HEAT AND MASS TRANSFER AND DURATION OF THE DESUBLIMATION OF WATER VAPOR IN VACUUM

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Certain features of the mechanism for the growth of the condensed phase during desublimation of water vapor in vacuum are examined. Approximate equations are found for the duration of water-vapor desublimation on a flat plate.

The development of highly efficient vacuum freezing condensers rests largely on physically justified ideas regarding the mechanism for the formation of a condensed system under these conditions.

1. Features of the Heat and Mass Transfer. The formation of ice from water vapor in vacuum below the triple point (desublimation) can be explained in the traditional manner on a P—t diagram (Fig. 1).

Spontaneous condensation (desublimation) sets in only if the temperature of the cooling surfaces lies above some curve CD for the given pressure [2, 3]. There is a region (between curves AB and CD) in which crystals do not form spontaneously (the metastable region); the boundary of this region is governed by the state of the condensation surface — whether there are adsorbed films, dust, ions, etc., on it. Near curve AB the desublimation occurs infinitely slowly.

The active formation of the condensed phase (ice) on the cooled surface can occur in two directions. A rapid change in the pressure, e.g., at t_V = const (line eF) leads to the rapid formation of a frost consisting of a thin, snowy, disperse dust, which forms a film over the entire condensation (desublimation) surface (Fig. 2a); this film subsequently becomes thicker [2].

The nature of the condensation (desublimation) at a constant pressure P_V (Fig. 1) depends on the rate of change of the temperature of the cooling surface (line kF). There is usually a localized spontaneous nucleation of the condensed phase in this process (Fig. 2b).

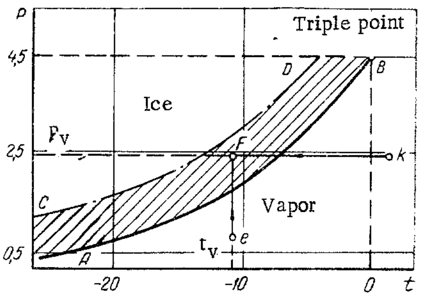

Fig. 1. Direction of the desublimation processes on the P—t diagram for water. The pressure P is in torr and the temperature t is Celsius degrees.

The first stage of the desublimation process — the nucleation of ice crystals and their growth — was studied in [2]. This stage is strongly influenced by the pressure P_S and the physical state of the surface. Experiments show that if the process follows line eF there is a certain probability for the homogeneous appearance of ice nuclei from the supersaturated vapor and the deposition of these nuclei on the working surface. If the process follows line kF, the appearance of nuclei from the supersaturated vapor can be heterogeneous; i.e., the nuclei of the new phase (ice) from at local centers, e.g., adsorbed water films on the working surface, as shown in Fig. 2b. In this case the shape of the crystals of the new phase is quite different.

Various investigators have observed alternating light and dark bands in a cross section of the ice and have offered various physical explanations for them. It was shown in [1] that if the temperature at the surface at which the phase transition occurs

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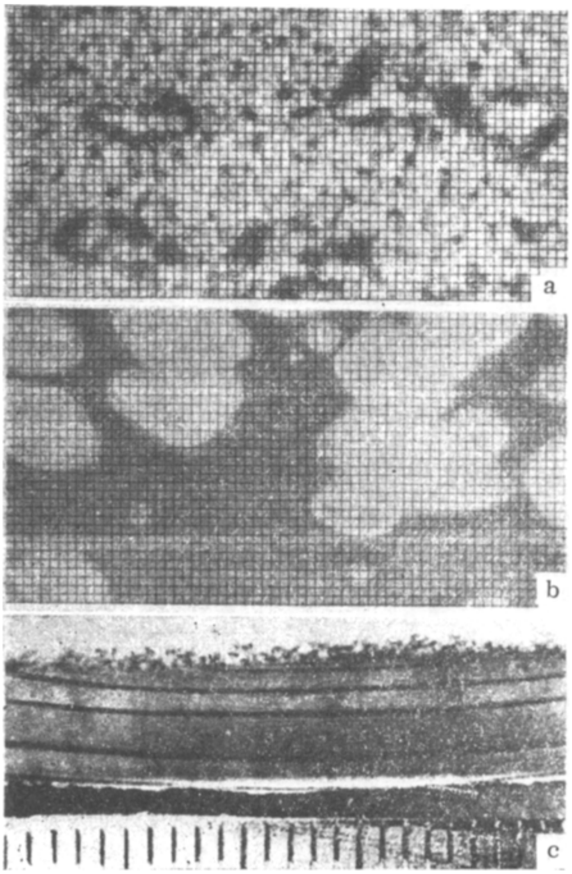

g. 2. Certain stages in the formation and state of the condensed phase as various parameters are changed. a) The pressure is changed (0.1-2 torr); b) the temperature of the working surface is changed (from −20 to −30°C, at P = 2 torr); c) there are periodic pressure changes. The distance between the lines in the grid is 10 μ.

(e.g., during the freezing of water) becomes variable, several thawed and frozen zones can form in an interstratified manner. This is probably the situation responsible for the formation of the dark bands in a section of the desublimed ice in the case in which the pressure in the condenser is raised, but not all the way to atmospheric pressure. The number of dark bands shows the number of times the pressure in the system was raised (Fig. 2c).

On the basis of these experiments on the desublimation of water vapor in vacuum [2] we can assume that the condensed phase forms in a two-stage mechanism: molecules from the gas phase initially condense into a movable film (an adsorbed film) and can either go from this film back to the gas phase or become attached to the surface (to a crystallization center).

Taking into account these arguments, and using the arguments of [8, 9], we can describe the condensation of water vapor in vacuum by

$$J = \alpha (2\pi m k T_v)^{-1/2} [P_S - P_d],$$

where α is a coefficient which is a measure of the condensation rate.

Numerical values of α could not be found from the experimental data and theory of [2, 3] for the case in which desublimed ice is formed in vacuum. Analysis of the experimental data of [2, 3] reveals that the condensation coefficient under the conditions of these experiments varied from 0.03 to 0.058 (over the pressure range 0.1-3 torr). These results agree well with the data of [6, 7].

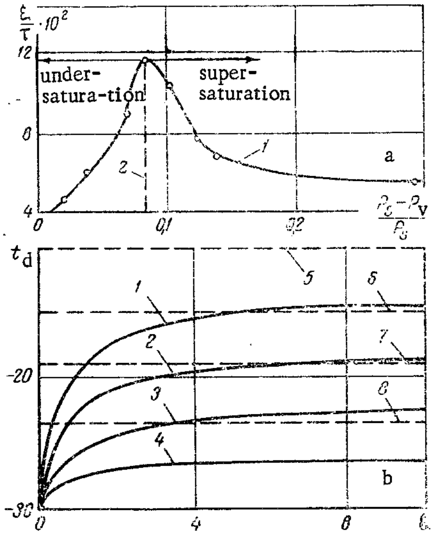

Fig. 3

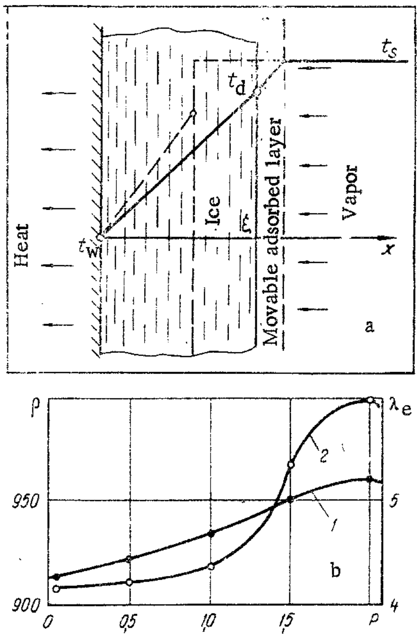

Fig. 4

Fig. 3. a) Ice growth rate as a function of the supersaturation of the incoming water vapor; b) temperature at the surface of the resulting ice layer as a function of the residual pressure and the thickness of the desublimed ice layer. a: 1) $t_v = -30°C$; 2) P = 2 torr; ξ/τ is given in millimeters per minute. b: 1) $t_{d\,P=2} = f(\xi)$; 2) $t_{d\,P=1} = f(\xi)$; 3) $t_{d\,P=0.5} = f(\xi)$; 4) $t_{d\,P=0.1} = f(\xi)$; 5) $t_{S\,P=2}$; 6) $t_{S\,P=1}$; 7) $t_{S\,P=0.5}$; 8) $t_{S\,P=0.1}$. Here t is in Celsius degrees and ξ is in millimeters ($P_v = P_d$).

Fig. 4. a) Physical model for the desublimation process; b) effective thermal conductivity and density of the desublimed ice as functions of the pressure during the growth of the ice layer. 1) $\rho = f(P)$ (for ice 10 mm thick); 2) $\lambda_e = f(P)$ (for ice thicknesses from 2 to 10 mm). Here ρ is in kilograms per cubic meter and λ is in watts per meter per Celsius degree.

The values of α which are much less than one during condensation in vacuum (desublimation) under these conditions can probably be explained by arguing that in this case there are both interactions of the molecules "escaping" from the adsorbed surface layer and collisions of these molecules in the vapor phase; only some of these molecules return to the desublimation surface. These arguments are confirmed by observations of the formation and growth of the eccentric ice profile on a tube under certain conditions in vacuum [2].

We believe that the external gasdynamic conditions during the formation of the condensed phase (the external problem of the desublimation process) require special thermal-physics research in order to determine α. Experiments as well as methodological studies in this field are very complicated.

Our experiments [2, 3] have shown that the rate at which the ice crystals grow in vacuum (for a constant wall temperature of the working surface, −30°C) depends strongly on the relative supersaturation $P_S - P_d/P_S$ (Fig. 3a) at the time at which the ice layer is 10 mm thick. The maximum rate for a given wall temperature (Fig. 3a) corresponds to a critical pressure of 2 torr.

The kinetics of the desublimation of water vapor in vacuum was analyzed in [2, 3] on the basis of the measured temperature fields in the condensed phase (the layer of ice which formed) and of the unsteady heat fluxes (the internal problem). The surface temperature of the resulting ice layer was also determined in these experiments as a function of the pressure in the sublimator and the thickness of the ice layer (Fig. 3b). A similar method for determining the surface temperature of a condensed phase was used in [4] to calculate the condensation coefficient.

2. Duration of the Desublimation Process.* The physical model for the desublimation (the internal

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*The studies in [2, 3] and the mathematical formulation of the problem refer to the condensation (desublimation of pure water vapor (without impurities of gases which do not condense).

problem) corresponding to these studies is illustrated in Fig. 4a.

According to this scheme the mathematical formulation of the conjugate problem (in which the first stage — the nucleation and growth of the crystals — is neglected) is

$$\frac{\partial T}{\partial \tau} = a \frac{\partial^2 T}{\partial x^2} \quad (0 \leqslant x \leqslant \xi). \tag{1}$$

The initial and boundary conditions are

$$T = T_{\mathrm{w}}; \quad x = 0; \quad \tau = 0; \tag{2}$$

$$T = T_{\mathrm{d}}(\xi); \quad x = \xi; \tag{3}$$

$$\lambda \left. \frac{\partial T(x, \tau)}{\partial x} \right|_{x=\xi-0} = \rho r_{\mathrm{d}} \frac{d\xi}{d\tau}. \tag{4}$$

The condition on the external mass transfer is

$$\rho \frac{d\xi}{d\tau} = \alpha \frac{[P_S - P_{\mathrm{d}}(\tau)]}{\sqrt{2\pi R T_{\mathrm{d}}(\tau)}}, \tag{5}$$

where P_S and $P_{\mathrm{d}}(\tau)$, the saturation vapor pressure above the ice and the pressure in the sublimator, are defined by [5]

$$\lg P_S = -2668{,}72/T_S + 10{,}43112; \tag{6}$$

$$\lg P_{\mathrm{d}}(\tau) = -2668{,}72/T_{\mathrm{d}}(\tau) + 10{,}43112.$$

Taking the experimental results of [2] into account, we choose a function which describes the time-evolving temperature field within the ice and which corresponds to Eq. (1) and to the initial and boundary conditions of problem (2)-(5) in the following nonlinear form:

$$T(x, \tau) = T_{\mathrm{w}} + (T_{\mathrm{d}}(\xi) - T_{\mathrm{w}}) \frac{x^n}{\xi}, \text{ where } n = n(\tau). \tag{7}$$

In this case, using (7), we can rewrite Eqs. (1) and (4) as*

$$\frac{d}{d\tau}\left[(T_{\mathrm{d}}(\xi) - T_{\mathrm{w}}) \frac{\xi}{n+1}\right] - (T_{\mathrm{d}}(\xi) - T_{\mathrm{w}}) \frac{d\xi}{d\tau} = \frac{an(T_{\mathrm{d}}(\xi) - T_{\mathrm{w}})}{\xi}; \tag{8}$$

$$\frac{\lambda_{\mathrm{e}} n(T_{\mathrm{d}}(\xi) - T_{\mathrm{w}})}{\xi} = \rho r_{\mathrm{d}} \frac{d\xi}{d\tau}. \tag{9}$$

Equations (5), (8), (9), and (2)-(4) constitute the conjugate problem of the desublimation of water vapor on a flat plate for computer solution. These equations are used to determine T_{d}, n, and ξ.

In this problem, in contrast with the standard problems of melting and freezing, the temperature at the ice front changes continuously as a function of the time. In accordance with [1] we adopt n = 1 in (7) as an approximate solution of the problem; then

$$T(x, \tau) = T_{\mathrm{w}} + (T_{\mathrm{d}}(\xi) - T_{\mathrm{w}}) \frac{x}{\xi}. \tag{10}$$

The temperature $T_{\mathrm{d}}(\xi)$ can be written

$$T_{\mathrm{d}}(\xi) = T_S - (T_S - T_{\mathrm{w}}) f(\xi). \tag{11}$$

In this case the function $f(\xi)$ must satisfy

$$\begin{gathered} f(\xi) = 1 \text{ as } \xi \to 0; \quad T_{\mathrm{d}}(0; \tau) = T_{\mathrm{w}}; \\ f(\xi) = 0 \text{ as } \xi \to \delta_{\mathrm{f}}; \quad x = \delta_{\mathrm{f}}; \quad T_{\mathrm{d}}(\delta_{\mathrm{f}}; \tau_{\mathrm{f}}) = T_S. \end{gathered} \tag{12}$$

Substituting (11) into (10), we find

$$T(x, \tau) = T_{\mathrm{w}} + \{(T_S - T_{\mathrm{w}})[1 - f(\xi)]\} \frac{x}{\xi}. \tag{13}$$

Substituting (13) into (9) we find, with n = 1,

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*Equation (1) is first written in integral form for this problem.

$$\tau = k_1 \int_0^{\bar{\xi}} \frac{\xi}{[1 - f(\xi)]} \, d\xi, \tag{14}$$

where $k_1 = \rho r_d / \lambda_e [T_S - T_W]$. On the basis of the experimental data (Fig. 3b) and their computer analysis we find

$$f(\xi) = \frac{A \exp(-a\xi) + B \exp(-b\xi) + C \exp(-c\xi)}{D}, \tag{15}$$

where A, B, C, D, a, b, c are constants specified desublimation conditions.

Substituting (15) into (14) we find

$$\tau = \frac{r_d \rho}{\lambda_e [T_S - T_w]} \int_0^{\bar{\xi}} \frac{\xi d\xi}{\left[1 - \frac{A \exp(-a\xi) + B \exp(-b\xi) + C \exp(-c\xi)}{D}\right]} = \frac{r_d \rho D}{\lambda_e [T_S - T_w]} \int_0^{\bar{\xi}} \Phi(\xi) \, d\xi. \tag{16}$$

The approximation of the experimental data on the function $\Phi(\xi)$ for the computer is

$$\Phi(\xi) \approx \tilde{a}\xi + \tilde{b}\xi^2, \tag{17}$$

where $\tilde{a}$ and $\tilde{b}$ are constants for given desublimation conditions.

Substituting (17) into (16), we finally find

$$\tau = \frac{r_d \rho D}{\lambda_e [T_S - T_w]} (a' \bar{\xi}^2 + b' \bar{\xi}^3). \tag{18}$$

Under the condition $D \approx T_S - T_W$, but $b' \bar{\xi}^3 \ll a' \bar{\xi}^2$, Eq. (18) becomes

$$\tau = 0{,}109 \frac{\rho r_d}{\lambda_e} \bar{\xi}^2, \tag{19}$$

where λ_e and ρ are the average effective thermal conductivity and the density of the desublimed ice, determined from Fig. 4b [2].

Equation (19) holds for a wall temperature of the working element down to about −30°C; this equation is also applicable over the following ranges: pressures of 3-0.1 torr, flow velocities of 1.2-10.7 m/sec for the low-density vapor, and ice thicknesses from 2 to 10 mm. Under these conditions Eq. (19) describes the duration of the desublimation of water vapor on a flat plate in vacuum within 10%. It is easy to show on the basis of (19) that for this problem we have $\xi = \beta\sqrt{\tau}$ where β = const. This results shows that this problem has similarities with the familiar Stefan problem of the freezing of soil [1].

The approximation found here, Eq. (19), can be used to seek new approximate analytic solutions of this conjugate problem.

NOTATION

m	is the mass of molecule;
T_W	is the wall temperature of the working surface;
T_S, t_S	are the saturation vapor temperature of the water vapor at pressure P_S;
T_d, t_d	are the surface temperature of the desublimed ice;
σ_f, τ_f	are the final thickness and time corresponding to the end of the formation of the ice film at temperature $T_d = T_S$;
a	is the thermal diffusivity of the desublimed ice;
ρ	is the ice density;
λ_e	is the effective thermal conductivity of the desublimed ice;
r_d	is the heat of desublimation (or sublimation);
ξ	is the coordinates of the front of the desublimed ice (the time-varying thickness of the ice layer).

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