ICE SUBLIMATION FROM FROZEN SALT SOLUTIONS

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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 $0.01 \le P \le 1.02$ 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 β. 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

$$\partial p/\partial\tau + v\partial p/\partial\xi = (D/\xi^n)(\partial/\partial\xi)(\xi^n\partial p/\partial\xi) \quad (\tau>0,\ \eta \leqslant \xi \leqslant a) \tag{1}$$

with boundary conditions

$$p(\eta,\ \tau) = p_b; \tag{2}$$

$$-(D/RT)\partial p/\partial\xi + vp/RT = (\beta/RT)(p - p_f) \quad (\tau > 0,\ \xi = a); \tag{3}$$

$$-(D/RT)\partial p/\partial\xi + vp/RT = \sigma\rho^d\eta/d\tau \quad (\tau > 0,\ \xi = \eta(\tau)), \tag{4}$$

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

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

where p is partial pressure of vapor; P is the total pressure of vapor–gas mixture; a is the characteristic dimension of body from which ice sublimes (radius of sphere or cylinder, thickness of plate); ξ is the generalized coordinate; η is the position of the phase-transition boundary; τ 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; ρ is the ice density; σ is the volume porosity of material; $T = (T_b + T_f)/2$ is the mean temperature of vapor–gas mix-

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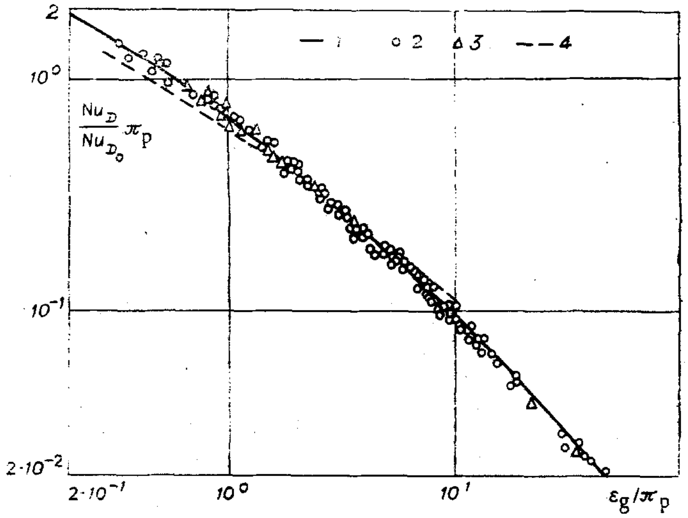

Fig. 1

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 β 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 β 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]:

$$\mathrm{Nu}_D/\mathrm{Nu}_{D_0} = 0.71\,\varepsilon_g^{-0.6}\pi_p^{-0.4} \quad \text{at} \quad 0.1 \leqslant \varepsilon_g/\pi_p \leqslant 1; \tag{6}$$

$$\mathrm{Nu}_D/\mathrm{Nu}_{D_0} = 0.71\,\varepsilon_g^{0.9}\pi_p^{-0.1} \quad \text{at} \quad 1 < \varepsilon_g/\pi_p < 3; \tag{7}$$

$$\mathrm{Nu}_D/\mathrm{Nu}_{D_0} = \varepsilon_g^{-1} \quad \text{at} \quad \varepsilon_g/\pi_p > 3, \tag{8}$$

where $\mathrm{Nu}_D = \beta l/D$ is the Nusselt diffusion number; Nu_{D_0} is the Nusselt diffusion number calculated by analogy to the Nusselt thermal number; l 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 β 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 δ 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]

$$m = \pm(D_0P/RT\delta)\ln[(P - p_w)/(P - p_f)],$$

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 $\delta = D_0/\beta_0$, the Stefan equation is written in the form

$$m = \pm\beta_0(P/RT)\ln[(P - p_w)/(P - p_f)]. \tag{9}$$

We will show that the quantity β_0 introduced in Eq. (9) is defined in a manner analogous to the heat-liberation coefficient and can replace the coefficient β in the boundary conditions of Eq. (3). To do this, we write the matter flow density expressed by Eq. (9) in the form

$$m = \pm(\beta/RT)(p_f - p_w). \tag{10}$$

Comparison of Eqs. (9) and (10) gives

$$\beta/\beta_0 \equiv \mathrm{Nu}_D/\mathrm{Nu}_{D_0} = \pm [P/(p_f - p_w)] \ln [(P - p_w)/(P - p_f)]$$

or, in the notation used in Eqs. (6)-(8) we may write

$$\mathrm{Nu}_D/\mathrm{Nu}_{D_0} = \pm (1/\pi_p) \ln (1 + \pi_p/\varepsilon_{gf}). \tag{11}$$

The values of $\mathrm{Nu}_D/\mathrm{Nu}_{D_0}$ are presented in Fig. 1: curve 1 corresponds to Eq. (11) of the present study (the same result is given by Eqs. (6)-(8) of [3]); curve 2 shows experimental data of [3]; curve 3, data of [6]; curve 4, equations of [7].

The good agreement of the calculated results with experimental data is justification for the conclusion that the mass output coefficient β_0 can be calculated with sufficient accuracy by analogy with the heat-liberation coefficient, and Eq. (9) can be used in place of the right side of Eq. (3). Moreover, instead of the separate equations (6)-(8), it will be convenient to use the single equation (11) in the range $\varepsilon_{gf}/\pi_p \geq 0.2$. It should be noted that with a small difference between partial pressures at the body surface and in the flow, i.e., when $\pi_p/\varepsilon_{gf} \ll 1$, Eq. (8) can be derived from Eq. (11) as a special case by retaining the first term in the expansion of the logarithm in a series.

The conclusion arrived at in considering the mass output coefficient permits writing boundary condition (3) in the form

$$-(D/RT)\partial p/\partial \xi + vp/RT = -\beta_0 (P/RT) \ln [(P - p)/(P - p_f)]. \tag{12}$$

In order to eliminate the square of the first derivative in Eq. (1) a new variable is introduced (Stefan substitution),

$$\varphi = \ln [(P - p)/(P - p_f)].$$

For the new variable, basic equation (1) and the boundary conditions (2), (12), (4) take the form

$$\partial\varphi/\partial\tau = (D/\xi^n)(\partial/\partial\xi)(\xi^n \partial\varphi/\partial\xi) \quad (\tau > 0,\ \eta \leqslant \xi \leqslant a); \tag{13}$$

$$\varphi(\eta, \tau) = \varphi_b; \tag{14}$$

$$D\partial\varphi/\partial\xi = -\beta_0\varphi \quad (\tau > 0,\ \xi = a); \tag{15}$$

$$DP\partial\varphi/\partial\xi = RT\sigma\rho d\eta/d\tau \quad (\tau > 0,\ \xi = \eta(\tau)), \tag{16}$$

where $\varphi_b = \ln [(P - p_b)/(P - p_f)]$.

Since the relaxation time of the partial vapor pressure field in the dehydrated zone is significantly less than the time for advancement of the phase-transition boundary, the derivative $\partial\varphi/\partial\tau$ may be omitted in Eq. (13), and the time can be found from Eq. (16). In this case solution of the homogeneous equation

$$(D/\xi^n)(d/d\xi)(\xi^n d\varphi/d\xi) = 0$$

with boundary conditions (14), (15) gives

$$\varphi = \varphi_b [(1 - n)D/a^n + \beta_0(a^{1-n} - \xi^{1-n})]/[(1 - n)D/a^n + \beta_0(a^{1-n} - \eta^{1-n})] \text{ for a plate and sphere;}$$

$$\varphi = \varphi_b \frac{1/\mathrm{Bi}_{D_0} + \ln (a/\xi)}{1/\mathrm{Bi}_{D_0} + \ln (a/\eta)} \quad \text{for a cylinder,}$$

where $\mathrm{Bi}_{D_0} = \beta_0 a/D$ is the Biot diffusion number.

Then integration of Eq. (16) allows us to find an expression for the total time for sublimation dehydration of salt solutions frozen in the form of a plate, cylinder, or sphere:

$$\tau = \frac{a^2 RT\sigma\rho}{(n + 1)\, DP \ln [(P - p_f)/(P - p_b)]} (1/\mathrm{Bi}_{D_0} + 1/2). \tag{17}$$

It should be kept in mind that in using Eq. (17) to calculate sublimation time it is first necessary to determine the partial vapor pressure value at the phase-transition boundary (p_b) from the thermal balance equation

$$\lambda(T_f - T_b) = [2PDr/R(T_f + T_b)] \ln [(P - p_f)/(P - p_b)],$$

where λ is the effective thermal-conductivity coefficient of the dehydrated zone; r is the heat of phase transition (sublimation); p_b and T_b are related by the Clapeyron–Clausius equation.

TABLE 1

$a \cdot 10^3$, m			6		3		0,5	0,2
			τ, sec					
			Results					
T, °K	P, Pa	ω, m/sec	theory	experiment	theory	experiment	theory	theory
268	1333,2	0,52	897	990	224	—	6,2	1.00
	6666,0		2899	3100	725	800	20,1	3,00
	15998,4		5443	5670	1361	1450	37,8	6,00
	102389,8		24081	25530	6020	6600	167,0	26,80
258	1333,2	0,52	2442	2670	611	680	17,0	2,70
	6666,0		7359	7980	1590	1710	51,1	8.00
	15998,4		15013	16130	3753	4130	104,2	16,70
	102389,8		59781	62170	14945	16080	415,1	66,40
268	1333,2	1,34	627	690	157	—	4.3	0,70
	6666,0		2201	2410	550	610	15,3	2.40
	15998,4		4352	4710	1088	1210	30,2	4,80
	102389,8		21287	21820	5322	5950	147,8	23,60
258	1333,2	1,34	1714	1840	429	480	11.9	1,90
	6666,0		5613	6250	1403	1520	39,0	6,20
	15998,4		12048	13100	3012	3260	83,6	13,30
	102389,8		52944	55490	13236	14190	367,6	58,80
268	1333.2	3,00	480	530	120	—	3.3	0,53
	6666,0		1821	2010	455	510	12.6	2.00
	15998,4		3755	4060	939	1100	26,0	4.10
	102389,8		19724	20730	4931	5540	137.0	21.90
258	1333,2	3,00	1315	1450	329	370	9.1	1.46
	6666.0		4653	5100	1163	1270	32.6	5.10
	15998,4		10429	11080	2607	2830	72,4	11.50
	102389.8		49192	50420	12298	12980	341.6	54.60
268	1333,2	5,00	412	450	103	—	2.9	0.46
	6666,0		1646	1780	412	440	11.4	1.80
	15998.4		3484	3700	871	1000	24.2	3.90
	102389,8		19025	19870	4756	5180	132.1	21.10
258	1333.2	5,00	1132	1250	283	340	7.1	1,20
	6666.0		4222	4530	1056	1180	29,3	4.70
	15998,4		9698	10480	2424	2570	67.3	10.80
	102389.8		47524	48570	11881	12830	330.0	52.80

Experiments were performed on sublimation dehydration of spherical granules obtained by freezing aqueous solutions of Mohr's salt in liquid nitrogen. Initial solution concentration was 14.7%. The experiments were performed in the following manner. Several granules were placed on a screen which served as the pan of a spring-type microscale installed in the experimental chamber. A draft of air at controlled velocity and pressure was passed over the granules. The air was dried in a zeolite column and cooled to the desired temperature in a thermostatic chamber connected to a cooler before entry into the experimental chamber. The scale indicator position was determined with a cathetometer. Dehydration was continued until there was no change of specimen weight with time. The porosity of the dehydrated material was determined from the weight difference before and after dehydration, and the known granule volume.

Drying time was calculated with Eq. (17) for the given experimental conditions. It was assumed that $p_f = 0$ in the calculations. Porosity was 0.85. The mass output coefficient β_0 entering into the Biot diffusion number was calculated by analogy with the heat-liberation coefficient for forced vapor flow [8]:

$$\mathrm{Nu} = 2 + 0.03\,\mathrm{Pr}^{0.33}\,\mathrm{Re}^{0.54} + 0.35\,\mathrm{Pr}^{0.36}\,\mathrm{Re}^{0.58}.$$

Results of the computation and experimental data are presented in Table 1. The completely satisfactory agreement between experiment and theory testifies to the correctness of the model chosen for the process and to the validity of the assumptions made in formulating the problem.

Equation (17) and the experimental data allow several conclusions as to the effects of various parameters on the duration of the sublimation dehydration process. For example, increase in vapor–gas mixture flow velocity leads to reduction in drying time down to the point where $1/\mathrm{Bi}_{D_0} << 1/2$. However, the theoretical and experimental data show that increase in flow velocity above 5 m/sec is not expedient.

Drying time is decreased by increase in solvent partial vapor pressure on the phase-transition boundary and by reduction to a minimum of the content of these vapors in the noncondensing gas ($p_f = 0$). This can be achieved by selection of a solvent with the highest partial pressure value at the chosen process temperature, or by increase in the temperature of the subliming body for a given solvent. In the latter case a limitation exists – the eutectic temperature of the frozen salt solution.

The binary diffusion coefficient proves to have a significant effect on the duration of sublimation dehydration. In particular, the dehydration time is decreased upon increase in the diffusion coefficient, which can be achieved by reduction in total pressure in the sublimator and selection of a corresponding solvent and noncondensing gas. It is desirable to use methane, hydrogen, or helium for the gas. As was reported in [9] and other studies, upon replacement of air by helium as the noncondensing gas, the duration of the dehydration process is decreased by a factor of more than three (with all other conditions equal).

In conclusion, we note that in preparation of materials with small pore dimensions (of the molecular sieve type), atmospheric sublimation drying is of great interest. In this case, for the majority of frozen solvents the partial vapor pressure is much less than atmospheric pressure. Then, preserving the first term in the expansion of the logarithm in the series, from Eq. (17) at high flow velocities for the dry noncondensing gas we obtain

$$\tau = a^2 RT\sigma\rho/2D(n+1)p_l.$$

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