent gas permeability of such a structure. The interphase zone is evidently also not entirely impermeable, because vapor bubbles forming at its surface can periodically escape through it.

In this way, heat during crystallization is picked off mainly by the generation and escape of vapor directly at the crystallization front. Let us determine the bulk rate of the freezing process on the basis of such a model. In the analysis we will assume the volume of the final solid phase to be equal to the initial volume of the liquid phase at the triple-point temperature, inasmuch as the upper surface of the solid phase remains in a fixed position during freezing. We will also disregard the heat capacity of the frozen gas, considering that the latter is subcooled negligibly only (this is valid at low evacuation rates).

The mass of vapor $\rho_V V_0 dt$ evacuated during time dt is equal to the decrease in mass of that liquid volume $x\rho_L dv$ which has crystallized during this time:

$$\rho_V V_0 dt = x\rho_L dv. \tag{1}$$

After integration over the entire volume of the solid phase, we have

$$v = \frac{1}{x} \cdot \frac{\rho_V}{\rho_L} \int_0^t V_0(t)\, dt. \tag{2}$$

The value of the integral $\int_0^t V_0(t)dt$ gives the volume of vapor evacuated during the freezing process, which is measured directly with the gas meter. At a constant evacuation rate, we obtain for a cylindrical vessel

$$h = \frac{1}{x} \cdot \frac{\rho_V}{\rho_L} \cdot \frac{V_0}{F} t. \tag{3}$$

In the derivation of formulas (2) and (3), the fraction of vapor formed during the freezing process has been considered constant with time. This assumption is valid also when the subcooling is only slight, and it has been made earlier.

The value of x can be easily found by equating the quantity of heat which the vapor carries off during evacuation to the heat of solidification plus the heat supplied to the vessel:

$$xm_0 r = (1-x)\, m_0 \lambda + Q.$$

From this we have

$$x = \frac{\lambda + \frac{Q}{m_0}}{\lambda + r} . \tag{4}$$

From relations (3) and (4) we obtain for the position of the crystallization front at a given instant of time the following expression:

$$h = \frac{\lambda + r}{\lambda + \dfrac{Q}{m_0}} \cdot \frac{\rho_V}{\rho_L} \cdot \frac{V_0}{F} t. \qquad (5)$$

The tests have shown that relation (5) is in accord with reality. The insignificant decreases in the freezing rate as well as in the evacuation rate (Fig. 2) are evidence of porosity and gas permeability of the building up solid layer. The hydraulic resistance of this layer is much lower than that of the solid–liquid interface. The freezing rate remains constant, therefore, even though the crystallization zone becomes deeper.

From the equality of the frozen gas volume and the initial liquid volume we can easily find also the mean-over-the-volume density of the solid phase:

$$\rho_0 = (1 - x)\,\rho_L. \qquad (6)$$

Relative to the crystal density, the density of frozen gas is

$$\bar{\rho} = \frac{\rho_L}{\rho_S} \cdot \frac{r - \dfrac{Q}{m_0}}{r + \lambda}. \qquad (7)$$

For nitrogen not supplied with heat we have $\bar{\rho} = 0.81$, which agrees closely with the test data.

The values of relative density for various frozen gases are given in Table 1, along with the fraction of initial liquid mass evaporated during the freezing process. These values have been calculated from relations (4) and (7) for the condition Q = 0.

It follows from Table 1 that 10-20% of the initial liquid mass evaporates during freezing at the triple-point temperature, while the density of gases frozen by the evacuation method does not exceed 73-80% of the crystal density.

NOTATION

T	is the temperature coordinate;
T_{3p}	is the triple-point temperature;
h_i, ΔT_i	are the thickness of and temperature drop across the dense layer of the solid phase at the boundary with the liquid phase;
$\varkappa$	is the thermal conductivity of frozen gas;
ρ_L	is the density of liquid at the triple point;
λ	is the heat of solidification;
h	is the depth of the solid phase;
t	is the time;
dh/dt	is the velocity of the crystallization front;
ρ_V	is the density of vapor (gas) under normal conditions;
V_0	is the evacuation rate, measured for vapor under normal conditions;
x	is the weight portion of liquid evaporating during the freezing process;
m	is the mass;
v	is the volume;
t_f	is the freezing time;
r	is the heat of evaporation at the triple-point temperature;
m_0	is the initial mass of liquid at the triple-point temperature;
ρ_S	is the density of the crystal at the triple-point temperature;
ρ_0	is the mean-over-the-volume density of frozen gas;
$\bar{\rho} = \rho_0/\rho_S$	is the relative density of the frozen gas;
p	is the pressure;
F	is the cross section area of the vessel;
Q	is the quantity of heat supplied.

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