MASS TRANSFER BETWEEN STREAMS OF LIQUID AND VAPOR DURING EVAPORATION FROM CAPILLARIES

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We have estimated the degree of departure from one-dimensionality of the relative humidity field during evaporation from a capillary, allowing for interaction of the vapor and liquid phases according to the Deryagin-Nerpin-Churaev theory. The boundary conditions for the non-one-dimensional problem have been formulated. An analytical solution has been obtained for a non-one-dimensional relative humidity field in a capillary under simplifying assumptions.

For a long time the transfer to the atmosphere of moisture situated deep in a capillary has been regarded as the motion of molecules evaporated from the meniscus of a liquid [1]. Appreciable contradictions between theory and experiment [3] have often been observed. The authors of references [4–6] have pointed out that the observed laws of evaporation from capillaries can be explained by the fact that, in addition to the above process in the transfer of mass to the capillary outlet, a part may be played by a stream of liquid caused by the disjoining pressure gradient [7], flowing in a film over the capillary walls. A considerable fraction of the total mass flux from the capillary is that due to evaporation from the film. Thus, phase transformations at the interface between film and vapor are a substantial component of the intracapillary mass transfer process, and in general a direct allowance should be made for interphase transfer.

In some cases (for example, for capillaries with a considerable ratio of distance from meniscus to capillary outlet l to radius R, with large drops of relative humidity φ between the meniscus and the outlet) there is reason to suppose that the rate of evaporation from the surface of the liquid film is small, and the gradients of φ over a cross section of the capillary are small in comparison with gradients of φ in the longitudinal direction. The process of intracapillary mass transfer in systems like this may be regarded, with sufficient approximation, as one-dimensional, while mass transfer between the liquid and the vapor is accounted for by introducing the condition of constant total flux of both phases at every section of the capillary. An analysis based on these assumptions was conducted in [4–6]. The question of the applicability of the numerical results of this analysis to specific conditions is closely connected with the degree of approximation of the field φ in these conditions to the one-dimensional.

We will examine the model (see figure) used in references [4–6]. Evaporation from a single capillary of radius R in the steady regime under isothermal conditions proceeds in such a way that the distance between the meniscus and the capillary outlet is constant. The capillary walls are covered by a film of liquid of thickness h, and the relative humidity of the air over the meniscus and the outlet of the capillary is constant.

A tentative estimate of the degree of one-dimensionality of the field of φ in the capillary may be obtained as follows. Since the angle of inclination of the film surface to the capillary axis is small, regarding the film as one-dimensional, we may write down the flow of liquid in the film as

$$g_l = L_l \frac{\partial \varphi}{\partial x},$$

$$L_l = \frac{2\pi R \rho^2 (h-h_0)^3}{3\nu} \frac{R_c T}{M \varphi}. \quad (1)$$

The x axis is directed along the capillary axis from the outlet to the meniscus.

The connection between φ and the disjoining pressure Π in the film is given by the well-known equation

$$\Pi + \frac{\sigma}{R} = -\frac{\rho R_c T}{M} \ln \varphi. \quad (2)$$

The total increment of vapor flow in the whole distance l is equal to the difference in liquid flow in the film between the level of the meniscus and the outlet. At the same time, this increment Δg_v is equal to the product of the conductivity of the vapor phase L_v and the radial gradient $\overline{\partial\varphi}/\partial r$, averaged over the phase interface, and the area of the phase interface area from meniscus to outlet:

$$\Delta g_v = L_v \frac{\overline{\partial \varphi}}{\partial r} 2\pi R l = -\Delta g_l = g_{l,\mathrm{m}} - g_{l,\mathrm{o}},$$

$$\bar{L}_v = \frac{DPM}{R_c T (P/p_s - \bar{\varphi})}. \quad (3)$$

From (3) it follows that

$$\frac{\overline{\partial \varphi}}{\partial r} = \left[L_{l,\mathrm{m}} \frac{\partial \varphi}{\partial x}\Big|_{\mathrm{m}} - L_{l,\mathrm{o}} \frac{\partial \varphi}{\partial x}\Big|_{\mathrm{o}} \right] \Big/ \bar{L}_v 2\pi R l. \quad (4)$$

The condition of one-dimensionality has the form

$$\left| \frac{\partial \varphi}{\partial r} \right| \ll \left| \frac{\partial \varphi}{\partial x} \right|. \quad (5)$$

The degree of one-dimensionality of the field φ at the level of plane x is determined by W_x:

$$W_x = \left| \frac{\partial \bar{\varphi}}{\partial r} \right| : \left| \frac{\partial \varphi}{\partial x} \right|_x = \frac{1}{2\pi R l} \times \quad (6)$$

$$\times \left[\frac{L_{l,\mathrm{m}}}{L_v} \left(\frac{\partial \varphi}{\partial x}\Big|_{\mathrm{m}} : \frac{\partial \varphi}{\partial x}\Big|_x \right) - \frac{L_{l,\mathrm{o}}}{L_v} \left(\frac{\partial \varphi}{\partial x}\Big|_{\mathrm{o}} : \frac{\partial \varphi}{\partial x}\Big|_x \right) \right].$$

The ratios of the gradients entering into (6) is given approximately from the equation

$$\Delta g_{v.x} = -\Delta g_{l.x} = L_{l.m}\frac{\partial\varphi}{\partial x}\Big|_{m} - L_{l.x}\frac{\partial\varphi}{\partial x}\Big|_{x} = \pi R^2\left[L_{v.x}\frac{\partial\varphi}{\partial x}\Big|_{x} - L_{v.m}\frac{\partial\varphi}{\partial x}\Big|_{m}\right].$$

We designate $L_l/2\pi R^2 L_v = H$, and, putting $L_{v,o} \approx L_{v,m} \approx L_{v,x} \approx L_v$, we write (6) in the form

$$W_x = \frac{R}{l}\,\frac{(2H_x+1)(H_m-H_o)}{(2H_m+1)(2H_o+1)}.$$

It is evident that the φ field may be made one-dimensional only in the region $W_x \ll 1$. We put $W_x \le 0.1$. Then the region of one-dimensionality of the field is determined by the condition

$$\frac{H_x-H_o}{H_o} = Q \leqslant \frac{2H_o+1}{2H_o}\left[0.1\,\frac{l}{R}\,\frac{2H_m}{H_m-H_o}-1\right]. \quad (7)$$

Assuming the values used in [4] for the appropriate parameters, we find that when $R \ge 10^{-5}$ cm, $H_m \approx 500$. When $\varphi_x \approx \varphi_o \approx 1$

$$\frac{H_x-H_o}{H_o} \approx \frac{h_x^3-h_o^3}{h_o^3} \approx -\ln\frac{\varphi_x}{\varphi_o}\Big/\ln\varphi_x \approx \frac{\varphi_x-\varphi_o}{\varphi_o(1-\varphi_x)}.$$

Then condition (7) may be written in the form

$$\varphi_o \leqslant \varphi_x \leqslant \frac{\varphi_o(Q+1)}{1+Q\varphi_o}.$$

In particular, when $\varphi_o = 0.9$, $l/R = 10$, $R = 10^{-5}$ cm, $0.9 \le \varphi_x \le 0.95$.

Thus, the inequality (7) permits us to estimate the range of variation of φ_x, from the total drop $\Delta\varphi = \Phi$, where the one-dimensional approximation is allowable. In the special case where we are directly at the meniscus, $W_x = \frac{R}{l}\,\frac{H_m-H_o}{2H_o+1}$ and when $R \ge 10^{-5}$ cm and $\varphi_o = 0.9$ $W_x \ge 50\,R/l$, i.e., the deviation of the field from the one-dimensional is large. At the same time, it is precisely in the region near the meniscus that there are especially large variations in the thickness of the film with height, so that evaporation from the film makes a relatively large contribution to the total flow.

If we estimate this contribution on the basis of considerations similar to the foregoing, we obtain

$$\Delta g_{l.x}/\Delta g_{l,o} = (H_m-H_x)(2H_o+1)/(H_m-H_o)(2H_x+1).$$

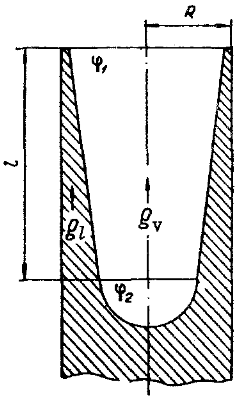
Thus, for $\varphi_o = 0.9$, $l/R = 10$, $R = 10^{-5}$ cm $\Delta g_{l,x}/\Delta g_{l,o} \approx 0.4$.

In other words, the contribution to the total flow of moisture due to evaporation from the film in the region where the field φ is not one-dimensional is quite large, and, in such cases of analysis of intracapillary mass transfer, it is necessary to allow for mass transfer between the phases in explicit form.

With this objective the condition of total flow of liquid and vapor at any cross section of the capillary should be replaced by the condition of conservation of mass, applied at the vapor-film interface,

$$-\frac{\partial g_l}{\partial x} = -2\pi(R-h)\,\frac{DPM}{R_cT(P/p_s-\varphi)}\,\mathrm{grad}_n\varphi. \quad (8)$$

Here $\mathrm{grad}_n\,\varphi$ is the gradient of Q in the direction of the interior normal to the film.



Capillary model with a wetting film in which the distance from the meniscus to the outlet remains constant [3].

For simplification, we will examine the region $0 \le x \le l$ in the capillary with plane surfaces at $x = 0$ and $x = l$. We assume that $x = l$, $\varphi \approx \varphi_2$, and when $x = 0$, $\varphi = \varphi_1$ (φ_1 is the given relative humidity of the air in the surrounding medium). According to the condition of conservation of mass in the capillary,

$$\mathrm{div}\cdot\mathrm{grad}\,g_v = 0. \quad (9)$$

Taking the nonlinear part of (9) to be small, we write

$$\mathrm{div}\cdot\mathrm{grad}\,\varphi = 0. \quad (10)$$

When $R \gg h$ or when there is little variation in film thickness along the capillary (when $[h(l) - h(0)]/l \ll 1$), the intracapillary vapor region may be approximated by a cylinder. Then $\mathrm{grad}_n\,\varphi = -\mathrm{grad}_r\,\varphi$, and condition (8) may be written in the form

$$-\frac{\partial g_l}{\partial x} = 2\pi(R-h)\frac{DPM}{R_cT\left(\frac{P}{p_s}-\varphi\right)}\frac{\partial\varphi}{\partial r}. \quad (11)$$

In differentiating (1) we take into account variation of h(x) and φ along the length of the capillary. Without allowing for the ion-electrostatic component of the disjoining pressure, $h = \sqrt[3]{k/\Pi}$, where k is constant, and

$$\frac{\partial h}{\partial x} = \frac{h\rho R_cT}{3M\Pi\varphi}\,\frac{\partial\varphi}{\partial x}. \quad (12)$$

We introduce the new variables $\xi = x/l$, $\eta = r/R$, the function $U = \varphi - \varphi_1$, and designate $\varphi_2 - \varphi_1 = \Phi$. In the new variables Eq. (11) with the appropriate boundary conditions may be written as

$$\frac{\partial^2U}{\partial\eta^2} + \frac{1}{\eta}\frac{\partial U}{\partial\eta} + \frac{R^2}{l^2}\frac{\partial^2U}{\partial\xi^2} = 0, \quad (13)$$

$$\left.\begin{array}{ll} U = \Phi, & \xi = 1 \\ U = 0, & \xi = 0 \end{array}\right\} 0 \leqslant \eta \leqslant 1, \tag{14}$$

$$H \frac{R^2}{l^2} \frac{\partial^2 U}{\partial \xi^2} + \frac{H}{\varphi} \frac{R^2}{l^2} V \left(\frac{\partial U}{\partial \xi} \right)^2 = \frac{\partial U}{\partial \eta},$$

$$V = \frac{\rho R_c T}{\Pi M} \frac{h}{h - h_0} - 1. \tag{15}$$

An analytical solution of the problem, with boundary conditions (14) and (15), is in general impossible because of the great mathematical difficulties. But we may obtain such a solution by making a number of approximations.

We make the following assumptions:

1. The coefficients of $\frac{\partial^2 U}{\partial \xi^2}$ and $\left(\frac{\partial U}{\partial \xi}\right)^2$ in the boundary condition (15) are constant and are assumed equal to their mean values along the capillary.

2. The nonlinear term in (15) is small and is taken into account as a perturbation in solving the problem by the method of successive approximations. Because of these assumptions, the examination is limited to the case of small changes of φ along the capillary ($\Phi/\varphi \ll 1$), and to small interchanges between the liquid and vapor-phase flows.

The solution of (13), with the appropriate boundary conditions and the above assumptions, gives the following first-order approximation for the φ field in the capillary:

$$\varphi - \varphi_1 = \Phi\xi + C \left[\eta^2 + 2 \left(\frac{l}{R} \right)^2 (\xi - \xi^2) + \right.$$

$$\left. + \sum_{n=1}^{\infty} L_n N_n \frac{I_0(\alpha_n \eta)}{I_0(\alpha)} \right],$$

$$C = \frac{H \Phi^2 V}{2(1 + 2H)} \frac{R^2}{l^2 \varphi}; \quad N_n = \operatorname{th} \frac{\beta_n}{2} \operatorname{sh} \beta_n \xi - \operatorname{ch} \beta_n \xi;$$

$$\beta_n = \alpha_n \frac{l}{R}; \quad L_n = \sum_{k \geqslant n}^{\infty} \frac{d_k}{f_k} \sigma_{k_n}. \tag{16}$$

The quantities d_k, f_k, σ_k are determined from the relations

$$\Theta_k = \sum_{\Theta=1}^{k} \sigma_{kn} \frac{I_0(\alpha_k)}{I_0(\alpha_n)} I_0(\alpha_n \eta) = I_0(\alpha_k \eta) -$$

$$- \sum_{i=1}^{k-1} \int_0^1 \eta I_0(\alpha_k \eta) \psi_i \, d\eta \, \psi_i,$$

$$\psi_i = \frac{\Theta_i}{\|\Theta_i\|}; \quad \|\Theta\|_k^2 = \int_0^1 \eta_k^2(\eta) \, d\eta = f_k I_0^2(\alpha_k),$$

$$d_k = \sum_{\Theta=1}^{k} \sigma_{kn} \gamma_n, \qquad \gamma_1 = \frac{1}{4}, \qquad \gamma_{n>1} = \frac{2 - H(\alpha_n^2 - 4)}{\alpha_n^2},$$

where α_n are the roots of the equation $I_1(\alpha_n) = -H\alpha_n \times I_0(\alpha_n)$; $I_0(\eta)$, $I_1(\eta)$ are Bessel functions of the first kind and of order zero and one.

The increment of vapor flow along the capillary due to evaporation from the film is given by

$$\Delta g_v = -\Delta g_l = \frac{2\pi R^2 \rho^2 (h - h_0)^3 R_c T V \Phi^2}{3\nu M \varphi^2 [1 + 2H] l} \times$$

$$\times \left[1 - H \frac{R^2}{l^2} \sum_n \beta_n \operatorname{tg} \frac{\beta_n}{2} L_n \right]. \tag{17}$$

It follows from the form of (16) that the equipotential lines of the field of φ in the capillary have a convex curvature toward the meniscus. For physical conditions in which assumptions 1 and 2 are valid, the curvature of the equipotential lines is insignificant.

In the general case the solution of the problem of mass transfer between phases during evaporation from a capillary may be obtained numerically by applying the boundary conditions indicated.

NOTATION

φ is the relative humidity of air; l is the capillary length; R is the capillary radius; R_c is the universal gas constant; M is the molecular weight of water; ν is the viscosity of water; ρ is the density of water; σ is the surface tension of water; h is the thickness of film of water on capillary wall; h_0 is the thickness of stationary film of water; Π is the disjoining pressure of water in film; g is the flux density; L is the phase conductivity; D is the diffusion coefficient for water vapor in air; P is the barometric pressure; p_s is the pressure of saturated water vapor; T is the temperature. Subscripts v, l denote, respectively, vapor and liquid phases; o and m are the coordinates of the outlet and the meniscus of the capillary.

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