

MECHANISM OF THE PHENOMENON OF VAPOR  
PERMEABILITY OF POROUS BODIES

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It is shown that the transport of film liquid and capillary condensate makes an important contribution to the coefficient of vapor permeability when the relative humidity in the surrounding medium is high.

Methods [1-7] consisting in the observation of the amount of water evaporated from a vessel covered by a film or layer of the test material into air containing a determined constant humidity  $\varphi_0$  are used for the characterization of vapor permeability. The vapor permeability coefficient  $K$  is determined as the ratio of the amount of moisture evaporated in a steady process to the time of observation and the relative humidity gradient of the air. In a number of reports [1, 2, 5, 6] it has been discovered that with high  $\varphi_0$  the evaporation rate exceeds the rate of vapor diffusion through the pore space. The increased vapor permeabilities may be connected with surface transport of adsorbed material and with capillary condensation.

Let us trace the effect of film flow of liquid over the pore surface on the vapor permeability, representing the porous body as consisting of cylindrical capillaries of radius  $r$ . We solve the one-dimensional isothermal problem (Fig. 1) of the evaporation of liquid from the level  $x = -L$  through the porous body, the lower and upper boundaries of which are  $x = 0$  and  $x = l$ , respectively. Taking the distance  $L$  as small, we neglect the effect of convection in the interlayer of gas between the liquid and the lower boundary of the porous body. Then in the steady state the mass flux in the section  $-L \leq x \leq 0$  is determined by the diffusion equation

$$j = D \frac{1 - \varphi_1}{L} . \quad (1)$$

We allow for convection at the boundary between the porous body and the surrounding medium and we introduce a boundary layer with an effective thickness  $x_0$ , within the limits of which the value of  $\varphi$  varies from  $\varphi_2$  at the upper boundary of the porous body to  $\varphi_0 = \text{const}$  in the surrounding medium. The flux through the boundary layer will equal

$$j = D \frac{\varphi_2 - \varphi_0}{x_0} . \quad (2)$$

Comparing (1) and (2), we obtain

$$\varphi_2 = \varphi_0 + (x_0/L) \cdot (1 - \varphi_1) . \quad (3)$$

Since as a rule  $\varphi_1$  is close to unity and  $x_0 \ll L$ , for simplicity one can take  $\varphi_2 \approx \varphi_0$ , i.e., neglect the resistance of the boundary layer. Because of the linearity of Eq. (3), however, an exact solution can also be obtained, if necessary, when  $\varphi_2 \neq \varphi_0$ . This pertains especially to cases of small  $\varphi_0$ , when one can no longer take  $\varphi_2 \approx \varphi_0$ .

For steady conditions the solution of the problem of internal mass exchange in a porous body is given by the equation

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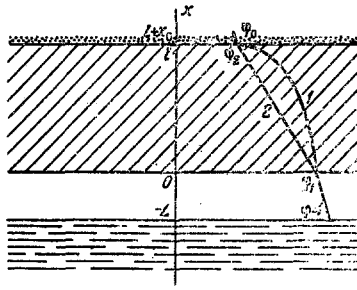


Fig. 1. Distribution of  $\varphi$  over thickness of model of porous body: 1) in the presence of transport in films; 2) with mass transport by vapor diffusion only.

$$j = -mD_*(\varphi) \frac{d\varphi}{dx} = \text{const}, \quad (4)$$

where  $D_*(\varphi)$  is the effective diffusion coefficient, which allows for both the vapor flux and transport in the liquid phase. Let us find an expression for  $D_*(\varphi)$  by considering, as earlier [8-10], the combined flow of film and vapor. For a cylindrical capillary of radius  $r$  the local flux equals

$$q = -\frac{\pi r^2 D \mu}{RT} \cdot \frac{dp}{dx} + \frac{2\pi r \rho h^3}{3\eta} \cdot \frac{d\Pi}{dx} = -\frac{\pi r^2 \mu D_*(\varphi)}{RT} \cdot \frac{d\varphi}{dx}. \quad (5)$$

Here the first term corresponds to the vapor diffusion flux and the second to the viscous flow in a surface film of thickness  $h$  on the assumption that  $h \ll r$ . Assuming that the chemical potentials of the substance in the liquid and gaseous phases are the same in each section, we find an equation connecting  $p$  and  $\Pi$ :

$$\Pi = -\frac{RT}{v_m} \ln \frac{p}{p_s} - \frac{\sigma}{r}. \quad (6)$$

Here  $\Pi$  pertains to a flat film, while  $\sigma/r$  allows for its curvature. As the isotherm of the disjoining pressure we take the dependence

$$\Pi = A/h^3. \quad (7)$$

As is known, an equation of this type, also called the Frenkel'-Halsey-Hill equation [11], is often used to describe polymolecular adsorption for values of  $\varphi$  close to unity.

Using Eqs. (6) and (7), we obtain in place of (5)

$$D_*(\varphi) = D \left[ 1 + (\alpha/r\varphi) \cdot \left( \ln \frac{1}{\varphi} - \frac{\beta}{r} \right)^{-1} \right]; \quad (8)$$

$$\alpha = \frac{2ART}{3\eta D p_s v_m}; \quad \beta = \frac{\sigma v_m}{RT}.$$

This equation gives the dependence of the effective diffusion coefficient  $D_*$  on  $\varphi$ . The values of the isotherm constant  $A$ , the temperature  $T$ , the capillary radius  $r$ , and the viscosity  $\eta$  of the liquid in the film must be known for the calculation of  $D_*(\varphi)$ .

Since  $D_*(\varphi) > 0$  for high  $\varphi$ , it follows from (4) that the function  $\varphi(x)$  has the following properties:  $\varphi'(x) < 0$ ,  $\varphi''(x) < 0$ . Consequently, the values of  $\varphi(x)$  within the porous body vary according to the law shown by curve 1 in Fig. 1. The second term in Eq. (8) approaches zero as  $r \rightarrow \infty$  or in the absence of a surface film ( $A = 0$ ). In this case the distribution  $\varphi(x)$  is linear (straight line 2, Fig. 1), which corresponds to the usual solution of the vapor diffusion problem when  $D = \text{const}$  and  $m = \text{const}$ .

Solving (4), with the fact that  $\ln(1/\varphi) \approx (1-\varphi)/\varphi$  for high  $\varphi$  also being used, we obtain for  $\varphi_1$  the expression

$$\varphi_1 = \varphi_0 + \gamma(1 - \varphi_0) \left\{ 1 + \gamma + \frac{\alpha}{r[1 - \varphi_0 - (\beta\varphi_0/r)]} \right\}^{-1}. \quad (9)$$

As seen from this equation, the values of  $\varphi_1$  decrease with an increase in the contribution of film flow (an increase in the constant  $A$  characterizing the film thickness, a decrease in the capillary radius).

Let us now proceed to find the corresponding expression for the vapor permeability coefficient  $K(\varphi_0)$ :

$$j = K(\varphi_0)(\varphi_1 - \varphi_0)/L. \quad (10)$$

Using (1), we obtain from the latter equation

$$K(\varphi_0) = Dm\gamma(1 - \varphi_1)/(\varphi_1 - \varphi_0). \quad (11)$$

Substituting (9) into (11), we have

$$K(\varphi_0) = Dm\{1 + (\alpha/r)[1 - \varphi_0 - (\beta\varphi_0/r)]^{-1}\}. \quad (12)$$

The solutions obtained above pertain to the region of values of  $\varphi$  close to unity. This is connected both with the assumptions made and with the fact that Eq. (7) describes only the region of polymolecular adsorption. For the usual values of the constant  $A \approx 10^{-14}$  erg [12] the film thickness  $h$  does not exceed one to two layers of molecules when  $\varphi \leq 0.95$ . To perform calculations when  $\varphi < \varphi_k = 0.95$  we neglect the effect of surface diffusion, which is valid for pores of radius  $r > 10^{-6}$  cm, and we will only allow for the vapor diffusion flux. We must then consider that in sufficiently fine pores capillary condensation can set in (primarily on the side facing the water surface). The condition of filling in of a pore is determined by the Kelvin equation

$$1 - \varphi_* = 2\sigma v_m / rRT = \delta / r. \quad (13)$$

It should be noted that the values of  $K(\varphi_0)$  are usually measured going from high values of  $\varphi_0$  to lower values. If the measurements are performed from low to high values, however, one can no longer use Eq. (13), since the effect of hysteresis of the filling-in may appear.

If the value of  $\varphi_*$  which follows from (13) lies between  $\varphi_1$  and  $\varphi_0$  then three zones should be distinguished in the porous body when  $\varphi_0 < \varphi_k$ :

- 1) a "dry zone," where  $\varphi < \varphi_k$ , with the coordinates  $l_0 \leq x \leq l$ ;
- 2) a zone of polymolecular films, where  $\varphi_* > \varphi > \varphi_k$  and  $l_* \leq x \leq l_0$ ;
- 3) a zone of viscous flow in the completely filled part of the capillary  $0 \leq x \leq l_*$ .

In zone 3 the transfer is accomplished under the effect of the capillary pressure gradient, equal to

$$\Delta P / l_* \simeq RT(\varphi_1 - \varphi_*) / v_m l_*.$$

From this we obtain the following expression for the mass flux:

$$j = mRT r^2 (\varphi_1 - \varphi_*) / 8v_m \eta l_*. \quad (14)$$

When the capillaries are completely filled with liquid, which occurs with the condition  $\varphi_0 \geq \varphi_*$ , the vapor permeability coefficient

$$K = mRT r^2 / 8\eta v_m \quad (15)$$

ceases to depend on  $\varphi_0$  and is determined only by the pore radius. It must be kept in mind, however, that in this case the pore radius in accordance with Eq. (13) must not exceed the value  $r_* = 2\sigma v_m / RT(1 - \varphi_0)$ . The vapor permeability coefficient in Eq. (15) is the maximum value of  $K$  for a fixed pore radius. For example,  $K = 0.67$  for  $r = 10^{-5}$  cm and  $K = 67$  for  $r = 10^{-4}$  cm.

Using (1), in zone 1 we obtain

$$mD(\varphi_h - \varphi_0)/(l - l_0) = D(1 - \varphi_1)/L$$

or

$$(\gamma - \gamma_0)(1 - \varphi_1) = \varphi_h - \varphi_0. \quad (16)$$

Replacing  $\varphi_1$  with  $\varphi_*$ ,  $\varphi_0$  with  $\varphi_k$ , and  $\gamma$  with  $\gamma_0 - \gamma_*$  in (9) and using (1), we obtain for zone 2

$$(\varphi_* - \varphi_k) \{1 + (\alpha/r) [1 - \varphi_k - (\beta\varphi_k/r)]^{-1}\} = (1 - \varphi_1)(\gamma_0 - \gamma_*) \quad (17)$$

For the zone of viscous flow, using (14) and (1), we find

$$\gamma_*(1 - \varphi_1) = \varepsilon(\varphi_1 - \varphi_k) \quad (18)$$

Here  $\varepsilon = mRTr^2/8v_m\eta D$ . From (16)-(18) we obtain the following equations:

$$\varphi_1 = 1 - \frac{\varepsilon(1 - \varphi_*)}{(\gamma_* + \varepsilon)}; \quad (19)$$

$$\gamma_0 = \gamma_* + \frac{\Lambda(\gamma_* + \varepsilon)}{\varepsilon D(1 - \varphi_*)}; \quad (20)$$

$$\gamma_* = \frac{\gamma - [(\Lambda + \varphi_k - \varphi_0)/(1 - \varphi_*)]}{1 + [(\Lambda + \varphi_k - \varphi_0)/(1 - \varphi_*)\varepsilon]}; \quad (21)$$

here

$$\Lambda = (\varphi_* - \varphi_k) \{1 + (\alpha/r) [1 - \varphi_k - (\beta\varphi_k/r)]^{-1}\}.$$

The latter equations allow one to conclude that  $\gamma > \gamma_0 > \gamma_*$ ,  $1 > \varphi_1 > \varphi_*$ . When  $\varphi_1 = \varphi_*$  it follows from (19) that  $\gamma_* = 0$ , i.e., the zone of complete filling of the capillaries disappears.

From (21) we find that  $\gamma_* > 0$  when

$$\gamma > (\Lambda + \varphi_k - \varphi_0)/(1 - \varphi_*) \quad (22)$$

and the zone with viscous flow is present up to  $\varphi_0 = \varphi_k + \Lambda - \gamma \times (1 - \varphi_*)$ . But if the condition

$$\gamma > (\Lambda + \varphi_k)/(1 - \varphi_*) \quad (22')$$

is satisfied then this zone is present for any  $\varphi_0$ . When  $\varphi_0 < \varphi_k$  and (22) is satisfied the vapor permeability coefficient from (11) and (19) is

$$K(\varphi_0) = m\gamma D\varepsilon(1 - \varphi_*)/[\gamma_*(1 - \varphi_0) + \varepsilon(\varphi_* - \varphi_0)]. \quad (23)$$

Using (21) and (23), one can show that when the condition

$$\varepsilon > \Lambda/(\varphi_* - \varphi_k) \quad (24)$$

is satisfied, i.e., when the permeability of the filled capillaries is greater than the maximum vapor permeability of the vapor and film,  $K(\varphi_0)$  increases with an increase in the size of the test model; when (24) is not satisfied it decreases. A finite limit (as  $\gamma \rightarrow \infty$ ) exists in any case:

$$\lim K(\varphi_0) = mD[\varphi_k + \Lambda - \varphi_0 + \varepsilon(1 - \varphi_*)]/(1 - \varphi_0). \quad (25)$$

The value  $\varepsilon = 1$  corresponds to  $r = 0.625 \cdot 10^{-5}$  cm.

Now let us consider the case of  $\varphi_* > \varphi_0 > \varphi_k$ ; in this case zone 1, the diffusion of vapor only, will be absent and, using equations analogous to (15)-(16), we find that  $K(\varphi_0)$  is expressed as before by Eq. (23), while

$$\gamma_* = (\gamma - \varepsilon\alpha)/(1 + \alpha). \quad (26)$$

Hence it follows that  $\gamma_* > 0$  with the condition

$$\gamma > \varepsilon\alpha = \frac{(\varphi_* - \varphi_0)}{(1 - \varphi_*)} \{1 + (\alpha/r) [1 - \varphi_0 - (\beta\varphi_0/r)]^{-1}\} = \frac{\Lambda_0}{1 - \varphi_*}. \quad (27)$$

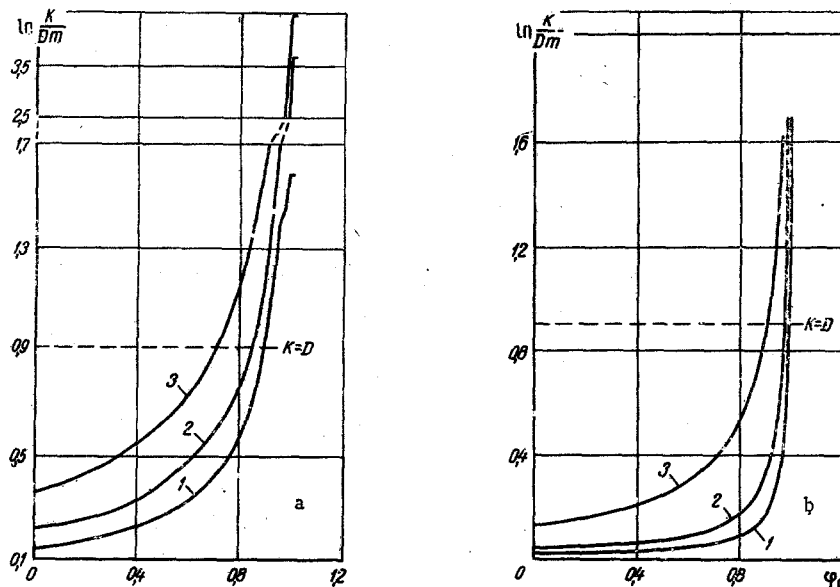


Fig. 2. Vapor permeability coefficient in the presence of transport through vapor, films, and capillaries partially filled with adsorbed liquid, calculated from Eqs. (25) and (28) with  $0 < \varphi_0 < \varphi_k$  and  $\varphi_k < \varphi_0 < \varphi_*$  (a), and vapor permeability coefficient in the presence of transport through vapor and films, calculated from Eqs. (30) and (11) (b): 1)  $r = 0.9 \cdot 10^{-5}$  cm; 2)  $3 \cdot 10^{-5}$  cm; 3)  $6 \cdot 10^{-5}$  cm.

It follows from (27) that  $\kappa = 0$  and  $\gamma_* = \gamma$  when  $\varphi_0 = \varphi_*$ , i.e., the entire capillary is filled and (23) changes into (15) — the equation for  $K$  in the presence of viscous flow. In the case under consideration  $K(\varphi_0)$  increases with an increase in the size of the model when the condition

$$\varepsilon > \Lambda_0 / (\varphi_* - \varphi_0)$$

is satisfied; otherwise,  $K(\varphi_0)$  decreases with an increase in size;

$$\lim_{\gamma \rightarrow \infty} K(\varphi_0) = Dm [\Lambda_0 + \varepsilon(1 - \varphi_*)] / (1 - \varphi_0). \quad (28)$$

The dependence of the vapor permeability coefficient on  $\varphi_0$  calculated from Eqs. (25) and (28) is presented in Fig. 2a. We took  $T = 293^\circ\text{K}$ ,  $\eta = 10^{-2}$  p,  $\sigma = 72$  dyn/cm, and  $m = 0.4$  in the calculation. As was shown in [12], in fine cylindrical capillaries one can take  $A = 8.6 \cdot 10^{-14}$  erg for water on a quartz surface. The results of the calculations showed that these equations are applicable when  $r \geq 0.9 \cdot 10^{-5}$  cm. As seen from Fig. 2a, the values of  $K$  grow with an increase in  $\varphi_0$ , becoming larger than  $D$  under certain conditions. In this case because of the transfer of liquid through the partially filled capillaries and films the porous body has a higher vapor permeability than a layer of air of the same thickness. In addition, Fig. 2a shows that for models of sufficient thickness, i.e., when the conditions (22) are satisfied,  $K(\varphi_0)$  grows with an increase in the pore radius, which is in agreement with experimental studies [5].

The case when the condition (22) is not satisfied remains to be examined. In this case only zones 1 and 2 exist. It is easy to obtain the expression for the vapor permeability coefficient in this case:

$$K(\varphi_0) = m\gamma D \frac{(1 - \varphi_0) + B(1 - \varphi_k)}{(1 - \varphi_0)\gamma + B(\varphi_k - \varphi_0)}, \quad (29)$$

where

$$B = (\alpha/r) [1 - \varphi_k - (\varphi_k \beta / r)]^{-1}.$$

When  $\gamma \gg 1$  but the condition (22) is still not satisfied the contribution of film flow continues to be appreciable even for low  $\varphi_0$ . The expression for  $K(\varphi_0)$  takes the following form:

$$K(\varphi_0) = mD \left\{ 1 + \frac{\alpha(1 - \varphi_h)}{r(1 - \varphi_0)[1 - \varphi_h - (\varphi_h \beta / r)]} \right\}. \quad (30)$$

When  $\varphi_k = \varphi_0$  this expression changes into Eq. (11) obtained earlier.

The dependence of  $K$  on  $\varphi_0$  plotted from Eqs. (11) and (30) for water evaporating in air at atmospheric pressure is shown in Fig. 2b. It is seen from Fig. 2b that in finely porous bodies and with  $\varphi_0$  close to unity the values of  $K$  grow, becoming larger than  $D$  for high  $\varphi_0$ . For example, for water  $K$  becomes larger than  $D$  for  $r = 0.5 \cdot 10^{-5}$  cm when  $\varphi_0 \geq 0.985$ . The phenomenon of anomalously high vapor permeability (analogous to the phenomenon of surface "superconductivity" in the theory of electrokinetic effects [13]) is confirmed experimentally in a number of reports [1, 2, 5, 6].

The appearance within the porous body of a zone where there are no wetting films leads to a decrease in the vapor permeability. If a value of  $\bar{\varphi}_0$  exists such that  $\gamma_0(\bar{\varphi}_0) = 0$ , then  $\varphi_1 < \varphi_k$  when  $\varphi_0 < \bar{\varphi}_0$  and the value of  $K$  ceases to depend on  $\varphi_0$  and is determined by the vapor diffusion flux  $mD$ . But if the conditions (22) or (22') are satisfied, then  $\varphi_1 > \varphi_k = 0.95$  and  $\varphi_1$  depends weakly on  $\varphi_0$  in the surrounding atmosphere. If  $\varphi_0$  is not close to unity, however, then  $\varphi_1$  is almost independent of  $\varphi_0$ . This phenomenon was discovered experimentally earlier but did not receive a proper explanation [7].

We note that the effect of the boundary layer is very important for small  $\varphi_0$ . In the theory presented it is not hard to allow for on the basis of (3) but all the equations become very cumbersome. Quantitatively the allowance for the boundary layer is equivalent to an increase in the thickness of the porous body being tested.

In conclusion, we note that the vapor permeability coefficient, as follows from Eqs. (23) and (29), is a function not only of  $\varphi_0$  but also of  $\gamma$ , i.e., of the size of the model. Therefore, the appropriateness of the use of the limiting equations (25), (28), and (30) must be evaluated from Eqs. (23) and (29) for each specific case.

#### NOTATION

$K$ , vapor permeability coefficient;  $\varphi = p/p_s$ ;  $p$ , water vapor pressure;  $p_s$ , saturated vapor pressure;  $T$ , temperature;  $j$ , flux;  $q$ , flow rate;  $D$ , vapor diffusion coefficient;  $m$ , porosity;  $v_m$ , molar volume of water;  $\rho$ ,  $\sigma$ ,  $\eta$ , density, surface tension, and viscosity of water;  $\Pi$ , disjoining pressure;  $\mu = \rho v_m$ ;  $\gamma = l/mL$ ;  $\gamma_0 = l_0/mL$ ;  $\gamma_* = l_*/mL$ .

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