VACUUM SUBLIMATION OF ICE AND WATER FROM A SINGLE MACROCAPILLARY SUPPLIED RADIATIVELY WITH HEAT

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A photographic study was conducted of the sublimation mechanism for water, in a single macroscopic capillary, under vacuum, supplied radiatively with heat. It was found that the sublimation in a capillary is analogous to that in a body with capillary pores.

Only temperature, pressure, and mass loss have been measured in most studies of sublimation in capillary porous colloidal materials. These measurements have been used to explain various aspects of the mechanism, and a mathematical model has been formulated to describe the heat and mass transfer.

The readings are inaccurate if temperature and pressure transducers are inserted in a capillary body, and this has sometimes led to incorrect explanations of the effects.

In order to formulate correct explanations of the sublimation mechanism contactless measurement methods and photographic observations are necessary. In a few papers [1, 2] large scale photographs have been used in order to examine the heat and mass transfer in the sublimation of ice under vacuum.

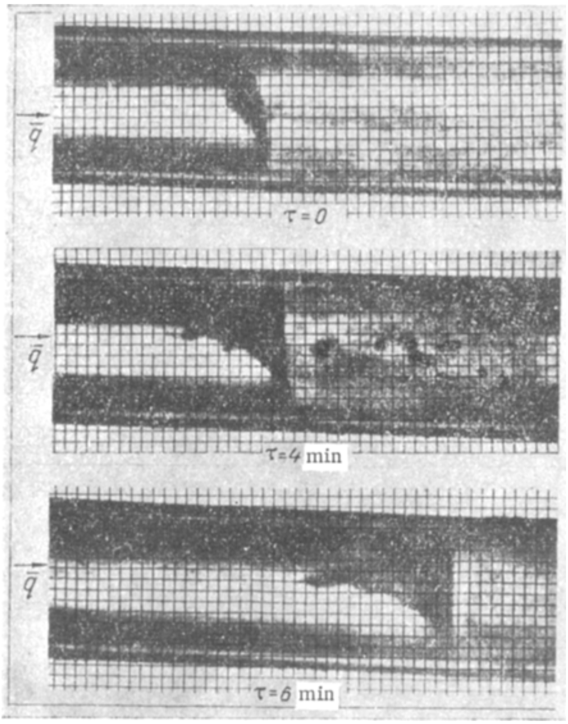

Fig. 1. Sublimation of ice in a capillary 400 μ in diameter from water previously frozen in the capillary.

Time-lapse cinephotography allows one to examine the evaporation kinetics [3]. We have made photographic studies on single glass capillaries 250-400 μ in diameter. The heat was applied by radiation when the water had been frozen into the capillary in a refrigerator and also when the water froze spontaneously in the sublimation chamber.

In Fig. 1 (the side of each square graduation is about 35 μ) the position of the boundary is shown in a

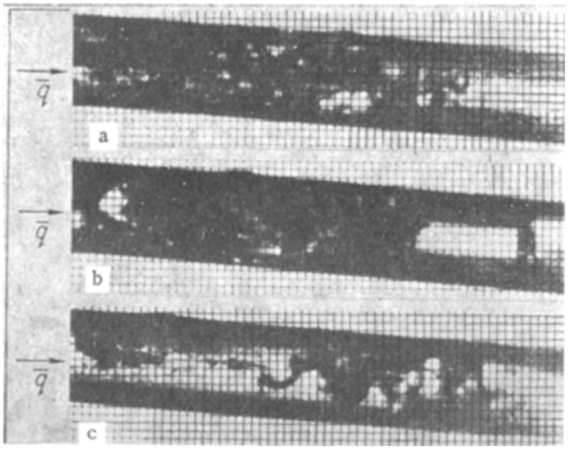

Fig. 2. Sublimation in a capillary 400 μ in diameter without previous freezing.

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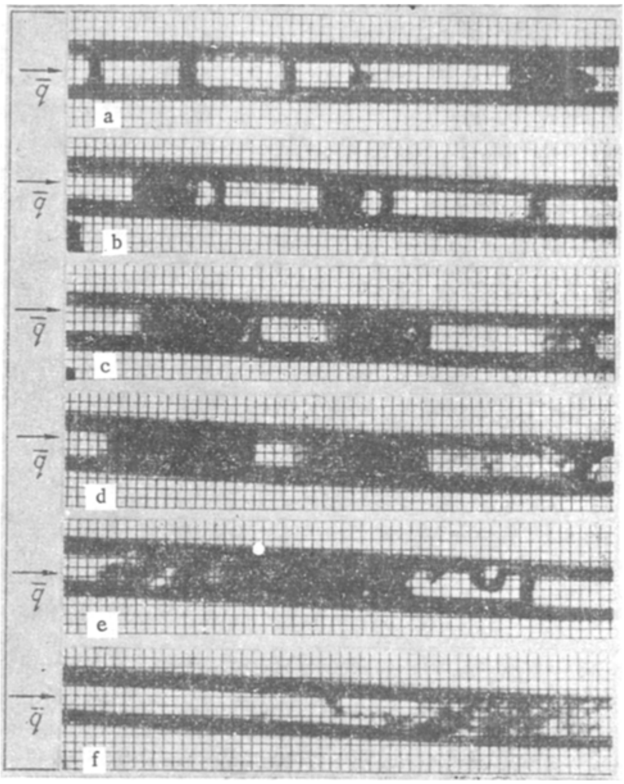

Fig. 3. Sublimation in a capillary 250 μ in diameter without previous freezing.

capillary 400 μ in diameter at 4 and 6 minutes after the start of sublimation at a pressure of 0.5 mm Hg (66.6 N/m^2). The water had previously been frozen into the capillary in a refrigerator. The mean sublimation rate with the radiator at 120°C was

$$v = \frac{\pi d_c^2}{4} \cdot \frac{\Delta l \gamma_l}{\Delta \tau} = \frac{\pi (4 \cdot 10^{-2})^2 \cdot 0.15 \cdot 0,92}{4 \cdot 2}$$

$$= 0.85 \cdot 10^{-4} \cdot \text{g/min.}$$

As is evident from Fig. 1, the sublimation is accompanied by the production of crystals at the surface. These crystals grow, break, and are carried away as the sublimation front advances. Previously [2], this crystallization occurred at the surface of an ice cube made from ordinary tap water, but within the capillary it occurred at the end surface of the ice rod arising from double distilled water.

We found no such crystallization when double-distilled water sublimed under these conditions in a capillary when the pressure and the radiator temperature were the same.

As can be seen in Fig. 1, the surface initially had a meniscus, which then flattened out as the crystals grew. In the steady state, the front advanced uniformly along the capillary (Fig. 1), and the front was covered with crystals that were seen to grow, break, and fly off continuously.

The growing crystals form a cone because of the influx of heat from the capillary wall. The conditions as the front advances therefore changed little from those for an ordinary cube evaporating with radiated supply of heat [2].

We have examined the evaporation in capillaries down to 250 μ in diameter, as against a mean diameter of about 70 μ in plant and animal cells. It has been supposed [4] that there could be a meniscus at the sublimation surface, and that the meniscus, in some way, effects the water vapor pressure within the capillary.

The meniscus arising from radiative heating increases the free energy of the system, i.e., the ice crystal and vapor within the capillary.

The free energy tends to a minimum, and so the meniscus tends to deteriorate. This result is represented by the Gibbs–Kelvin thermodynamic equation [4]

$$RT \left[\ln \frac{P_r}{P_\infty} \right] = -2\sigma \overline{V}/r.$$

Equilibration at the front implies that

$$P_r \to P_\infty; \quad \ln \frac{P_r}{P_\infty} \to 0; \quad \sigma \to \sigma_{\min}.$$

Our photographs show an essentially different behavior at the front when ice sublimes in a capillary in which no freezing had previously occurred. We made these measurements at 0.5 mm Hg = 66.6 N/m^2. Figure 2 shows the main stages in the process at intervals of 10 sec (a square has a side equivalent to about 45 μ).

The water in the capillary freezes when it is inserted in the vacuum chamber and the freezing starts from the side facing the vacuum.

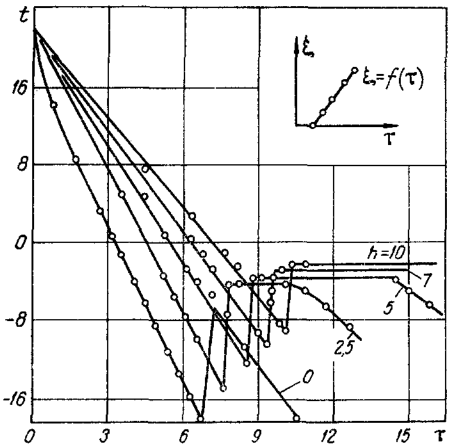

Fig. 4. Temperature distribution in a capillary body showing spontaneous freezing (results of E. I. Popova). The numbers on the curves are values of h mm, ξ mm, τ min, t°C.

This freezing results in sublimation, partly because of the directional radiation flux, and small ice crystals are formed (Fig. 2a).

The boundary between the fine-grained ice and the unfrozen water can be seen clearly in Fig. 2b. The radiation flux, warming the walls of the capillary, creates the conditions for the reheating of the unfrozen liquid and the formation of a vapor bubble. The growth of this bubble produces a region of elevated pressure in the capillary.

The single bubble (Fig. 2c) moves towards the sublimation surface, where the pressure is lower, and stops at the dense barrier of porous ice.

As the ice sublimes, it becomes thinner and at a certain instant the pressure from the vapor bubble expels it explosively from the capillary, as shown in Fig. 2c.

This cycle is repeated continuously, and at each stage the sublimation zone advances into the capillary.

The time for one cycle is dependent on the heat input, pressure, the chemical composition of the water, etc. The sublimation is, to some extent, a random process, and at higher heat inputs it takes a rather different form from that shown in Fig. 3 (side of square about 45 μ). Here the photographs were taken at intervals of 15 sec, and the pressure was 0.5 mm Hg. The higher heat flux led to a succession of vapor bubbles between columns of liquid. Such a group is shown in Fig. 3a. The sections of liquid move towards the vacuum under the pressure difference, and may freeze at the same time (Fig. 3b) and sublime to form porous ice (Fig. 3c, d). Radiation causes the pressure in a bubble under the ice to increase as described above. The ice plugs adhere less firmly to the capillary walls as the ice sublimes and the porosity increases; finally, the pressure difference ejects the porous ice from the capillary (Fig. 3f).

The heat input and the pressure determine whether the process occurs as in Fig. 2 or in Fig. 3, or by a combination of the two.

Some experiments due to E. I. Popova illustrate spontaneous freezing in a capillary body under vacuum [5]. It was found that such a body has considerable temperature gradients, and it was pointed out that the temperature at any point falls roughly linearly, and when a certain negative value is reached, it suddenly rises by 12°. This rise occurs mainly well below 0°C (Fig. 4). These steps are ascribed to crystallization accompanied by heat release.

Our visual observations indicate that this temperature jump is due to the pulsations, which are similar to those in single capillaries. This is confirmed by our observations on the temperature pulsations in a porous cermet. The temperature pulsations are due to periodic migration and freezing of water in the capillaries, with subsequent advance of the sublimation zone. These directional vapor pulsations in capillaries move the sublimation zone explosively and may disrupt the skeleton of the material, as occurs, for example, in fish drying without preliminary freezing.

Previous freezing in such a material results in continuous and stable sublimation without damage to the capillaries.

NOTATION

v	is the sublimation rate, g/min;
d_c	is the diameter of capillary, cm;
$\Delta\tau$	is the time interval, min;
Δl	is the displacement of sublimation front in capillary in $\Delta\tau$, cm;
γ_l	is the density of ice, g/cm^3;
P_r, P_∞	are the vapor pressure on concave and flat surfaces;
R	is the universal gas constant;
σ	is the surface free energy of solid body in equilibrium with vapor;

V is the molar volume of evaporating substance;
T is the absolute temperature;
T_s is the temperature of screen.

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