ICE SUBLIMATION FROM FROZEN SALT SOLUTIONS

N. F. Bogomolov, A. Z. Volynets, and V. K. Safonov

The sublimation method of drying is finding ever wider application in scientific and technical fields. For example, one of the newest fields employing this method is cryochemical synthesis of inorganic materials, with sublimation dehydration as the basis of the process. Sublimation of ice from rapidly frozen salt solutions produces powders with a component distribution close to that existing in the solution. We will consider the problem of ice sublimation from salt solutions frozen in the form of a plate, cylinder, and sphere in a flow of noncondensing gas at a pressure of \(0.01 \leq P \leq 1.02\) bars. The noncondensing gas contains vapors of the subliming material at a partial pressure of \(p_f\). Comparison of theoretical and experimental data reveals completely satisfactory agreement. The mass output coefficient, which is usually determined experimentally for mass-exchange processes with phase transitions, can be found in a manner analogous to the heat-liberation coefficient for a volume content of noncondensing gas between 25 and 100%.

Experiments have revealed that in sublimation dehydration of various materials with porous structure the temperature difference between the phase-transition boundary and the heat-exchange medium is small [1]. This allows neglect of the convective component of heat transfer as compared to the heat of phase transition. Vapor transfer is accomplished not only by molecular diffusion, but also by a Stefan flow, which produces a change in the mass output coefficient \(\beta\). The effect of the material's porous structure on the diffusion process within the limits of the dehydrated zone is considered by means of an effective diffusion coefficient \(D = kD_0\), where \(D_0\) is the diffusion coefficient in a free volume and \(k\) is a proportionality coefficient dependent on the structure of the material. The following assumptions are also made: the vapor-gas mixture surrounding the subliming body is a two-component ideal gas; the temperature change at the phase-transition boundary is negligibly small; thermodiffusion and radiative heat transfer are absent.

In this case the basic equation of the problem has the form

\[
\frac{\partial p}{\partial \tau} + v \frac{\partial p}{\partial \xi} = (D/\xi^2) \left( \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial p}{\partial \xi} \right) \right) \quad (\tau > 0, \ \eta < \xi < \sigma) \tag{1}
\]

with boundary conditions

\[
p(\eta, \tau = \tau_0) = p_0; \tag{2}
\]

\[
-(D/RT) \frac{\partial p}{\partial \eta} + \frac{v p}{RT} = (\beta/RT)(p - p_f) \quad (\tau > 0, \ \xi = \eta); \tag{3}
\]

\[
-(D/RT) \frac{\partial p}{\partial \xi} + \frac{v p}{RT} = \sigma \eta p/\tau \quad (\tau > 0, \ \xi = \eta(\tau)), \tag{4}
\]

where \(v\) is the velocity of the Stefan flow, defined by the expression [2]

\[
v = -[D/(P - p)] \frac{\partial p}{\partial \xi}; \tag{5}
\]

where \(p\) is partial pressure of vapor; \(P\) is the total pressure of vapor-gas mixture; \(\sigma\) is the characteristic dimension of body from which ice sublimes (radius of sphere or cylinder, thickness of plate); \(\xi\) is the generalized coordinate; \(\eta\) is the position of the phase-transition boundary; \(\tau\) is the time; \(n\) is the form constant, equal to 0, 1, and 2 for a plate, cylinder, and sphere, respectively; \(R\) is the specific gas constant of vapor; \(p\) is the ice density; \(\eta\) is the volume porosity of material; \(T = (T_b + T_f)/2\) is the mean temperature of vapor-gas mix-
ture; the subscript b refers to conditions in the frozen zone, including the phase-transition boundary; subscript f refers to the flow of noncondensing gas.

The difficulty of solving this equation lies in its nonlinearity [in light of Eq. (5), Eq. (4)] and the fact that the mass output coefficient $\beta$ in Eq. (3) is not a constant, but is dependent in a complex fashion on total partial pressures of the vapor–gas mixture.

Usually, the value of the coefficient $\beta$ cannot be determined by analytic methods. In the majority of cases it is necessary to use various empirical equations. A characteristic example are the criterial equations recently obtained by generalization of a large amount of experimental data on vapor condensation from vapor–gas mixtures [3]:

$$\frac{Nu_D}{Nu_{D_0}} = 0.71 \varepsilon_g^{-0.6} \pi_p^{-0.4} \text{ at } 0.1 \leq \frac{\varepsilon_g}{\pi_p} \leq 1;$$

$$\frac{Nu_D}{Nu_{D_0}} = 0.71 \varepsilon_g^{0.6} \pi_p^{-0.1} \text{ at } 1 < \frac{\varepsilon_g}{\pi_p} < 3;$$

$$\frac{Nu_D}{Nu_{D_0}} = \varepsilon_g^{-1} \text{ at } \frac{\varepsilon_g}{\pi_p} > 3,$$

where $Nu_D = \beta I / D$ is the Nusselt diffusion number calculated by analogy to the Nusselt thermal number; $I$ is the characteristic dimension of body; $\pi_p = (p_f - p_w) / P$ is the dimensionless difference of vapor partial pressure in the flow and at the condensation surface; $\varepsilon_g = (P - p) / P$ is a dimensionless quantity characterizing the volume gas content in the vapor–gas mixture. It is obvious that use of $\beta$ from these equations creates practically insurmountable difficulty in solving the problem, which could be avoided if there were an expression for the mass output coefficient in which at a Lewis–Semenov number near unity the coefficient could be defined analogously to the heat-liberation coefficient. With this purpose in mind, the concept of corrected film thickness $\delta$ has been used [2, 4, 5]. The transfer mechanism in the film is considered not only molecular, but also convective. The density of matter flow transferred through the film in the direction perpendicular to the body surface is expressed by the well-known Stefan equation [2]

$$m = \pm (D_\delta (P/RT) \delta \ln [(P - p_w) / (P - p_f)]),$$

where the plus sign corresponds to the case of desublimation (condensation) of vapor, and the minus sign to the case of sublimation (evaporation); $p_{w}$ is partial vapor pressure at the body surface.

Since for the corrected film $\delta = D_\delta / \beta_\delta$, the Stefan equation is written in the form

$$m = \pm \beta_\delta (P/RT) \ln [(P - p_w) / (P - p_f)].$$

We will show that the quantity $\beta_\delta$ introduced in Eq. (9) is defined in a manner analogous to the heat-liberation coefficient and can replace the coefficient $\beta$ in the boundary conditions of Eq. (3). To do this, we write the matter flow density expressed by Eq. (9) in the form

$$m = \pm (\beta/RT)(p_f - p_w).$$