STABILITY OF THE PHASE-TRANSITION SURFACE IN VACUUM DRYING

A. Z. Volynets, A. V. Rozhdestvenskii, and Yu. M. Gavrilov

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A criterion is proposed and stability conditions are defined for the phase-transition surface in the sublimation drying of solid or granulated materials supplied with heat by radiation and conduction.

Proper organization of sublimation drying is important in the sublimation treatment of organic and inorganic materials.

Traditional models are based on the presence of a stable one-dimensional transition front [1, 2], but these are inadequate, since they do not reflect the effects of deviations in conditions at the boundary or the structure of the material. Quite recently, an approach has been proposed that incorporates these deviations related to production conditions [3]. However, inhomogeneities may arise without dependence on external factors, since there may be instability arising from the physical nature of the process.

Possible instability in drying has been pointed out in [4]; a stability criterion was derived for a planar sublimation front under conditions of conductive heat input through a solid frozen layer. However, one cannot make direct use of the results of [4] to examine real processes because the proposed stability criterion contains a certain quantity Δx characterizing the extent of the initial fluctuations, whose choice is essentially arbitrary. Instead, the stability criterion for a planar front may be taken as

$$\frac{d}{dh}\left(\frac{dh}{d\tau}\right)=\frac{dv}{dh}, \tag{1}$$

which defines the change in the rate of advance for the sublimation front as it penetrates into the specimen; some conclusions can be drawn from this on the behavior of the phase boundary. Under real conditions, there are always geometrical fluctuations in the form of pits, cracks, and so on at the transition surface. If $dv/dh > 0$, the speed in a pit will be greater than that of the front itself, so any fluctuation will grow, which increases the unevenness. Conversely, if $dv/dh < 0$, fluctuations are damped out and the one-dimensional front is restored. Then the stability condition may be put as follows: $dv/dh > 0$ for an unstable front and $dv/dh < 0$ for a stable one, with $dv/dh = 0$ indefinite (passive front). In other words, accelerated advance corresponds to instability and vice versa. Under passive conditions, any unevenness in the structure does not die out or develop during sublimation because the temperature pattern in the frozen material remains one-dimensional on random change in the phase boundary relief.

Practical interest attaches to stability for solid and granulated materials, where simple models are used to examine the stability for the main energy input methods. We restrict consideration to planar specimens.

1. Conductive Heat Input to a Frozen Solid Layer (Fig. 1a). In the quasistationary approximation, where the thermophysical properties are constant and one neglects the phase resistance [5], we write the equation for the speed of the front as

$$\frac{dh}{d\tau}=\frac{(T_{\mathrm{h}}-T_{\mathrm{e}})\lambda_{\mathrm{f}}}{(H-h)L\gamma\rho_{\mathrm{i}}}. \tag{2}$$

The temperature at the phase boundary is given by

$$\frac{(T_{\mathrm{h}}-T_{\mathrm{e}})\lambda_{\mathrm{f}}}{(H-h)L}=\frac{(P_{\mathrm{e}}-P_{\mathrm{in}})\varkappa}{h}. \tag{3}$$

Simple steps then give the following equation for the stability criterion:

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$$\frac{dv}{dh}=\frac{(T_h-T_e)\lambda_f}{(H-h)^2L}\left\{1-\left(1+\frac{H-h}{h}\right)\left[1+\left(\frac{H-h}{h}\right)\frac{\varkappa L}{\lambda_f}\frac{dP_e}{dT_e}\right]^{-1}\right\}. \quad (4)$$

The sign of this is determined by

$$\xi_{cl}=\frac{\varkappa L}{\lambda_f}\frac{dP_e}{dT_e}. \quad (5)$$

Then for $\xi_{cl} > 1$ we have accelerated advance, for $\xi_{cl} < 1$ retarded, and for $\xi_{cl} = 1$ uniform, so the type of front movement is defined.

This ξ differs from the criterion of [4] in that it contains only quantities that in general can be determined quite reliably.

2. Conductive Input to a Frozen Granulated Material (Fig. 1b). The equations for the front speed and temperature at the phase boundary are

$$\frac{dh}{d\tau}=\frac{(T_h-T_e)\lambda_d}{hL\gamma\rho_i}, \quad (6)$$

$$\frac{(T_h-T_e)\lambda_d}{hL}=\frac{(P_e-P_{in})\varkappa}{H-h}. \quad (7)$$

Similar transformations give

$$\frac{dv}{dh}=-\frac{(T_h-T_e)\lambda_d}{h^2L}\left\{1-\left(1+\frac{h}{H-h}\right)\left[1+\left(\frac{h}{H-h}\right)\frac{\varkappa L}{\lambda_d}\frac{dP_e}{dT_e}\right]^{-1}\right\}. \quad (8)$$

We get the stability condition in the same form as for a solid material: $\xi_g = (\kappa L/\lambda_d)(dP_e/dT_e)$, but here stability occurs for $\xi_g > 1$ and instability for $\xi_g < 1$.

These simple models do not reduce the generality of the results. For example, if one incorporates the thermal resistance of the vapor layer between the subliming material and the heat-supplying surface, (2) becomes

$$\frac{dh}{d\tau}=\frac{(T_h-T_e)\lambda_f}{(H+\Delta h-h)L\gamma\rho_i}, \quad (9)$$

where Δh is the thickness of the frozen material whose thermal resistance is equal to that of the vapor gap. Here the temperature at the thickness $H + \Delta h$ may be considered as the temperature of the heat-supplying surface. The stability condition is clearly not altered. One can also show that the general structure of the stability condition persists for one-dimensional patterns in cylindrical and spherical coordinates.

3. Radiative Input to a Solid (Granulated) Frozen Material (Fig. 1c). The equations for the front speed and temperature at the boundary take the form

$$\frac{dh}{d\tau}=\frac{(T_h-T_e)\lambda_d}{hL\gamma\rho_d}, \quad (10)$$

$$\frac{(T_h-T_d)\lambda_e}{hL}=\frac{(P_e-P_{in})\varkappa}{h}. \quad (11)$$

We see that $T_h - T_e$ is independent of h, which enables us to find the stability condition directly by differentiating (1) with respect to h term by term:

$$\frac{dv}{dh}=-\frac{(T_h-T_e)\lambda_d}{h^2L\gamma\rho_i}<0. \quad (12)$$

This shows that the front always remain stable here.

These results can be given a clear physical interpretation. Consider a depression arising by fluctuation. The sense of development (increase or decrease) is dependent on the relation between the rates of approach to the heating surface for the boundary of the depression and for the planar front. The reason for the front advancing, which determines the speed, is the local temperature gradient, which in turn is influenced by two factors opposite in sense. On the one hand, a recess in the material reduces the distance to the heating surface, and so it increases the temperature gradient. On the other hand, it increases the distance that the vapor must travel to escape to the environment, which raises the temperature of the interface (because of increase in the pressure needed for the vapor to escape) and thus reduces the

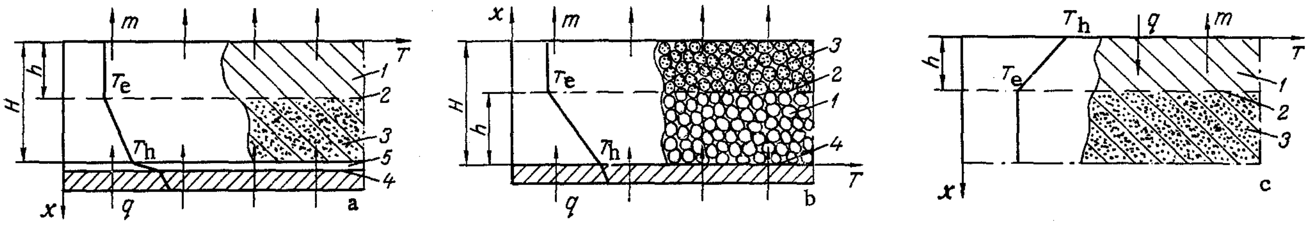

Fig. 1. Physical models for sublimation drying (P_{in} = const): a, c) continuous material; b) granulated; a, b) conductive input; c) radiative; 1) dried material; 2) transition surface; 3) frozen material; 4) heating surface; 5) gap.

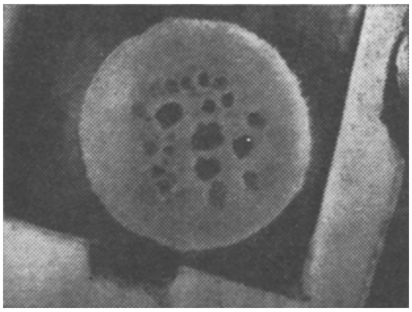

Fig. 2. Surface of pure ice with unstable sublimation front.

temperature gradient. The relation between the two trends determines the course. Clearly, the sublimation front will not alter in shape if the temperature pattern remains unaltered, which requires a balance between the fluxes of outgoing and incoming vapor. One thus should have

$$|\varkappa \operatorname{grad} P_e| = \left| \frac{\lambda}{L} \operatorname{grad} T_e \right|, \tag{13}$$

and so

$$\xi = \frac{\varkappa L}{\lambda} \frac{dP_e}{dT_e} = 1. \tag{14}$$

If this equation is violated in either direction, the front geometry should alter.

Data have been presented on the stability in drying granules with conductive input [6], and the same for solid or granulated material with radiative heating [7]. The front remains stable almost throughout the entire range of working conditions for a granulated material with conductive input [6]. Our theoretical results also indicate this. Our forecasts for radiative heating indicate that a planar front always persists. Similar conclusions have been drawn in [7] for drying organic materials. Much less is known about solid frozen layers with conductive input, although here the stability is of particular interest. Theoretical arguments show that the stability limit is set by $\xi = 1$; the process may clearly switch from stable to unstable or vice versa in response to minor changes in pressure or in the temperature at the heating surface, or else in h. A special study was made of the front for various ξ to check the theoretical results for this case.

The main parts of the apparatus were as follows: vacuum working chamber, vacuum pump, and set of measuring instruments. The working chamber was made of stainless steel as a cube of side 100 mm, with the side faces fitted with windows, and the base having two copper current leads of diameter 10 mm. The leads were connected to a strip of steel foil, which was firmly pressed onto a polished copper plate, which was heated on passing the current through the foil, where the high conductivity of copper meant that there was almost a uniform temperature distribution in the plate.

We examined thesublimation of pure ice and of a frozen solution of Mohr's salt, which was taken as a model substance. About 0.1% cobalt chloride was introduced into the solutions to indicate the phase boundary.

The solutions were frozen in a refrigerator at 263°K as disks of diameter 30 mm and thickness 10 mm.

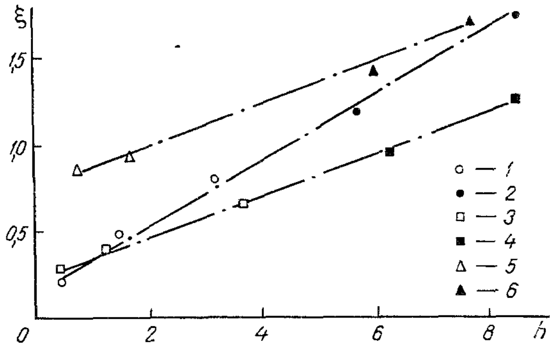

Fig. 3

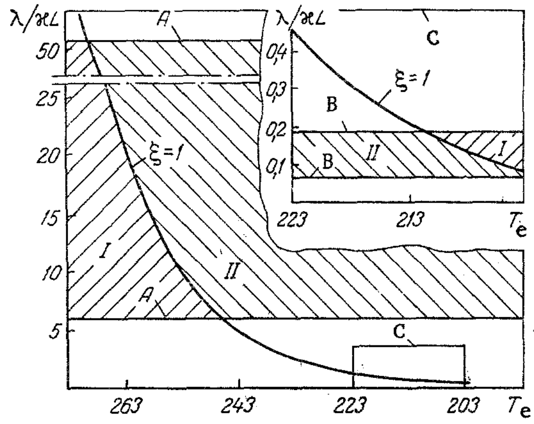

Fig. 4

Fig. 3. Values of ξ and observed boundary state in relation to depth of dried layer for a frozen aqueous solution of Mohr's salt ($c = 10\%$, $\kappa = 50 \cdot 10^{-9}$ kg/sec•m•Pa): 1, 2) $P_{in} = 26.6$ Pa, $T_h = 268$°K; 3, 4) 26.6 and 263; 5, 6) 133.3 and 268 (1, 3, and 5 planar front; 2, 4, and 6 zonal sublimation); h in 10^{-3} m.

Fig. 4. Boundaries to the regions of unstable sublimation front (I) and stable front (II) on conductive heat input for characteristic commercial materials (solid A—A, granulated B—B, C part of graph); $\lambda/\kappa L$ in Pa/K and T_e in °K.

One of the definitive factors is the surface temperature adjoining the conducting plate. This is very difficult to measure because of the uncertainty over the contact resistance. Therefore, T_h was determined directly. For this purpose, two thermocouples of diameter 100 μm were frozen into each specimen. The junctions were not more than 1 mm from the lower surface of the disk, while the leads were approximately in a plane of constant temperature. The temperature was measured with a KSP-4 potentiometer.

The specimens were dried at various external pressures and surface temperatures; a specimen was placed on the polished copper plate, where a set pressure was provided by the vacuum pump and adjustable leak. The set temperature at the lower surface was maintained by adjusting the heater power. At various times, the partially sublimed specimen was removed from the chamber and broken along a diameter. The cross section was examined with a KM-8 cathetometer. The cobalt chloride changes in color on drying and gives a clear indication of the boundary between the dried and frozen layers, thus indicating whether there is zonal sublimation. The thickness of the sublimated layer was also determined with the cathetometer.

The main conclusions are as follows.

For pure ice ($\kappa \to \infty$, $\xi \to \infty$), the front is unstable throughout the working parameter range, in complete agreement with the theoretical discussion (Fig. 2).

Figure 3 shows results obtained with the solutions of Mohr's salts at various stages. An unstable front occurs for $\xi > 1$, which confirms the above argument.

A solid layer with conductive input can thus be discussed in terms of the above stability condition, which gives a reliable prediction.

The importance of dv/dh is not exhausted by the stability. A passive front behaves in a fashion not explicitly determined by the macroscopic factors ($\xi = 1$) and is very sensitive to others. As dv/dh approaches zero, the fine structure of the material begins to become decisive (composition inhomogeneity, or spatial or energy inhomogeneities).

Stability aspects must be considered directly in designing such apparatus and defining optimum working conditions. For example, drying with conductive input can be conducted under conditions corresponding to the unstable state, in which case the total drying time will be increased substantially by comparison with the calculated values, since the drying rates (completion of drying) for the dispersed frozen parts are usually very low on account of the low thermal conductivity of the dried zone. One can choose parameters eliminating this from Fig. 4, which gives the results on the stability for solid and granulated materials as used in industry and employed here with conductive input.

With an accuracy sufficient for one to use the diagram, one can take T_e for a solid material as equal to T_h given by the condition. The maximum $T_h - T_e$ (the difference over the thickness of the frozen layer) is very small (about 2-3°K) by comparison with T_h because of the comparatively high conductivity of the frozen layer. Therefore, one can usually take T_h as the abscissa of the desired point on using the diagram.

The diagram shows regions corresponding to the parameters realized in industry. A solid material used at temperatures characteristic of industrial plant (233-273°K) may show stable or unstable fronts. For a granulated material, on the other hand, the instability region is narrow and lies outside the industrial range (213°K and below). Therefore, it is better to process the material in granulated form in most cases from the viewpoint of run time and energy consumption.

NOTATION

H, sample thickness; h, dried layer thickness; v, propagation velocity of one-dimensional sublimation front; τ, time; L, specific sublimation time; T_h ice temperature on heating side; T_e, equilibrium temperature at sublimation boundary; P_e, saturation pressure; P_{in}, pressure in apparatus; λ_f, thermal conductivity of frozen material; λ_d, thermal conductivity of dried material; κ, mass conductivity; γ, relative content per unit volume; ρ_i, density of ice; c, concentration.

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