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Fig. 1

Figure 1: Fig. 1

Abstract

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THE MECHANISM OF MOISTURE TRANSFER IN CAPILLARY-POROUS BODIES

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Moisture transfer during evaporation from capillaries can occur not only by vapor diffusion, but also as a result of film motion of the liquid. To estimate the contribution of the latter transfer mechanism to the total moisture flux, the Derjaguin-Nerpin equation can be used (^{1}). The calculations carried out for this purpose were performed for the case of complete wetting of the capillary walls by water and under isothermal conditions, i.e., without taking into account the possible influence of thermal moisture conductivity.

The vapor consumption in a section located at a distance y from the mouth of the capillary (Fig. 1a), according to Stefan' s equation, is

$$G = \frac{\pi r^2 DP}{RT\,(P/P-\varphi)}\,\frac{d\varphi}{dy}\ \text{g/sec}, \tag{1}$$

where φ is the relative humidity of the air; r is the capillary radius; D is the coefficient of vapor diffusion in air; P is atmospheric pressure; P is the partial pressure of saturated vapor at temperature T, and R is the gas constant.

Fig. 1

The amount of moisture moving in the liquid film in the same section is equal to

$$G = -\frac{2\pi r\rho\,(h-h_0)^3}{3\eta}\,\frac{d\Pi}{dy}\ \text{g/sec}, \tag{2}$$

where h is the film thickness and h_0 is the thickness of the adsorption-water layer (boundary phase); ρ is the density and η the viscosity of the moving water; $d\Pi/dy$ is the gradient of the disjoining pressure in the plane film.

By virtue of the continuity of the flux in any section of the capillary:

$$G\ + G\ = G. \tag{3}$$

As a result of evaporation of moisture from the film, an equilibrium vapor pressure is established above its surface, determined from the condition of equality of the potentials in the liquid and vapor phases:

$$\Pi = -\rho RT \ln \varphi - \sigma / r \text{ dyn/cm}^2, \tag{4}$$

where σ/r is the Laplace pressure associated with the curvature of the film in the capillary.* Owing to the small dimensions of the pore space, the values of φ may be regarded as identical within each section, which reduces the problem to a linear one.

* For convenience of calculation, the disjoining and capillary pressures are everywhere taken as positive.

Replacing in equation (2) $d\Pi/dy = -(\rho RT/\varphi)(d\varphi/dy)$ and taking, in accordance with (^{1,2}), $h = \sqrt[3]{K/\Pi^*}$, where K is a constant coefficient depending on the properties of the liquid and the solid substrate (the capillary wall), after substituting (1) and (2) into (3) we obtain the differential equation

$$\frac{2\pi r \rho^2 RT}{3\eta} \int_{\varphi_1}^{\varphi} \frac{\left(\sqrt[3]{\frac{K}{-\rho RT \ln \varphi - \sigma / r}} - h_0 \right)^3}{\varphi} d\varphi + \frac{\pi r^2 DP}{RT} \int_{\varphi_1}^{\varphi} \frac{d\varphi}{P/P_{\text{H}} - \varphi} = \int_0^y G\, dy. \tag{5}$$

Under constant external conditions, determined by the value of the relative humidity of the air in the surrounding medium $\varphi_1 = \text{const}$ and $Y = \text{const}$, the total moisture flow rate is also constant, $G = \text{const}$. The solution of equation (5) for these conditions, after replacing φ by Π according to (4), can be obtained in the form:

$$-y = \frac{2\pi r \rho}{3\eta G} \left[K \ln \frac{\Pi}{\Pi_1} - 9K^{2/3} h_0 \left(\Pi^{1/3} - \Pi_1^{1/3} \right) + 4.5 K^{1/3} h_0^2 \left(\Pi^{2/3} - \Pi_1^{2/3} \right) - h_0^3 (\Pi - \Pi_1) \right] + \frac{\pi r^2 DP}{RTG} \ln \frac{P/P_{\text{H}} -}{P/P_{\text{H}} -} \tag{6}$$

From (5) one can also find a solution for G, carrying out the integration over the limits from φ_1 to φ_2 and from $y_1 = 0$ to $y_2 = Y$.

Differentiating the obtained equation (6) with respect to Π or with respect to φ (replacing Π by φ according to (4)), we find the distribution, arising under the assumptions made, of the potential gradients in the liquid film and in the vapor along the length of the capillary:

$$-\frac{dy}{d\Pi} = \frac{2\pi r\rho}{3\eta G}\,[h(\Pi) - h_0]^3 + \frac{\pi r^2 DP}{\rho R^2 T^2 G\,[(P/P_{\text{H}})\exp[(\Pi + \sigma/r)/\rho RT] - 1]} = F(\Pi); \tag{7}$$

$$\frac{dy}{d\varphi} = \frac{2\pi r\rho^2 RT}{3\eta\varphi G}\,[h(\varphi) - h_0]^3 + \frac{\pi r^2 DP}{RTG\,(P/P_{\text{H}} - \varphi)} = \psi(\varphi), \tag{8}$$

whence $-d\Pi/dy = 1/F(\Pi)$ and $d\varphi/dy = 1/\psi(\varphi)$.

Substituting the values $d\varphi/dy$ and $d\Pi/dy$ into equations (1) and (2), we obtain the expressions of interest to us, determining the contribution of each of the fluxes to the total moisture flux through the capillary:

$$q_{\text{l}} = \frac{G_{\text{l}}}{G} = 1\Big/\left\{\frac{3\eta rDP}{2(\rho RT)^2(h - h_0)^3\,[(P/P_{\text{H}})\exp[(\Pi + \sigma/r)/\rho RT] - 1]} + 1\right\}; \tag{9}$$

$$q_{\text{v}} = \frac{G_{\text{v}}}{G} = 1\Big/\left\{\frac{2(\rho RT)^2(h - h_0)^3(P/P_{\text{H}} - \varphi)}{3\eta\varphi rDP} + 1\right\}. \tag{10}$$

Putting $\Pi = \Pi_1$ and $\varphi = \varphi_1$ in equations (9) and (10), one can find the values $q_{\text{l}1}$ and $q_{\text{v}1}$, corresponding to the share of each of the fluxes in section 1, i.e., at the mouth of the capillary. Taking $\Pi = \Pi_2$ and $\varphi = \varphi_2$, one can in the same way calculate the corresponding values $q_{\text{l}2}$ and $q_{\text{v}2}$ for section 2 at the meniscus (see Fig. 1a). These data make it possible to determine: 1) the amount of moisture evaporating from the surface of the meniscus in the capillary $q_{\text{I}} = q_{\text{v}2}$; 2) the total amount of moisture evaporating inside the capillary from the liquid film, $q_{\text{II}} = q_{\text{l}2} - q_{\text{l}1} = q_{\text{v}1} - q_{\text{v}2}$; 3) the amount of moisture delivered to the mouth of the capillary by the film mechanism, $q_{\text{III}} = q_{\text{l}1}$. In this case $q_{\text{I}} + q_{\text{II}} + q_{\text{III}} = 100\%$. It should be noted that formulas (9) and (10) make it possible to calculate the values q_{v} and q_{l} in any section of the capillary. For this purpose the distribution of Π and φ along the length of the capillary must first be found from equation (6).

Table 1 and Fig. 2 give the results of calculations of q_{I}, q_{II}, and q_{III}, made for a number of values of φ_1 and different capillary sizes. In the calcula- thus it was adopted: $K = 4.9 \cdot 10^{-12}$ dyne • cm (1,3) (for an aqueous solution of $10^{-4}N$ NaCl on glass); $h_0 = 1.5 \cdot 10^{-7}$ cm (1); $D = 0.28$ cm^2/sec (4); $P = 760$ mm Hg; $P_{\text{n}} = 17.54$ mm Hg; $T = 293^\circ$ K; $\rho = 1$ g/cm^3; $\eta = 0.01$ P; $\sigma = 73$ dyne/cm and $R = 0.46 \cdot 10^7$ cm^2/sec^2 · deg. The values of φ_2 were determined from the

* Without allowance for the ion-electrostatic component of the disjoining pressure.

Thomson-Gibbs equation, taking the radius of curvature of the meniscus to be equal to r.

In capillaries of size $r \ll 10^{-5}$ cm the calculations were carried out for the Knudsen regime of vapor transfer. In this case, instead of equation (1), in deriving the calculation formulas the following equation was used

$$G_{\text{p}} = \frac{8\sqrt{\pi}\, P_{\text{n}} r^3}{3\sqrt{2RT}} \frac{d\varphi}{dy}. \tag{11}$$

Table 1

Ratio between the different mechanisms of moisture transfer in capillaries at $\varphi_1 = 0.9$

r, cm	$h_1 \cdot 10^7$, cm	$h_2 \cdot 10^7$, cm	q_{I}, %	q_{II}, %	q_{III}, %
10^{-1}	3.1	188	0.01	99.91	0.08
10^{-2}	3.1	87.5	0.02	99.17	0.81
10^{-3}	3.1	40.5	0.05	92.4	7.57
10^{-4}	3.1	18.8	0.1	54.8	45.1
10^{-5}	3.14	8.8	0.2	12.0	87.8
10^{-6}	3.79	4.1	0.04	0.06	99.9

The calculation formulas for q and q then take the form

$$q \ \ = 1 \Bigg/ \left\{ \frac{4\pi P r^2 \exp[-(\Pi + \sigma/r)/\rho RT]}{\sqrt{2\pi\rho^2 (RT)^{1/2} (h - h_0)^3}} + 1 \right\}; \tag{12}$$

$$q \ \ = 1 \Bigg/ \left\{ \frac{\sqrt{2\pi\rho^2 (RT)^{3/2} (h - h_0)^3}}{4\pi P r^2 \varphi} + 1 \right\}. \tag{13}$$

In Fig. 2 the results of calculations with allowance for Knudsen vapor transfer are shown by dashed lines.

As is seen from the data given in Table 1, the contribution of moisture evaporating from the surface of the meniscus, q_{I}, is insignificant, which is explained (in sufficiently narrow capillaries) by the influence of the adjoining film, above which a value of the relative humidity of the air close to φ_2 is established. In the case of appreciable pore sizes, when the influence of the liquid film on the formation of the φ gradient in the pore space of the capillary may be neglected, calculations of the amount of evaporated moisture should be carried out by equation (1), taking $d\varphi/dy = \text{const}$, as was done, for example, in (^{4}).

As follows from the data obtained, the processes of evaporation of moisture from the film inside the capillary (q_{II}) and the movement of water in the liquid film (q_{III}) are of primary importance in moisture transfer in capillaries. Figure 2 shows how these values change depending on the size of the capillary and the external conditions (φ_1). Since q_{I} is small, in constructing the graphs it was assumed that $q_{\mathrm{II}} + q_{\mathrm{III}} \simeq 100\%$.

Fig. 2. Values of φ_1: 1 –0.5; 2 –0.7; 3 –0.9; 4 –0.97; 5 –0.99; 6 –0.999

Analysis of the graphs shows that in larger pores the principal transfer mechanism is the evaporation of moisture from the liquid film on the capillary walls; in pores of smaller size, moisture transfer in the liquid film predominates. The role of this transfer mechanism increases still more with increasing φ_1, which is associated with the growth of the film thickness determining its water-conducting capacity. At $\varphi < 0.5$, depletion of the film occurs–

$(h - h_0 \to 0)$, as a result of which movement in the liquid phase toward the mouth of the capillary ceases.

In the transfer of moisture in unsaturated capillary-porous bodies, when the moisture is separated by small air gaps, φ_1 and φ_2 become close in magnitude (see Fig. 1b). In this case, as follows from Fig. 2, the principal mechanism of moisture transfer in the capillaries must be film motion. These data are in good agreement with the results of the work of B. V. Deryagin, S. V. Nerpin, and M. K. Mel' nikova ([2,5]), who were the first to note the essential role of film motion in the processes of moisture transfer in fine-porous bodies. Moisture transfer by means of a successive series of multievaporations and condensations ([6]) is of limited importance here. As follows from the calculations performed, the role of the latter mechanism can be appreciable only in coarse-porous bodies and at low humidities, when the length of the air-conducting pores is sufficiently large.

The data obtained are also in good agreement with the results of experiments on the mechanism of moisture transfer during isothermal drying of peat and clays, carried out with the use of a radioactive label ([7,8]). As a result of considerable shrinkage of these materials during drying, there occurs a sharp decrease in pore size, leading to a change in the transfer mechanism. The predominant transfer of moisture in the form of vapor at the initial stage of drying, which does not lead to a noticeable increase in the specific activity of the surface of the specimen, is gradually replaced by the film mechanism of transfer. This is evidenced by the sharp increase in the specific activity of the surface of the specimen, which occurs as a result of evaporation of water labeled with the indicator, delivered there by a liquid film flow. The change of the transfer mechanism corresponds to the first critical point on the drying-rate curves. The decrease in the drying rate is explained by the lower rate of moisture motion in the liquid film as compared with its transfer through the pore channels in the form of vapor.

The established relationships may also be applied in considering the processes of moisture condensation in porous bodies. The data obtained indicate the possibility of preferential condensation of moisture in the surface film, with its subsequent transfer in the liquid phase to the meniscus, which may substantially affect the kinetics of this process, especially in fine-porous bodies.

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