SUBLIMATION OF ICE UNDER VACUUM

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It is shown that the form of the sublimation process in which phase transformation takes place not from the geometric surface but in a certain layer of finite thickness is a stable one.

A whole series of phenomena observed in connection with the sublimation of ice – the porosity of the surface, the presence of a sublimation zone, etc. – are usually attributed to its nonuniform structure. We will show that these phenomena often have a more general origin associated with the penetration of energy into the thickness of the material. For this purpose we will examine the temperature field in a subliming specimen.

We assume that the attenuation of the energy flux can be described with sufficient accuracy by an exponential law. The relatively high values of the linear correlation coefficients (0.6-0.8), obtained from a statistical analysis of the experimental data of a number of authors [1, 2] for the integral energy flux, indicate that this assumption is quite acceptable for the purposes of a quantitative evaluation. Each method of energy supply can be characterized by a certain absorption coefficient k, which varies from almost zero (for example, in the case of a high-frequency energy supply for ice) to very large values (for a convective energy supply).

With the above assumption the distribution of the internal heat sources for a plate with a bilateral energy supply has the form:

$$M(x) = kq_0\{\exp[-k\rho(\xi - x)] + \exp[-k\rho(\xi + x)]\}. \tag{1}$$

Correspondingly (assuming that the temperature field corresponds to the steady state), the differential equation of heat conduction is written in the form:

$$\frac{\partial^2 T}{\partial x^2} + \frac{kq_0}{\lambda}\left\{\exp[-k\rho(\xi - x)] + \exp[-k\rho(\xi + x)]\right\} = 0. \tag{2}$$

We assume that sublimation and hence the removal of energy proceed from the geometric surface of the specimen. Then the boundary conditions take the form:

$$\begin{aligned} &\text{when} \quad x = 0 \quad \frac{\partial T}{\partial x} = 0, \\ &\text{when} \quad x = \xi \quad T = T_\xi. \end{aligned} \tag{3}$$

The solution is easily obtained. We have

$$T - T_\xi = \frac{q_0}{k\lambda}\{\exp(-2k\rho\xi) - \exp[k\rho(x - \xi)] - \exp[-k\rho(\xi + x)] + 1\}. \tag{4}$$

If the temperature at the center of the plate is given (for example, if the process is such that it does not exceed a certain value T_0), then we can give expression (4) the form:

$$\theta = \frac{T - T_\xi}{T_0 - T_\xi} = \frac{\operatorname{ch} k\rho x - \operatorname{ch} k\rho\xi}{1 - \operatorname{ch} k\rho\xi}. \tag{5}$$

Having an expression for the temperature field, we can easily determine the nature of the equilbrium pressure distribution in the specimen. If, in accordance with the Clapeyron–Clausius equation (assuming that

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TABLE 1. Mean Period (τ, min) of Existence of Excess Temperature at Center of Ice Specimen

Temperature difference $T_0 - T_\xi$	Pressure	High-frequency electric field		SHF electric field		"Bright" emitters	
		Plate 20×80×80	Cylinder d=15 h=60	Cylinder d=15 h=50	Cylinder d=10 h=50	Plate 15×80×80	Cylinder d=10 h=50
5°	266	9,5	3,3	9,6	3	0,6	3
	67	43	51,3	46,3	30,6	2,6	12
	13,3	>120	>120	115	80	11,6	9,6
	6,7	>120	>120	>120	69,6	13,6	14
10°	67	20,6	8,5	25,3	23,3	1,3	2,6
	13,3	38,6	41,3	23,6	4,6	0,5	—
	6,7	71	80	90,3	36,6	3,3	3,3
20°	13,3	7,3	9	—	—	—	0
	6,7	28,3	8,6	2	—	0,6	0,3

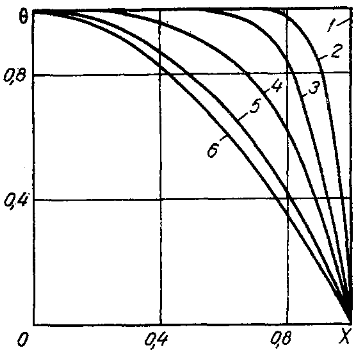

Fig. 1. Theoretical temperature distribution in half-plate: 1) $k\rho\xi \to \infty$; 2) $k\rho\xi = 20$; 3) 10; 4) 5; 5) 2; 6) $k\rho\xi \to 0$.

the heat of evaporation does not depend on temperature), we set

$$\ln P = A - \frac{B}{T}, \tag{6}$$

we find

$$P = \exp\left\{A - B\left[\frac{(T_0 - T_\xi)(\operatorname{ch} k\rho x - \operatorname{ch} k\rho\xi)}{1 - \operatorname{ch} k\rho\xi} + T_\xi\right]^{-1}\right\}. \tag{7}$$

For the temperature interval from 233 to 268°K A = 24.38 and B = 6236. Expressions for the temperature and pressure gradients are easily obtained by differentiating (5) and (7). The results of a calculation based on expression (5) are presented in Fig. 1.

It follows from the expressions obtained that under the conditions of evaporation of ice from the geometric surface of the specimen considerable temperature and pressure gradients, producing high stresses, must exist in the body. At a fixed value of the excess temperature, these gradients increase with increase in k. The pressure gradients, moreover, increase with increase in the surface temperature. The maximum temperature should be observed at the center of the plate.

We note that the principal results following from this reasoning remain valid even if a nonexponential expression is used in the approximation. Qualitatively, the results also apply to bodies of other shapes (cylinders, spheres, etc.).

The object of the experimental investigation was to establish the possibility of realizing a form of process in which evaporation takes place from the geometric surface of determining its duration. The experiment reduced to determining the temperature fields at different frequencies of the electromagnetic energy supply: 38-40 MHz (LD1-2 oscillator), 2375 ± 50 MHz ("Luch-58" oscillators), and in the infrared frequency spectrum with maximum wavelength near 1 μ created by an ordinary incadescent lamp with a filament temperature 2800°K ("bright emitters") and with a maximum wavelength near 6 μ created by a blackened metal plate at a temperature of 500°K ("dark emitters").

The temperatures in electric fields of high and superhigh frequencies were measured with special thermocouples designed to eliminate both local overheating of the material and self-heating of the thermocouple in the electromagnetic fields [3]. Seven thermocouples were available for measuring the temperatures in the high-frequency electric field for the plate and five for the cylinder. The distribution of the thermocouples (two or three thermocouples in the equipotential plane of the temperature and electric fields) made it possible to monitor the uniformity of the energy supply over the thickness of the plate. For preparing the ice samples we used a solution of the following composition: distilled water – 1000 g, sodium chloride – 10 g, potassium chloride – 0.5 g, calcium carbonate – 0.25 g, sodium bicarbonate – 0.5 g, and glucose – 2 g.

The use of this solution (employed in medicine as a physiological solution) leads to impregnation of the ice with unfrozen moisture. This makes it possible to supply the specimen with a sufficient amount of

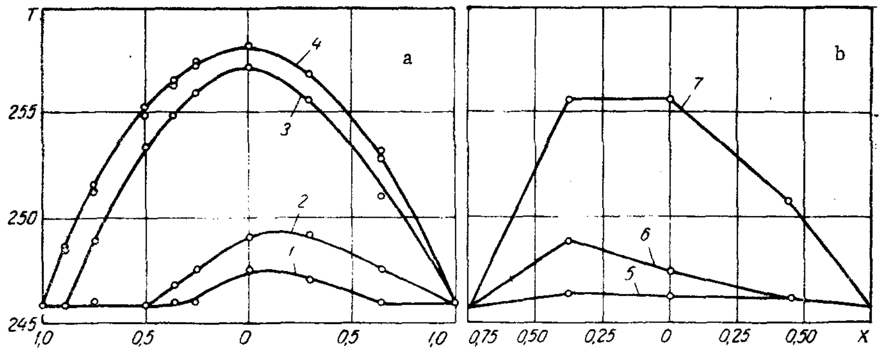

Fig. 2. Variation of temperature (°K) in plate (cm) with time: a) in high-frequency electric field; b) "bright" emitters [1) $\tau = 50$; 2) 40; 3) 30; 4) 10 and 15; 5) 9; 6) 7; 7) 4].

energy in a high- or superhigh-frequency electric field. At the same time, the composition of the experimental ice approaches the composition of the ice in products subjected to freeze drying. The ice was cooled in such a way as to reduce as far as possible the stresses created in the freezing process.

In the experiments with "dark" emitters it was not possible to achieve a significant temperature rise in the center of the specimen. With the other methods, however, this did prove possible.

Table 1 shows the mean of three measurements of the period of existence of an elevated temperature in the specimen of ice. The period of existence of the maximum temperature at the center of the specimen was determined as the interval during which the temperature fell to 10% of the original value.

We also investigated the variation of the temperature field in time. The nature of the temperature variation in the specimen during sublimation in a high-frequency electric field is shown with reference to one of the experiments in Fig. 2a. When bright emitters are used as the energy source, the temperature variation is usually more rapid (Fig. 2b).

As the experiments show, in the case of sublimation in a high-frequency electric field a parabolic distribution exists for a certain time.

The parabolic distribution corresponds to the theoretical distribution and is easily obtained from (2) on the assumption that the sources are uniformly distributed over the volume or from (5) as $k \to 0$.

The results show that under conditions of evaporation from the geometric surface the sublimation process is unstable and in the case of traditional methods of energy supply can exist only for a short time. Subsequently, approximately the same temperature is established over the thickness of the specimen. This is due to the formation within the ice of cavities, fissures and cracks that permit the escape of vapor from the interior of the specimen, i. e., to the presence of a certain sublimation zone of finite thickness. The depth of this zone is determined by the penetrating powder of the radiation. For example, in the case of a high-frequency energy supply, as soon as a uniform temperature is established in the specimen, this zone extends over its entire depth.

The formation of a sublimation zone may be accompanied by a number of phenomena, for example, supersonic jet flow effects and the spalling and separation of ice particles. In fact, in any cavity created by a temperature difference the vapor tries to escape into the surrounding medium, which may cause particles to break away. This conclusion is consistent with an earlier hypothesis [4, 5]. In freeze drying practice the ice specimens already have a certain porosity. However, this does not imply that the effects due to the existence of temperature and pressure gradients cease to operate: in this case they are observed in the individual continuous regions of the specimen.

In conclusion, we note that the investigator should not overlook the possibility of specific effects associated with the penetration of energy into the thickness of the material.

NOTATION

k is the absorption coefficient, $cm^{-1} \cdot g^{-1}$;
q is the surface energy density, W/cm^2;
ξ is the thickness of half-plate, cm;

T	is the temperature, °K;
T_0	is the temperature at center, °K;
T_ξ	is the surface temperature, °K;
λ	is the thermal conductivity, W/m · deg;
A, B	are the empirical coefficients;
P	is the pressure, N/m^2;
τ	is the time, min;
x	is the distance from center of plate, cm;
$X = x/\xi$	is the relative thickness;
ϑ	is the dimensionless temperature;
ρ	is the density, g;
d	is the diameter of the cylinder, mm;
h	is the height of the cylinder, mm.

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