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ROLE OF THE DIFFUSION MECHANISM OF MASS-TRANSFER PROCESSES IN CONIC CAPILLARIES SUBMERGED IN A LIQUID

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A study is made of one possible mechanism explaining the phenomenon of bilateral filling of dead-end conic capillaries submerged in a liquid: diffusion and recondensation of a liquid vapor from a meniscus with a small curvature to a meniscus with a larger curvature. A theory of this process has been constructed and the rate of growth of the near-vertex liquid column has been calculated based on this theory. A comparison with experiment shows that although the law of growth of the column predicted by the theory coincides with the experimental one, the numerical values of the rate are nearly two orders of magnitude lower. Conditions under which one can detect this mechanism experimentally are discussed.

Introduction. An extensive amount of experimental material on the results of research into the phenomenon of bilateral filling of dead-end conic capillaries with liquid has been obtained at present (this phenomenon was disclosed in [1] for the first time). The kinetic regularities of the process have been established; it has been shown that in some cases we have filling of the capillary channel predominantly on the source side of the vertex of a cone having no direct contact with the liquid around the capillary [2–4].

It is clear that the appearance and growth of a liquid column in the dead-end point of the cone can be caused by two physical mechanisms. The first of them is evaporation of the liquid from a meniscus of smaller curvature and condensation of its vapor on a meniscus of larger curvature, which are caused by the difference in the pressures of a saturated vapor above the two menisci. The second mechanism is based on the presence of film liquid flow toward the vertex of the cone under the action of the pressure gradient caused by the decrease in the pressure in it with increase in the curvature of the meniscus.

In [4–5], conclusions on the prevailing role of the processes of evaporation and condensation in the phenomenon of bilateral filling of conic capillaries with liquids are drawn based on the available experimental data. The first of the above mechanisms is investigated below theoretically. Consideration is given to mass transfer due to both the diffusion of the vapor in a compressed vapor-air mixture and the diffusion of a gas dissolved in the liquid at the outlet from the capillary, i.e., the process determining diffusion impregnation.

The geometry of the problem with the corresponding notation is presented in Fig. 1. We will consider a spherical coordinate system whose origin coincides with the vertex of a conic capillary.

Formulation of the Problem in a General Statement. Consideration is given to two interrelated processes: diffusion of air (gas) from the gas cavity of the capillary through a liquid column in the channel (the concentration of the dissolved air at the outlet from the capillary is assumed to be equilibrium) and diffusion of a liquid vapor through the gas cavity due to dissimilar curvatures of the menisci at the gas–liquid boundaries. The problems of diffusion are formulated in a one-dimensional isothermal statement.

The one-dimensional equations of diffusion in a moving medium for the gas dissolved in the liquid and for the vapor in the gas cavity in the above spherical coordinate system are written in standard form:

$$\frac{\partial c_{\mathrm{g}}(t,r)}{\partial t}+v_{\mathrm{f}}\frac{\partial c_{\mathrm{g}}(t,r)}{\partial r}=D_{\mathrm{g}}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_{\mathrm{g}}(t,r)}{\partial r}\right),\quad r\in[R_2,R_{\mathrm{c}}]\,, \tag{1}$$

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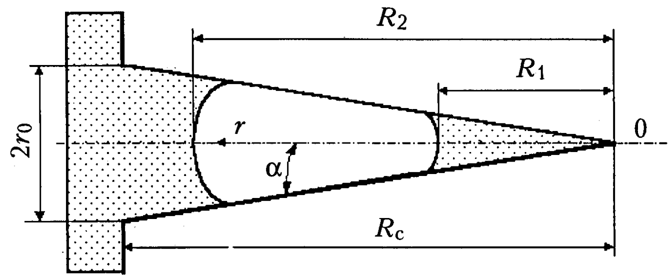

Fig. 1. Scheme of bilateral filling of a conic capillary with liquid.

$$\frac{\partial c_v(t,r)}{\partial t} + v_g \frac{\partial c_v(t,r)}{\partial r} = D_v \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial c_v(t,r)}{\partial r}\right), \quad r \in [R_1, R_2] . \tag{2}$$

The meaning of the variables in (1) and (2) is clear from Fig. 1.

The coordinates of the menisci R_1 and R_2 depend only on time. In what follows, we agree to denote the time derivatives for variables dependent only on time by points above symbols unlike functions of both the time and the coordinates for which the corresponding derivatives are denoted in the ordinary manner (see (1) and (2)).

System (1) and (2) must be supplemented with a set of the corresponding initial and boundary conditions. The initial conditions have the form

$$t = 0: \begin{cases} c_g(0, r) = c_{g0} \equiv k_H \left[p_a + p_c \dfrac{R_c}{R_2(0)}\right], \quad r \in [R_2(0), R_c]; \\ c_v(0, r) = \rho_s = \dfrac{p_s \mu_f}{R_g T}, \quad r \in [R_1(0), R_2(0)] . \end{cases}$$

The initial coordinate of the inlet meniscus is computed from the known expression [5]

$$R_2(0) = R_c \left\{\left[\frac{1}{2} - \left(\frac{m}{3}\right)^3 + \sqrt{\frac{1}{4} - \left(\frac{m}{3}\right)^3}\right]^{1/3} + \left[\frac{1}{2} - \left(\frac{m}{3}\right)^3 - \sqrt{\frac{1}{4} - \left(\frac{m}{3}\right)^3}\right]^{1/3} - \frac{m}{3}\right\},$$

where

$$m = \frac{p_c}{p_a + p_{v0}}, \quad p_c = \frac{2\sigma \cos\theta}{R_c \tau}, \quad \tau = \tan\alpha .$$

The boundary conditions for the vapor phase are determined on the basis of the well-known formula of Kelvin and Thompson for the pressure of a saturated vapor p_{r_c} above a curved surface with a radius of curvature r_c:

$$p_{r_c} = p_s \exp\left(-\frac{\rho_s}{p_s}\frac{p_c}{\rho_f}\frac{R_c}{r_c}\right). \tag{3}$$

Introducing the notation $\gamma = \dfrac{\rho_s}{\rho_f}\dfrac{p_c}{p_s}$, using (3) and the equation of state of the vapor we write the boundary conditions at the boundaries of the gas cavity:

$$r = R_1(t): \quad c_v(t, R_1(t)) = \rho_s \exp\left(-\gamma \frac{R_c}{R_1(t)}\right),$$

$$r = R_2(t): \quad c_v(t, R_2(t)) = \rho_s \exp\left(-\gamma \frac{R_c}{R_2(t)}\right).$$

For the equation of diffusion of the gas in the liquid column bounded by the meniscus $R_2(t)$ we have the following boundary conditions with allowance for Henry's law:

$$r = R_2(t): \quad c_g(t, R_2(t)) = k_H \left(p_a + p_c \frac{R_c}{R_2(t)\,\tau} + p_{v0} - p_s\right),$$

$$r = R_c: \quad c_g(t, R_c) = k_H p_a .$$

We use a continuity equation to calculate the velocity field. In view of the incompressibility of the liquid in the inlet column, it has the form

$$\frac{1}{r}\frac{\partial (r v_f)}{\partial r} = 0 .$$

Whence

$$v_f(t, r) = \frac{c(t)}{r} . \tag{4}$$

From the condition on the external meniscus we have

$$v_f(t, R_2(t)) = \dot{R}_2(t) - \frac{D_v}{\rho_f}\frac{\partial c_v(t, r)}{\partial r}\bigg|_{r=R_2(t)} . \tag{5}$$

Substituting (4) into (5), we find the integration constant C:

$$C(t) = R_2(t)\left[\dot{R}_2(t) - \frac{D_v}{\rho_f}\frac{\partial c_v(t, R_2(t))}{\partial r}\right].$$

Then, in accordance with (4), the velocity field of the liquid is expressed as

$$v_f(t, r) = \frac{R_2(t)}{r}\left[\dot{R}_2(t) - \frac{D_v}{\rho_f}\frac{\partial c_v(t, R_2(t))}{\partial r}\right]. \tag{6}$$

Let us turn to the continuity equation for the gas (air) closed in the cavity of the capillary. Since the capillary pressure above the external meniscus can substantially change as the capillary is filled, we must take into account the compressibility of the gas. Also, we allow for the fact that the relative change in the partial pressure of the vapor along the gas cavity is low ($\gamma \sim 10^{-5}$); the partial pressure of the vapor itself is much lower than the pressure of the gas ($p_v / p_g \sim 10^{-1}$–10^{-2}). And since the total pressure along the gas cavity is constant, with an accuracy no worse than hundredths of a percent, we can consider the pressure and hence the density of the gas in the cavity to be homogeneous, i.e., $\partial\rho_g / \partial r = 0$. With allowance for what has been said above, the continuity equation for the closed gas takes the form

$$\dot{\rho}_g + \rho_g \frac{1}{r}\frac{\partial (r v_g)}{\partial r} = 0 ,$$

where ρ_g is a function of only the time. Integrating this equation, we obtain

$$v_g(t, r) = -\frac{r}{2}\frac{\dot{\rho}_g}{\rho_g} + \frac{C_1(t)}{r}. \tag{7}$$

By analogy with (5), on the external meniscus we have the condition

$$v_g(t, R_2(t)) = \dot{R}_2(t) - \frac{D_g}{\rho_g}\frac{\partial c_g(t, r)}{\partial r}\bigg|_{r=R_2(t)}. \tag{8}$$

Substituting (7) into (8), we find the integration constant:

$$C_1(t) = R_2(t)\left[R_2(t) - \frac{D_g}{\rho_g}\frac{\partial c_g(t, R_2(t))}{\partial r} + \frac{R_2(t)}{2}\frac{\dot{\rho}_g(t)}{\rho_g(t)}\right]. \tag{9}$$

With account for (9), expression (7) for the velocity distribution of the gas in the cavity takes the following form:

$$v_g(t, r) = \frac{\dot{\rho}_g(t)}{2\rho_g(t)}\left[\frac{R_2^2(t)}{r} - r\right] + \frac{R_2(t)}{r}\left[\dot{R}_2(t) - \frac{D_g}{\rho_g(t)}\frac{\partial c_g(t, R_2(t))}{\partial r}\right]. \tag{10}$$

The rate of growth of the liquid column at the vertex of the capillary is determined by the diffusion vapor flow to it:

$$\rho_f \dot{R}_1(t) = D_v \frac{\partial c_v(t, R_1(t))}{\partial r}. \tag{11}$$

For the density of the gas closed in the cavity of the capillary, from the equation of state of the gas we have

$$\rho_g(t) = \rho_{g0}\left[1 + m\frac{R_c}{R_2(t)}\right]. \tag{12}$$

The change in the sum of the masses of the gas closed in the cavity and of the gas dissolved in the internal liquid column is due to its diffusion flow through the boundary of the external meniscus of the gas cavity:

$$\frac{d}{dt}\left\{\rho_g \frac{\pi\tau^2}{3}[R_2^3(t) - R_1^3(t)] + \frac{\pi\tau^2}{3}R_1^3(t)\, k_H p_a\left[1 + m\frac{R_c}{R_2(t)}\right]\right\} = \pi[\tau R_2(t)]^2 D_g \frac{\partial c_g(t, r)}{\partial r}\bigg|_{r=R_2(t)}.$$

Substituting ρ_g from (12) into this equation and computing the time derivative, upon simple transformations we obtain

$$\rho_{g0}\dot{R}_2(t)\, R_2^2(t)\,[R_2^3(t) - (1-\beta)R_1^3(t)] +$$

$$+\left(1 + m\frac{R_c}{R_2(t)}\right)[3R_2^2(t)\,\dot{R}_2(t) - 3(1-\beta)R_1^2(t)\,\dot{R}_1(t)] = \frac{3D_g R_2^2(t)}{\rho_{g0}}\frac{\partial c_g(t, R_2(t))}{\partial r}, \tag{13}$$

where $\beta = k_H p_a/\rho_{g0}$.

Substitution of $\dot{R}_1(t)$ from (11) into (13) yields the equation for the motion of the meniscus $R_2(t)$:

$$\dot{R}_2(t) = \frac{\dfrac{D_g}{\rho_{g0}} \dfrac{\partial c_g(t, R_2(t))}{\partial r} + \dfrac{D_v}{\rho_f}(1-\beta)\left(1 + m\dfrac{R_c}{R_2(t)}\right)\dfrac{R_1^2(t)}{R_2^2(t)} \dfrac{\partial c_v(t, R_1(t))}{\partial r}}{1 + \dfrac{mR_c}{3R_2(t)}\left[(1-\beta)\dfrac{R_1^3(t)}{R_2^3(t)} - 2\right]} . \tag{14}$$

With account for (14) we can rewrite expressions (6) and (10) for $v_g(t, r)$ and $v_f(t, r)$ in the form

$$v_f(t, r) = \frac{R_2(t)}{r}\left[\frac{\dfrac{D_g}{\rho_{g0}} \dfrac{\partial c_g(t, R_2(t))}{\partial r} + \dfrac{D_v}{\rho_f}(1-\beta)\left(1 + m\dfrac{R_c}{R_2(t)}\right)\dfrac{R_1^2(t)}{R_2^2(t)} \dfrac{\partial c_v(t, R_1(t))}{\partial r}}{1 + \dfrac{mR_c}{3R_2(t)}\left[(1-\beta)\dfrac{R_1^3(t)}{R_2^3(t)} - 2\right]} - \frac{D_v}{\rho_f}\frac{\partial c_v(t, R_2(t))}{\partial r}\right], \tag{15}$$

$$v_g(t, r) = \frac{R_2(t)}{r\left[1 + m\dfrac{R_c}{R_2(t)}\right]}\left\{\frac{1 + \dfrac{mR_c}{R_2(t)}\left[1 + \dfrac{r^2}{R_2^2(t)}\right]}{1 + \dfrac{mR_c}{3R_2(t)}\left[(1-\beta)\dfrac{R_1^3(t)}{R_2^3(t)} - 2\right]}\left[\frac{D_g}{\rho_{g0}} \frac{\partial c_g(t, R_2(t))}{\partial r} + \frac{D_v}{\rho_f}(1-\beta)\left(1 + m\frac{R_c}{R_2(t)}\right)\times\right.\right.$$

$$\left.\left.\times\frac{R_1^2(t)}{R_2^2(t)} \frac{\partial c_v(t, R_1(t))}{\partial r}\right] - \frac{D_v}{\rho_{g0}}\frac{\partial c_g(t, R_2(t))}{\partial r}\right\} . \tag{16}$$

Summing up what has been said above, we formulate the problem in a general statement in the form of the system of equations consisting of (1) and (2) to which we add the following equations:

$$\dot{R}_1(t) = \frac{D_v}{\rho_f}\frac{\partial c_v(t, R_1(t))}{\partial r} , \tag{17}$$

$$\dot{R}_2(t) = \frac{\dfrac{D_g}{\rho_{g0}} \dfrac{\partial c_g(t, R_2(t))}{\partial r} + \dfrac{D_v}{\rho_f}(1-\beta)\left(1 + m\dfrac{R_c}{R_2(t)}\right)\dfrac{R_1^2(t)}{R_2^2(t)} \dfrac{\partial c_v(t, R_1(t))}{\partial r}}{1 + \dfrac{mR_c}{3R_2(t)}\left[(1-\beta)\dfrac{R_1^3(t)}{R_2^3(t)} - 2\right]} , \tag{18}$$

where $v_f(t, r)$ and $v_g(t, r)$ are determined by relations (15) and (16).

The initial conditions have the form

$$t=0:\quad \begin{cases} c_g(0,r)=k_H\left[p_a+p_c\dfrac{R_c}{R_2(0)}\right], & r\in[R_2(0),R_c]\,; \\ c_v(0,r)=\rho_s, & r\in[R_1(0),R_2(0)]\,; \\ R_1(0)=\delta\,; \\ R_2(0)=R_0\,. \end{cases} \tag{19}$$

The boundary conditions are written as follows:

$$r=R_1(t):\quad c_v(t,R_1(t))=\rho_s\exp\left(-\gamma\frac{R_c}{R_1(t)}\right), \tag{20}$$

$$r=R_2(t):\quad \begin{cases} c_v(t,R_2(t))=\rho_s\exp\left(-\gamma\dfrac{R_c}{R_2(t)}\right), \\ c_g(t,R_2(t))=k_H\left[p_a\left(1+\dfrac{mR_c}{R_2(t)}\right)+p_{v0}-p_s\right], \end{cases} \tag{21}$$

$$R=R_c:\quad c_g(t,R_c)=k_Hp_a\,. \tag{22}$$

Simplification of the Model. In the complete formulation, the problem in question contains two small parameters: $\beta\sim10^2$ and $\gamma\sim10^{-4}$–10^{-5}; therefore, we can simplify it, having set $\beta = 0$ and having linearized the exponents in boundary conditions (20) and (21)*. Furthermore, we reduce the problem to dimensionless form by employing the dimensionless variables

$$\tilde R=\frac{R}{R_c},\quad \tilde r=\frac{r}{R_c},\quad \tilde t=\frac{tD_g}{R_c^2},\quad \tilde c_g=\frac{c_g}{k_Hp_a},\quad \tilde c_v=\frac{c_v}{\rho_s},\quad \tilde v=\frac{vR_c}{D_g}$$

and the parameters

$$\chi_g=\frac{\rho_s}{\rho_g};\quad \chi_f=\frac{\rho_s}{\rho_f};\quad \chi_D=\frac{D_g}{D_v}\,.$$

Then instead of Eqs. (1), (2), (17), and (18) and (15) and (16) we obtain respectively

$$\frac{\partial\tilde c_g(\tilde t,\tilde r)}{\partial\tilde t}+\tilde v_f(\tilde t,\tilde r)\frac{\partial\tilde c_g(\tilde t,\tilde r)}{\partial\tilde r}=\frac{1}{\tilde r^2}\frac{\partial}{\partial\tilde r}\left[\tilde r^2\frac{\partial\tilde c_g(\tilde t,\tilde r)}{\partial\tilde r}\right],\quad \tilde r\in[\tilde R_2(\tilde t),1]\,;$$

$$\chi_D\left[\frac{\partial\tilde c_v(\tilde t,\tilde r)}{\partial\tilde t}+\tilde v_g(\tilde t,\tilde r)\frac{\partial\tilde c_v(\tilde t,\tilde r)}{\partial\tilde r}\right]=\frac{1}{\tilde r^2}\frac{\partial}{\partial\tilde r}\left[\tilde r^2\frac{\partial\tilde c_v(\tilde t,\tilde r)}{\partial\tilde r}\right],\quad \tilde r\in[\tilde R_1(\tilde t),\tilde R_2(\tilde t)]\,;$$

$$\dot{\tilde R}_1(\tilde t)=\frac{\chi_f}{\chi_D}\frac{\partial\tilde c_v(\tilde t,\tilde r)}{\partial\tilde r}\,;$$

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* We cannot set $\gamma = 0$, since in this case the mechanism of recondensation in question drops out.

$$\dot{\tilde{R}}_2(\tilde{t}) = \frac{\beta \dfrac{\partial \tilde{c}_g(\tilde{t}, \tilde{R}_2(\tilde{t}))}{\partial \tilde{r}} + \dfrac{\chi_f}{\chi_D} \dfrac{\tilde{R}_1^2(\tilde{t})}{\tilde{R}_2^2(\tilde{t})} \left(1 + \dfrac{m}{\tilde{R}_2(\tilde{t})}\right) \dfrac{\partial \tilde{c}_v(\tilde{t}, \tilde{R}_1(\tilde{t}))}{\partial \tilde{r}}}{1 + \dfrac{m}{3\tilde{R}_2(\tilde{t})} \left[\dfrac{\tilde{R}_1^3(\tilde{t})}{\tilde{R}_2^3(\tilde{t})} - 2\right]} ;$$

$$\tilde{v}_f(\tilde{t}, \tilde{r}) = \frac{\tilde{R}_2(\tilde{t})}{\tilde{r}} = \left[\frac{\beta \dfrac{\partial \tilde{c}_g(\tilde{t}, \tilde{R}_2(\tilde{t}))}{\partial \tilde{r}} + \left(1 + \dfrac{m}{\tilde{R}_2(\tilde{t})}\right) \dfrac{\tilde{R}_1^2(\tilde{t})}{\tilde{R}_2^2(\tilde{t})} \dfrac{\chi_f}{\chi_D} \dfrac{\partial \tilde{c}_v(\tilde{t}, \tilde{R}_1(\tilde{t}))}{\partial \tilde{r}}}{1 + \dfrac{m}{3\tilde{R}_2(\tilde{t})} \left[\dfrac{\tilde{R}_1^3(\tilde{t})}{\tilde{R}_2^3(\tilde{t})} - 2\right]} - \frac{\chi_f}{\chi_D} \frac{\partial \tilde{c}_v(\tilde{t}, \tilde{R}_2(\tilde{t}))}{\partial \tilde{r}}\right] ; \tag{23}$$

$$\tilde{v}_g(\tilde{t}, \tilde{r}) = \frac{\tilde{R}_2(\tilde{t})}{\left[1 + \dfrac{m}{\tilde{R}_2(\tilde{t})}\right] \tilde{r}} \left\{ \frac{1 + \dfrac{m}{2\tilde{R}_2(\tilde{t})} \left[1 + \dfrac{\tilde{r}^2}{\tilde{R}_2^2(\tilde{t})}\right]}{1 + \dfrac{m}{3\tilde{R}_2(\tilde{t})} \left[\dfrac{\tilde{R}_1^3(\tilde{t})}{\tilde{R}_2^3(\tilde{t})} - 2\right]} \left[\beta \frac{\partial \tilde{c}_g(\tilde{t}, \tilde{R}_2(\tilde{t}))}{\partial \tilde{r}} + \frac{\chi_f}{\chi_D} \left(1 + \frac{m}{\tilde{R}_2(\tilde{t})}\right) \frac{\tilde{R}_1^2(\tilde{t})}{\tilde{R}_2^2(\tilde{t})} \times \right.\right.$$

$$\left.\left. \times \frac{\partial \tilde{c}_v(\tilde{t}, \tilde{R}_1(\tilde{t}))}{\partial \tilde{r}}\right] - \beta \frac{\partial \tilde{c}_g(\tilde{t}, \tilde{R}_2(\tilde{t}))}{\partial \tilde{r}} \right\} .$$

The initial conditions have the form

$$t = 0 : \begin{cases} \tilde{c}_g(0, \tilde{r}) = 1 + \dfrac{p_c}{p_a \tilde{R}_0} , \quad \tilde{r} \in [\tilde{R}_0, 1] ; & (24) \\ \tilde{c}_v(0, \tilde{r}) = 1 , \quad \tilde{r} \in [\tilde{\delta}, \tilde{R}_0] ; & (25) \\ \tilde{R}_1(0) = \tilde{\delta} ; & (26) \\ \tilde{R}_2(0) = \tilde{R}_0 ; & (27) \end{cases}$$

here $\tilde{\delta} = \delta / R_c$.

Boundary conditions (20)–(22) in a form dimensionless and linearized in γ will be written as

$$\tilde r = \tilde R_1(\tilde t):\quad \tilde c_{\rm v}(\tilde t, \tilde R_1(\tilde t)) = 1 - \frac{\gamma}{\tilde R_1(\tilde t)}\,, \tag{28}$$

$$\tilde r = \tilde R_2(\tilde t):\quad \begin{cases} \tilde c_{\rm v}(\tilde t, \tilde R_1(\tilde t)) = 1 - \dfrac{\gamma}{\tilde R_2(\tilde t)}\,, \\ \tilde c_{\rm g}(\tilde t, \tilde R_2(\tilde t)) = 1 + \dfrac{m}{\tilde R_2(\tilde t)} + \chi_{\rm v} + \chi_{\rm s}\,, \end{cases} \tag{29}$$

$$\tilde r = 1:\quad \tilde c_{\rm g}(\tilde t, 1) = 1\,, \tag{30}$$

where $\chi_{\rm v} = p_{\rm v0}/p_{\rm a}$ and $\chi_{\rm s} = p_{\rm s0}/p_{\rm a}$.

In view of the smallness of the parameter χ_D ($\chi_D \sim 10^{-2}$), we can disregard the left-hand side in the second equation of (23) and solve it as the stationary one, considering the time as the parameter. The general solution of such an equation has the form

$$\tilde c_{\rm v}(\tilde t, \tilde r) = -\frac{C_1^*(\tilde t)}{\tilde r} + C_2^*(\tilde t)\,. \tag{31}$$

From boundary conditions (28) and (29) it follows that

$$-\frac{C_1^*(\tilde t)}{\tilde R_1(\tilde t)} + C_2^*(\tilde t) = 1 - \frac{\gamma}{\tilde R_1(\tilde t)}\,;\quad -\frac{C_1^*(\tilde t)}{\tilde R_2(\tilde t)} + C_2^*(\tilde t) = 1 - \frac{\gamma}{\tilde R_2(\tilde t)}\,.$$

Whence

$$C_1^* = \gamma\,,\quad C_2^* = 1\,, \tag{32}$$

and consequently from (31) and (32) we obtain

$$\tilde c_{\rm v}(\tilde t, \tilde r) = -\frac{\gamma}{\tilde r} + 1\,,$$

whence

$$\dot{\tilde R}_1(t) = \frac{\chi_{\rm f}}{\chi_D}\,\frac{\gamma}{\tilde R_1^2(t)}\,. \tag{33}$$

Setting $\delta = 0$ for the sake of simplicity, we write the solution of (33) with account for initial condition (26):

$$\tilde R_1(\tilde t) = \sqrt[3]{3\,\frac{\chi_{\rm f}}{\chi_D}\,\gamma\tilde t}\,.$$

In dimensional form, it takes the form

$$R_1(t) = \sqrt[3]{\frac{6D_{\rm v}\,\sigma\cos\theta}{p_{\rm s}\tau}\left(\frac{\rho_{\rm s}}{\rho_{\rm f}}\right)^2 t} = \sqrt[3]{\frac{6D_{\rm v}\,\sigma\cos\theta\mu_{\rm f}\,\rho_{\rm s}}{\tau R_{\rm g}T\rho_{\rm f}^2}\,t}\,. \tag{34}$$

TABLE 1. Values of the Parameter q_τ for Capillaries of Different Geometry

q_τ, μm^3/sec	123	175	155	173
R_c, μm	760	310	805	800
$R_0 = \tau R_c$, μm	14	14.6	14	14.5

where the left expression has been obtained with the use of the equation of state of the vapor.

Comparison with Experiment. Expression (34) reveals two features that are in qualitative agreement with the properties of the process of filling of conic capillaries observed experimentally. This is, first, the fact that the volume of the liquid in the dead end of the capillary is in proportion to the time (i.e., $R_1^3 \sim t$) or, in other words, the volumetric flow rate of the liquid refilling its column at the vertex of the capillary is constant with time. We can express this flow rate as follows:

$$Q = \frac{dV}{dt} = \frac{d}{dt}\left(\frac{\pi\,(R_1\tau)^2\,R_1}{3}\right) = \frac{d}{dt}\left(\frac{\pi\tau^2}{3}\,R_1^3\right) = \frac{2\pi\tau D_v\,\sigma\cos\theta\mu_f\,\rho_s}{\rho_f R_g T}\,. \tag{35}$$

As we see, the time drops out of this formula and the flow rate remains constant with time.

The other feature is the proportionality of this flow rate to the angle of opening (vertex angle) of the capillary, which is directly exemplified by (35). Such a dependence has been confirmed by experiment.

Nonetheless, there is a significant quantitative difference of the mass flow rates predicted by diffusion-condensation theory from the flow rates observed in experiments.

To compare experimental data for different angles of opening of capillaries it is convenient to calculate the following quantity:

$$q_\tau = \frac{Q}{\tau} = \frac{\pi}{3}\,\frac{\tau R_1^3}{t} = \pi\,\frac{2D_v\,\sigma\cos\theta\mu_f\,\rho_s}{RT\rho_f}\,. \tag{36}$$

When the values of the parameters involved in this formula are $D_v = 2\cdot10^4$ m^2/sec, $\mu_f = 18$, $\sigma = 0.07$ N/m, $\cos\theta = 1$, $\rho_s = 0.026$ kg/m^3, $T = 295$ K, and $\rho_f = 1000$ kg/m^3, we obtain $q_\tau = 0.84$ μm^3/sec for water.

From the data of the experiments conducted in filling different dead-end conic capillaries with water, the parameter q_τ was calculated on the basis of the expression after the second sign of equality in (36). The geometric parameters of the capillaries and the corresponding values of the parameter q_τ are given in Table 1.

As we see, $q_\tau = 0.84$ μm^3/sec differs by more than two orders of magnitude from the experimental values. Consequently, the diffusion flow of the liquid vapor is obviously inadequate to explain the experimentally observed rates of filling of the conic capillaries on the source side of the dead end. This means that it is necessary to search for another mechanism explaining this phenomenon, for example, the film one that has been dealt with earlier. We mention in passing that, although in actual practice the diffusion vapor flow does occur and makes its contribution to the rate of filling of capillaries, nonetheless in considering other mechanisms of this phenomenon we can disregard it since, as has been shown above, its contribution is less than one percent of the flow observed in actual practice. However, the experimental data of [5] demonstrate that for certain (nonpolar) liquids no bilateral filling of conic capillaries is observed. To be more precise, we are dealing with the fact that the rate of growth of the inlet column of the liquid due to the dissolution of the gas closed in the capillaries is much higher than the rate of growth of the column at the vertex of the capillary. Apparently, the alternative mechanism of bilateral filling does not work for such liquids. Nonetheless, the above mechanism of recondensation must occur here and can be detected experimentally if we ensure the conditions either inhibiting the growth of the inlet column of the liquid (for example, a poorly soluble gas in the selected pair gas–liquid) or intensifying the process of recondensation (for example, a highly volatile liquid or increased temperature under experimental conditions). In some of such cases it will be required that the complete system (23) be solved.

NOTATION

t, time; c_g and D_g, concentration and diffusion coefficient of the gas dissolved in the liquid; c_v and D_v, concentration and diffusion coefficient of the liquid vapor in the gas cavity; v_f, velocity of the liquid in the column on the source side of the capillary mouth; v_g, velocity of the gas in the gas cavity; r, coordinate (spherical system); R_1 and R_2, coordinates of the menisci; p_a, dry atmospheric pressure; k_H, Henry constant; ρ_s and p_s, density and pressure of the saturated vapor, respectively, at a given temperature; μ_f, molecular weight of the liquid; R_g, universal gas constant; T, temperature; $R_1(0) = \delta$, quantity corresponding to the radius of the meniscus formed before the capillary is submerged in the liquid due to capillary condensation; $R_2(0) = R_0$, initial coordinate of the inlet meniscus; θ, wetting angle; p_{v0}, partial pressure of the liquid vapor in the ambient medium; σ, coefficient of surface tension of the liquid; α and $\tau = \tan \alpha$, angle of opening of the capillary and its tangent; p_{r_c}, pressure of the saturated vapor above the curved surface; ρ, density; p, pressure; $C_1(t)$, $c(t)$, C_1^*, and C_2^*, integration constants; r_c, radius of curvature of the surface; R_c, capillary length; Q, volumetric flow rate of the liquid; $q_\tau = Q/\tau$; V, volume of the liquid in the dead end of the capillary; m, β, γ, χ_g, χ_f, and χ_D, dimensionless parameters. Subscripts: g, gas; v, vapor; f, liquid (fluid); s, saturated; c, capillary; g0, gas at the initial instant of time; v0, vapor in the ambient medium; a, atmosphere.

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