CALCULATION OF INTERNAL-MASS-TRANSFER COEFFICIENTS IN POROUS BODIES ON THE BASIS OF ADSORPTION ISOTHERMS

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Formulas relating the mass-transfer coefficients in porous bodies to the adsorption isotherms and coefficients of internal diffusion of vapor and adsorbed material are derived.

For a number of materials, for example, polymer dispersions, medicinal preparations, etc., the residual mass content on drying should not exceed a fraction of a percent. The most prolonged stage is the last, which may be called deep drying. It involves the removal of molecules strongly adsorbed on the surface of the solid phase. Accordingly, it is expedient to calculate the rate of deep drying by methods used to solve problems of desorption kinetics (see [1], for example).

The mathematical description of the process differs from the well-known equations of isothermal mass transfer in that, in the theory of sorption processes, the solution is sought in terms of the concentration of vapor c in the pore space:

$$(\partial a/\partial\tau)+(\partial c/\partial\tau)=\nabla(D_i\nabla c);\ j=-D_i\nabla c, \tag{1}$$

whereas in mass transfer it is sought in terms of the mass content U:

$$(\partial U/\partial\tau)=\nabla(a_m\nabla U);\ j=K\nabla\mu. \tag{2}$$

The concentration of adsorbed material a is related to the vapor concentration c by the adsorption equation, which must be given in the form of a function $a = f(c)$ determined theoretically or experimentally. It is evident that

$$a+c=\gamma_0 U;\ U=[f(c)+c]/\gamma_0. \tag{3}$$

In the theory of drying it is usual to assume that $a \gg c$ and to take $U \simeq a/\gamma_0$. However, in the case of deep drying the difference between a and c decreases, and hence it is necessary to use the more general form (3).

For calculations of drying processes, naturally, desorption isotherms should be used. However, in the region of mass contents corresponding to deep drying there is no hysteresis of capillary condensation and the adsorption and desorption branches usually coincide.

At high U (or a) there is evidently serious difficulty in determining D_i, since the main transfer is in the liquid phase. Similar difficulty arises in mass-transfer theory at low U, when the main mechanism of transfer is vapor diffusion. It is therefore expedient to use Eq. (2) for calculations of deep drying. However, since it is desirable to consider the whole of the drying process (from high to low U) in the framework of a single theory, mass-transfer theory may also be extended to the case of low U, determining a_m and K from the kinetic-desorption equations. It is clear that retaining the symbols a_m and K here is of purely formal significance.

As is evident from Eq. (3), c and U are analytically related by the adsorption isotherm. Hence it is also possible to establish relations between a_m and K, on the one hand, and D_i and a(c), on the other, by comparing the mass-flow relations in Eqs. (1) and (2). Thus,

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TABLE 1. Calculation of Internal-Mass-Transfer Coefficients for AR-100 Silica Gel with Specific Surface 640 m^2/g (T = 300°K)

Parameter	Relative vapor pressure p/p_s									
	0,05	0,15	0,25	0,35	0,45	0,55	0,65	0,75	0,85	0,912
U, %	2,8	7,5	11	14	17	20	22,7	26,5	34	45
a, g/cm^3	0,031	0,85	0,123	0,158	0,193	0,225	0,258	0,30	0,385	0,50
$c \cdot 10^5$, g/cm^3	0,05	0,152	0,253	0,355	0,457	0,558	0,66	0,761	0,863	0,965
$\beta \cdot 10^{-4}$	6,12	4,18	3,56	3,40	3,28	3,1	3,4	4,8	12,6	45,2
θ	0,15	0,41	0,60	0,77	0,94	1,1	1,25	1,45	1,9	2,45
$D_s \cdot 10^6$, cm^2/sec	0,85	2,2	3,15	3,8	4,45	5,0	5,4	5,9	6,9	7,95
$(D_K + \beta D_s) \cdot 10^2$	6,3	10,3	12,3	14,0	15,7	16,5	19,5	29,5	88,1	361
$D_i \cdot 10^2$, cm^2/sec	3,15	5,15	6,15	7,0	7,85	8,25	9,7	14,75	44	180.5
$a_m \cdot 10^6$, cm^2/sec	0,515	1,23	1,73	2,06	2,4	2,66	2,85	3,07	3,5	4,0
$K \cdot 10^{18}$, sec · mole/cm^3	0,65	2,2	6,2	10	14,5	18,5	26,0	45,4	154	680
$C_m \cdot 10^{12}$, mole/erg	1,11	2,28	3,24	4,3	5,3	6,1	8,0	13	37	150

multiplying both sides of the first relation in Eq. (2) by γ_0 = const and using Eq. (3), a relation analogous to Eq. (1) is obtained, and hence it follows that

$$a_m = K/c_m\gamma_0 = D_i/(1+\beta). \tag{4}$$

Furthermore, so as to express K in terms of the parameters of Eq. (1), the corresponding expressions for the mass flow j in Eqs. (1) and (2) are compared. Using the known expression for μ [2] and the equation of state of an ideal gas, we have

$$\mu = RT \ln \frac{p_s}{p}; \quad \nabla\mu = \frac{\partial\mu}{\partial p}\nabla p; \quad \frac{\partial\mu}{\partial p} = -\frac{RT}{p}; \quad p = \frac{RTc}{M}.$$

Taking into account this equation, comparison of the expressions for j in Eqs. (1) and (2) gives

$$K = D_i Mp/(RT)^2 = D_i c/RT. \tag{5}$$

Correspondingly, for the specific mass content $C_m = -dU/d\mu$ [2], we obtain

$$C_m = -\frac{d[f(c)+c]}{\gamma_0(\partial\mu/\partial p)\,dp} = \frac{(1+\beta)c}{\gamma_0 RT}, \tag{6}$$

where $\beta = \partial f(c)/\partial c$.

Thus, it is possible using Eqs. (4)-(6) to express all the coefficients of isothermal mass transfer in terms of physical constants, the equation of the adsorption isotherm, and the values of the diffusion coefficient D_i, which may include not only diffusion of vapor in the pore space, but also surface diffusion of adsorbed material:

$$D_i = D_* m = (D + \beta D_s)\, m. \tag{7}$$

In the case of sufficiently fine pores ($r \leq 10^{-5}$ cm), D may be taken to be the coefficient of Knudsen diffusion in a cylindrical capillary:

$$D_K = \frac{8r}{3m}\sqrt{\frac{RT}{2\pi M}}. \tag{8}$$

Thus, to calculate deep-drying processes of a finely porous body it is sufficient to have the equation of the desorption isotherm and the parameters of the porous-body structure.

In Table 1 examples of the calculation of D_i, a_m, K, and c_m for various mass contents U are given for a sample of AR-100 silica gel, for which the adsorption isotherm $a(c)$, the dependence of the surface-diffusion coefficient on the adsorption $D_s(a)$, and the structural parameters are known [3]. The specific surface is S = 640 m^2/g and the porosity m = 0.5. Then the mass of the solid phase in unit volume of sample is $\gamma_0 = \rho(1-m) = 1.13$ g/cm^3, where $\rho = 2.25$ g/cm^3 is the density of the SiO_2 solid phase. The mean radius of the cylindrical pores $r = 2m/S\gamma_0 = 14$ Å. From Eq. (8), D_K for the values of r considered is found to be $1.1 \cdot 10^{-2}$ cm^2/sec for water at T = 300°K.

The first row of Table 1 gives values of U corresponding to different values of the relative vapor pressure p/p_s of the sample. These values were obtained using the graph of the adsorption isotherm in [3]. The next rows give values of a and c calculated from the formulas

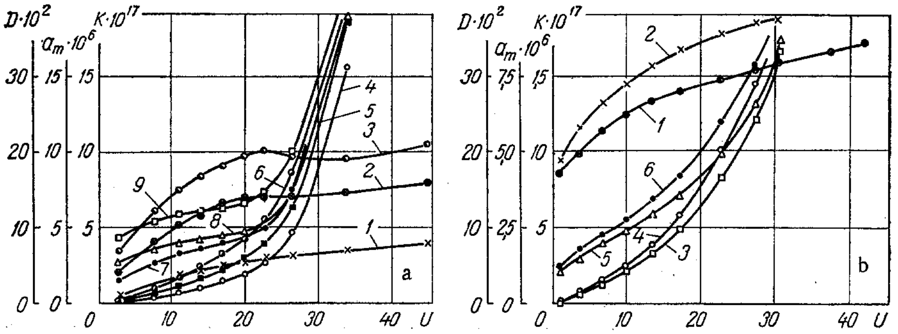

Fig. 1. Curves (calculated from adsorption isotherms) of the internal-mass-transfer coefficients a_m, cm²/sec, K, sec•(mole/cm³), and D_i, cm²/sec, against the moisture content U, %: a) AR-100 silica gel (curves 1, 4, 7: S = 640 m²/g, m = 0.5, r = 14 Å, j_0 = 1.13 g/cm³; curves 2, 5, 8: S = 344 m²/g, m = 0.7, r = 60 Å, j_0 = 0.68 g/cm³; curves 3, 6, 9: S = 206 m²/g, m = 0.7, r = 100 Å, j_0 = 0.68 g/cm³); a_m is shown in curves 1-3, K in curves 4-6, and D_i in curves 7-9; b) ARCC-7 silica gel (curves 1, 3, 5: S = 300 m²/g, m = 0.7, r = 70 Å, j_0 = 0.68 g/cm³; curves 2, 4, 6: S = 206 m²/g, m = 0.7, r = 100 Å, j_0 = 0.68 g/cm³); a_m is shown in curves 1 and 2, K in curves 3 and 4, and D_i in curves 5 and 6.

$$a \simeq \gamma_0 U; \tag{9}$$

$$c = \frac{mMp_s}{RT}\left(\frac{p}{p_s}\right). \tag{10}$$

Then for each interval of U the ratio $\Delta a/\Delta c$ is calculated. The results for $\Delta a/\Delta c$ are plotted against U. The fourth row of Table 1 gives smoothed (after drawing a smooth curve) values of $\beta = da/dc$.

The values of the surface-diffusion coefficient D_s are also taken from [3], where they are given as a function of the number of statistical monolayers of adsorbate θ. The monolayer thickness for water is taken equal to the mean molecular diameter 2.86 Å. Then βD_s is calculated and hence $D_K + \beta D_s$, and finally Eq. (7) gives D_i as a function of U.

The internal-mass-transfer coefficients are then calculated from Eqs. (4)-(6). The curves of D_i, a_m, and K against the moisture content U obtained are shown in Fig. 1. Curves 1, 4, and 7 in Fig. 1a refer to the sample of AR-100 silica gel for which the results shown in Table 1 were obtained. Analogous calculations on the basis of the same primary data (adsorption isotherms, dependences of the surface-diffusion coefficient on the mass content) were also carried out for other values of the structural parameters: S = 344 m²/g, m = 0.7, and r = 60 Å (curves 2, 5, and 8, Fig. 1a) and S = 206 m²/g, m = 0.7, and r = 100 Å (curves 3, 6, and 9, Fig. 1a). Here the main interest was in the effect of the pore structure on the curves of $D_i(U)$, $a_m(U)$, and K(U).

As is evident from a comparison of the curves in Fig. 1, a_m, K, and D_i increase with increase in the mean pore radius. The effect of change in pore radius is greatest at low mass contents.

The results shown in Fig. 1b are of analogous calculations for a sample of ARCC-7 silica gel, which differs in the form of the adsorption isotherm [3]. The adsorption isotherm $U(p/p_s)$ for AR-100 silica gel has a plateau. The initial convex section of the isotherm changes after the plateau into a concave section. For ARCC-7 silica gel the isotherm is entirely concave; with increase in p/p_s, U increases monotonically. Comparison of the curves of $a_m(U)$ in Fig. 1a and Fig. 1b shows that the form of the isotherm affects the form of the dependence $a_m(U)$. For AR-100 the value of a_m passes through a maximum, and for ARCC-7 it increases monotonically with increase in moisture content.

The investigation carried out shows that it is possible, in principle, to determine the coefficients of internal mass transfer on the basis of adsorption isotherms, pore dimensions, and surface-diffusion coefficients. The theory developed allows the effect of these basic characteristics of porous bodies on the transfer properties to be traced. By altering the adsorptive capacity and porosity of the structure of the samples, it is possible to change the transfer coefficients in the required direction and so create optimal conditions for the drying process.

NOTATION

S, specific surface, m^2/g; m, porosity; ρ, density of solid phase, g/cm^3; r, pore radius, cm; D_S, surface-diffusion coefficient, cm^2/sec; D, vapor-diffusion coefficient, cm^{-2}/sec; a, mass of adsorbed material per unit volume of porous body, g/cm^3; γ_0, mass of solid phase per unit volume of porous body; R, universal gas constant, erg/mole; T, absolute temperature, °K; M, mass of a mole of evaporating material, g/mole; U, mass content, g/g of solid phase; $\beta = da/dc$, adsorption-isotherm parameter; c, mass of vapor in pore space per unit volume of porous body, g/cm^3; D_i, effective internal-diffusion coefficient, cm^2/sec; a_m, coefficient of liquid diffusion, cm^2/sec; K, mass-conduction coefficient, $sec \cdot (mole/cm^3)$; C_m, specific mass capacity, mole/erg; p, vapor pressure above adsorbate; p_s, saturated vapor pressure; j, mass flow, $g/(cm^2 \cdot sec)$; θ, number of statistical monolayers of adsorbate; μ, chemical potential, erg/mole; τ, time, sec.

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METHOD OF ESTIMATING CHANGE IN FILTRATIONAL CHARACTERISTICS OF DISPERSE SYSTEMS CAUSED BY WATER-SOLUBLE POLYMERS

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It is shown that the filtration coefficients of polymer-modified disperse systems can be determined directly from calculations of their specific surface.

The influence of water-soluble polymers and electrolytes on the permeability of weakly filtering disperse systems (Na forms of montmorillonite) was studied in [1], where the data of filtrational, adsorption, and electron-microscopic investigations were used to construct a mechanism (a physical model) of the interaction of polymer macromolecules with the active centers of clay minerals and the concentrations of these polymers corresponding to maximum permeability were determined.

The main aim of the present work is to generalize the results of investigations of various rock-forming clay minerals, formulating a method of calculating the change in the filtration coefficients of soils on adding organomineral complexes.

In the investigations, natural forms of kaolinite and montmorillonite and the Na form of kaolinite were taken as the clay minerals, and polyacrylamide, K-4, and K-9 were chosen as the polymer additives.

Filtrational, adsorption, and electron-microscopic investigations of the system were carried out.

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