# VAPOR DIFFUSION IN EVAPORATION OF LIQUIDS FROM CAPILLARIES UNDER NONISOTHERMAL CONDITIONS

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The process of vapor transfer in the Stefan regime under the influence of a temperature gradient is considered. Expressions are found for the meniscus displacement rate and time required for liquid evaporation from a capillary. Conditions under which vapor condenses in the channel are determined.

Transfer of water in the form of vapor in a porous medium at temperatures lower than the liquid boiling point occurs due to diffusion of vapor in the air-filled pore space. The process of drying of capillary-porous bodies is often accompanied by development of a temperature gradient within the body. Thus, the process of diffusion transfer of vapor within a capillary is a subject of interest, to which the present study will be dedicated.

We will consider a cylindrical capillary of specified radius ($Kn \ll 1$), filled with a liquid, from the open surface of which evaporation occurs. We direct the coordinate axis from the channel mouth ($x = 0$) toward the liquid meniscus ($x = l$). A constant vapor pressure $P_{01} < P_s$ is maintained in the channel mouth (where $P_s$ is the saturated vapor pressure at the temperature of the liquid meniscus $T(l)$). Let the temperature change linearly along the channel by a law $T(x) = T_0(1 + \nabla T x/T_0)$, never exceeding the liquid boiling point.

In order to determine the meniscus displacement rate $dl/dt$, we will commence from the concept that the redistribution of partial pressures of vapor and air produced by change in $l$ and $P_s(l)$ due to motion of the liquid-phase boundary occurs much more rapidly than the displacement itself, so that for any $l$ the vapor flux is described by Stefan's expression [1]

$$j = \rho(l)\frac{dl}{dt} = \frac{D\mu P}{RTl}\ln\frac{P - P_{01}}{P - P_s(l)}. \tag{1}$$

The temperature and vapor diffusion coefficient in air are taken as averaged values over the air-filled portion of the channel:

$$T = \frac{T_0 + T(l)}{2} = T_0\left(1 + \frac{\nabla T l}{2T_0}\right), \tag{2}$$

$$D = \frac{D_0 + D(l)}{2} = \frac{D_0}{2}\left[1 + \left(1 + \frac{\nabla T l}{T_0}\right)^m\right] \tag{3}$$

(where m is a constant number, empirically determined values of which are presented in [2]).

With increase in $l$, as follows from the Clayperon–Clausius equation, the saturated vapor pressure above the meniscus will change by a law [3]

$$P_s(l) = P_s(0)\exp\left\{\frac{L_0\nabla T l}{RT_0^2\left(1 + \frac{\nabla T l}{T_0}\right)}\right\}. \tag{4}$$

If we neglect thermodiffusion fluxes of vapor and air, then from Eq. (1) with consideration of Eqs. (2)-(4), we can define the dependence of meniscus displacement rate on $l$:

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$$\frac{dl}{dt}=\frac{D_0\mu P\left[1+\frac{(m-1)\nabla Tl}{2T_0}\right]}{\rho(l)RT_0 l}\ln\frac{P-P_{01}}{P-P_s(0)\exp\left\{\frac{L_0\nabla Tl}{RT_0^2\left(1+\frac{\nabla Tl}{T_0}\right)}\right\}}. \quad (5)$$

Separating the variables and integrating both parts of the equation, we obtain an expression for the time t required for removal of water to a depth $l$ in integral form

$$t=\frac{RT_0}{D_0\mu P}\int_0^l\left\{\ln\frac{P-P_{01}}{P-P_s(0)\exp\left[\frac{L_0\nabla Tl}{RT_0^2\left(1+\frac{\nabla Tl}{T_0}\right)}\right]}\right\}^{-1}\frac{\rho l dl}{\left[1+\frac{(m-1)\nabla Tl}{2T_0}\right]}. \quad (6)$$

The right side of this expression can be integrated by numerical methods. In order to obtain an approximate value of the integral it is sufficient to limit ourselves to terms of second order smallness in the series expansions of the exponential and logarithmic functions in the integrand. Estimates performed indicate that the uncertainty in t determination does not exceed 1% at

$$l<\frac{0,15[P-P_s(0)]}{P_s(0)}\frac{RT_0}{L_0}\frac{T_0}{|\nabla T|}\ln\frac{P-P_{01}}{P-P_s(0)}. \quad (7)$$

If the value of $l$ does not satisfy this last expression, $l$ can be represented in the form of a sum

$$l=\sum_{i=0}^{n-1}(l_{i+1}-l_i),$$

where $l_0 = 0$, $l_n = l$,

$$l_{i+1}-l_i=\Delta l_{i+1}\leqslant\frac{0,15[P-P_s(l_i)]}{P_s(l_i)}\frac{RT(l_i)}{L(l_i)}\frac{T(l_i)}{|\nabla T|}\ln\frac{P-P_{01}}{P-P_s(l_i)}.$$

In this case an expression for t can be obtained by successive integrations of the right side of Eq. (6) over each $\Delta l_i$ and summation of the integrals

$$t=\sum_{i=0}^{n-1}\frac{\gamma_i}{2\alpha_i\beta_i}\ln(1+\alpha_i\Delta l_{i+1}+\alpha_i\beta_i\Delta l_{i+1}^2)+$$

$$\frac{\gamma_i}{\beta_i\sqrt{4\alpha_i\beta_i-\alpha_i^2}}\left(\operatorname{arctg}\frac{2\alpha_i\beta_i\Delta l_{i+1}+\alpha_i}{\sqrt{4\alpha_i\beta_i-\alpha_i^2}}-\operatorname{arctg}\frac{\alpha_i}{\sqrt{4\alpha_i\beta_i-\alpha_i^2}}\right)(2\beta_i l_i-1), \quad (8)$$

where

$$\alpha_i=\left[\ln\frac{P-P_{01}}{P-P_s(l_i)}\right]^{-1}\frac{P_s(l_i)}{[P-P_s(l_i)]}\frac{L(l_i)}{RT(l_i)}\frac{\nabla T}{T(l_i)},$$

$$\beta_i=\left\{\frac{L(l_i)}{2RT(l_i)}\frac{P}{[P-P_s(l_i)]}-1\right\}\frac{\nabla T}{T(l_i)},$$

$$\gamma_i=\frac{\rho(l_i)RT_0\left[1-\frac{(m-1)}{4}\frac{\nabla T}{T_0}(l_i+l_{i+1})\right]}{D_0\mu P\ln\frac{P-P_{01}}{P-P_s(l_i)}}.$$

It should be noted that for the case $\nabla T > 0$ at a certain value of $l$ the vapor begins to condense on the channel walls, which places a limit on the applicability of Eqs. (5) and (8). Conditions for condensation develop when the partial vapor pressure is not less than the saturated vapor pressure not only at the meniscus ($x = l$), but also in some intermediate region ($x < l$). This is possible when

$$\left.\frac{dP_1(x)}{dx}\right|_{x=l}\leqslant\left.\frac{dP_s(x)}{dx}\right|_{x=l}. \quad (9)$$

The right side of this inequality is determined from Eq. (4):

$$\left.\frac{dP_s(x)}{dx}\right|_{x=l} = P_s(l)\frac{L_0 \nabla T}{RT_0^2\left(1+\dfrac{\nabla T l}{T_0}\right)^2}\,. \tag{10}$$

The partial vapor pressure distribution is practically indistinguishable from the isothermal distribution at the liquid meniscus temperature. From this fact we can find the total vapor flux [4]

$$j = \frac{D\mu P}{RT}\,\frac{dP_1}{(P-P_1)\,dx}\,. \tag{11}$$

Solving this equation with consideration of Eq. (1), separating the variables and integrating, we obtain

$$P_1(x) = P-(P-P_{01})\left(\frac{P-P_s}{P-P_{01}}\right)^{\frac{x}{l}} \tag{12}$$

or

$$\left.\frac{dP_1(x)}{dx}\right|_{x=l} = -(P-P_s)\ln\frac{P-P_s(l)}{P-P_{01}}\,. \tag{13}$$

With consideration of Eqs. (10) and (13) inequality (9) takes on the form

$$[P-P_s(l)]\ln\frac{P-P_{01}}{P-P_s(l)} \leqslant P_s(l)\,\frac{L_0\nabla T l}{RT_0^2\left(1+\dfrac{\nabla T l}{T_0}\right)^2}\,. \tag{14}$$

Together with Eq. (4) this inequality defines the range of $l$ values at which vapor condensation occurs. In particular, for $P_s \ll P,\ P_{01}=0,\ \nabla T l/T_0 \ll 1$, Eq. (14) simplifies significantly:

$$l \geqslant \frac{RT_0^2}{L_0|\nabla T|}\,. \tag{15}$$

Vapor may condense on the inner surface either in the form of individual droplets (in wide capillaries) or with formation of liquid layers which coat the entire channel section (in narrow ones). In both cases the vapor flux in the capillary mouth is determined by Stefan's Eq. (1) as before. The vapor flux at the meniscus is greater than the flux in the mouth (the difference between the two fluxes being greater, the more intensely condensation occurs). Equation (5) and, thus, Eq. (8) become inapplicable, since the rate of meniscus displacement is determined by the vapor flux at the meniscus. Since under condensation conditions

$$\frac{dP_1(x)}{dx} = \frac{dP_s(x)}{dx}\,,$$

the vapor flux can be found from Eq. (11) with consideration of Eq. (10):

$$j = \frac{D_0\mu P\,P_s(l)}{RT_0\,[P-P_s(l)]}\,\frac{L_0\nabla T}{RT_0^2\left(1+\dfrac{\nabla T l}{T_0}\right)^2} \tag{16}$$

To verify the results obtained experiments were performed with an apparatus in which capillaries were located in cylindrical grooves in a massive brass plate. A temperature gradient was created on the plate directed along the capillary axes. The value of this gradient, determined by thermocouples, was maintained constant over the course of the experiment. During the experiment a cathetometer was used to determine the meniscus positions at various times, allowing determination of the rate of meniscus descent as a function of meniscus distance from the capillary mouth. Experiments were performed in capillaries with $r = 20$ μm at a mouth temperature $T_0 = 333$°K and partial vapor pressure at the mouth of zero. The experimental data are compared to calculations with Eqs. (5) and (8) in Figs. 1 and 2 (curves 1, 2, 3, 4 for $\nabla T$ = 300, 0, −300, and −600°K/m, respectively). Under nonisothermal conditions the dependence of $dt/dl$ and $\sqrt{t}$ on $l$ is nonlinear, in contrast to the isothermal case, which is due to the known dependence of saturated vapor pressure on meniscus coordinate. The amount and direction of the deviation from linearity are determined by the magni-

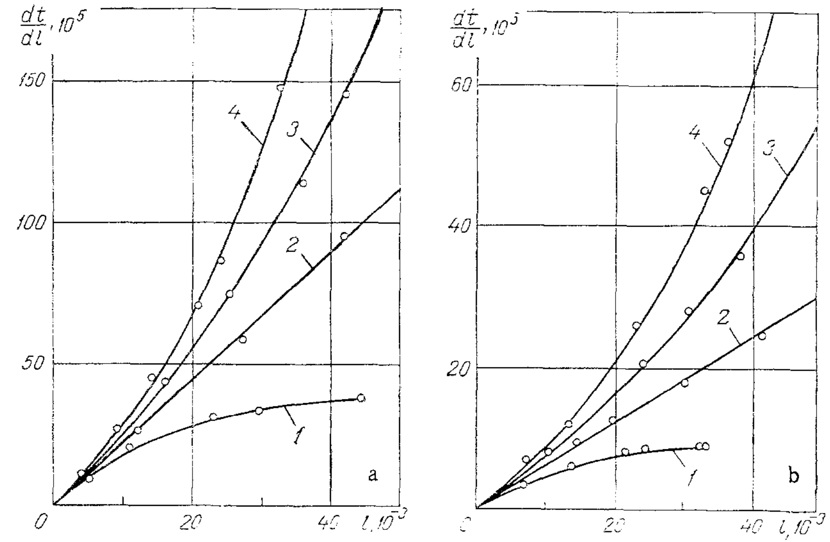


Fig. 1. Inverse meniscus displacement rate $dt/dl$ ($10^5$ sec/m) vs meniscus coordinate $l$ ($10^{-3}$ m) for evaporation of distilled water (a) and isopropyl alcohol (b).

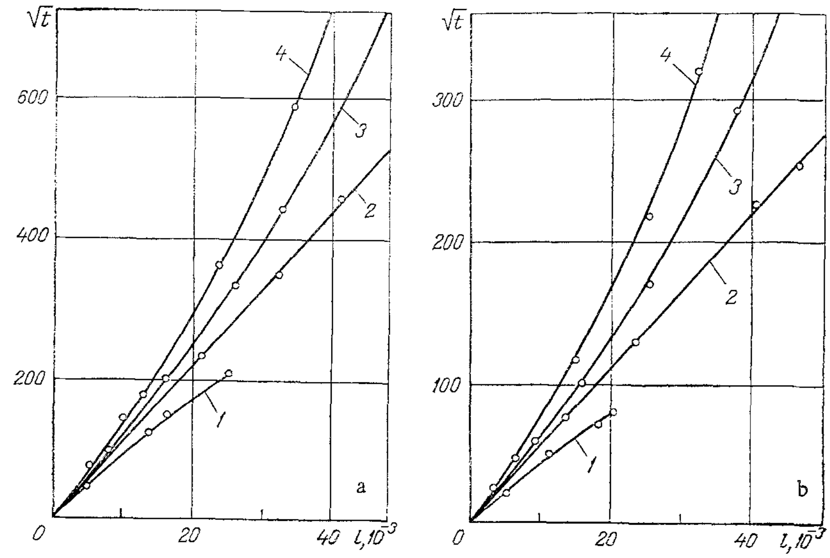


Fig. 2. Square root of evaporation time $\sqrt{t}$ ($sec^{1/2}$) for distilled water (a) and isopropyl alcohol (b) vs meniscus coordinate $l$ ($10^{-3}$ m). Points, experiment; solid lines, calculation (Figs. 1 and 2).

tude and sign of the temperature gradient. For evaporation of isopropyl alcohol the deviations from linearity are greater than for water. This is because with other characteristics approximately equal the difference between the boiling point and the temperature at the capillary mouth is less for the alcohol than the water, so that the saturated vapor pressure is higher. The breakoff of the curves at $\nabla T > 0$ indicates the beginning of the vapor condensation process. The difference between experimental and theoretical data is no greater than 5%, which is within the limits of experimental error. The same can be said of the differences in $l$ values at which vapor condensation was observed within the tube experimentally and those calculated with Eq. (14).

## NOTATION

$P_{01}$, vapor pressure at capillary mouth; $P_S$, saturated liquid vapor pressure; P, atmospheric pressure; x, current coordinate; $l$, meniscus coordinate; $T_0$, temperature of capillary mouth; $\nabla T$, temperature gradient; j, vapor flux; $\mu$, molecular weight of vapor; D, vapor diffusion coefficient in air; $L_0$, molar heat of evaporation at temperature $T_0$; t, evaporation time; $\rho$, liquid density; Kn, Knudsen number; r, capillary radius.

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