COEFFICIENTS OF ISOTHERMAL MASS TRANSFER IN A POROUS BODY COMPOSED OF SPHERICAL PARTICLES

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The mass transfer coefficients are calculated for a model porous body composed of identical spherical particles. The results apply to low fluid levels in the threshold space.

The gist of the calculation is to determine the relation P(U), which characterizes the state of a fluid in a system composed of spherical particles, and then to determine the mass transfer coefficients for this model body. The first part of the problem is solved rather easily, because corresponding expressions have already been derived for a bulk of capillary liquid condensing at contact surfaces between particles [1-7]. A comparison shows that, within the volume of liquid held by capillary action [4, 6], the rigorous solutions [2, 4, 5] do not differ much from the approximate solutions [1, 3, 6] where a complex meniscus profile has been replaced by a circular arc. We will, therefore, use the appropriate solution in [1] for the volume of liquid at a single contact surface v under a capillary pressure with complete wetting:

$$v=\frac{\pi d^3}{4}\left(\frac{1-\cos\varphi}{\cos\varphi}\right)^2\left[1-\left(\frac{\pi}{2}-\varphi\right)\operatorname{tg}\varphi\right]; \tag{1}$$

$$P=\frac{2\sigma}{d}\cdot\frac{(2\cos\varphi-\cos\varphi\sin\varphi)}{(1-\cos\varphi)(\cos\varphi+\sin\varphi-1)}. \tag{2}$$

We will consider a porous body composed of particles having all the same diameter d (Fig. 1). The number of contacts between each particle and adjacent ones (coordination number N) depends on their packing pattern. For a regular packing this number varies from N = 4 to N = 12, which corresponds to a variation in the system porosity from n = 0.66 to n = 0.26 [8]. For a random packing the value N is a statistical one, corresponding to an average number of contacts per particle. A volume element of the porous medium is contained within the dashed contour line in Fig. 1. Assuming that all contacts are solid, one can express the porosity in terms of the coordination number approximately as follows:

$$n=1-\frac{1}{8}\left(1+\frac{N}{2}\right).$$

The liquid content in the system corresponding to a specific magnitude of the contact angle φ and, consequently, to a specific capillary pressure level P is

$$U=\frac{6vN\rho}{\pi d^3\rho_0\,[1+(N/2)]}+\frac{6h\rho C}{\rho_0 d}. \tag{3}$$

Here the first term represents the quantity of capillary condensate and the second term represents the quantity of film moisture. Coefficient $C = 1-N(1-\cos\varphi)/2$ accounts for the incomplete coverage of a particle surface with film, namely at areas free of capillary moisture only. Just as in [7], the film thickness h will be calculated here with the aid of the breakdown-pressure isotherm for a plane film [9]:

$$h=(A/\Pi)^{1/3}. \tag{4}$$

Considering now only the case of large particles, we may disregard the effect of their surface curvature on the liquid film thickness and the pressure in it. During equilibrium $\Pi = -P$.

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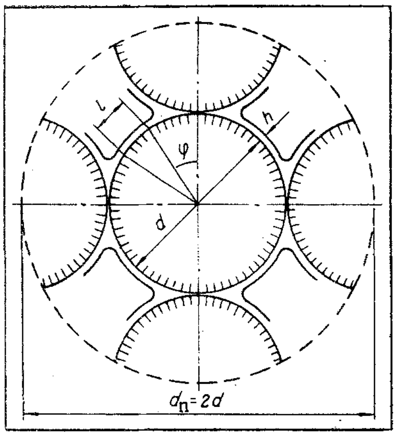

Fig. 1. Section through a model porous body composed of spherical particles with the same diameter d.

These expressions yield the specific mass capacity of a system $c_m = \partial U/\partial P$. In order to calculate the latter, we find the derivatives $\partial U/\partial\varphi$ and $\partial P/\partial\varphi$ from Eqs. (3) and (2) respectively, their ratio then being equal to c_m:

$$c_m = \frac{3\rho d(1-\cos\varphi)}{2\rho_0\sigma\cos^3\varphi(1+N)}\left\{(1-\cos\varphi)\left[\sin\varphi - \frac{(\pi/2)-\varphi}{\cos\varphi}\right] + 2\sin\varphi\left[1-\left(\frac{\pi}{2}-\varphi\right)\operatorname{tg}\varphi\right]\right\}\left[\frac{1+\sin\varphi}{(\cos\varphi+\sin\varphi-1)^2}\right.$$
$$\left. + \frac{\sin\varphi}{(1-\cos\varphi)^2}\right]^{-1} + \frac{6\rho A^{1/3}}{\rho_0 d}\left[\frac{1-(1-\cos\varphi)(N/2)}{3P^{4/3}} - \frac{3\sin\varphi}{P^{1/3}(\partial P/\partial\varphi)}\right]. \tag{5}$$

In Fig. 2a, b are shown $P(U)$ and $c_m(U)$ curves calculated for various particle sizes.

Henceforth we will consider a quartz–water system at T = 293°K with $\rho_0 = 2.7$ g/cm^3, $A = 5\cdot 10^{-13}$ erg [10], n = 0.5, and N = 6. The choice of N = 6 is based on its closeness to the average coordination number of actual contacts for random packed spherical particles [11].

It is evident, according to Fig. 2a, b, that these theoretical P(U) and $c_m(U)$ relations approach the respective relations established experimentally for several porous media [12-15]. Sirotkin has recently found a similarly close agreement between the P(U) relations calculated according to Eqs. (1), (2) and the test data for quartz powders of various dispersivities [7].

It must be noted, however, that calculations according to Eqs. (1), (2) can be made only for moisture contents below a certain critical level U_{cr}, which corresponds to a merger of adjacent capillary interstices and a filling of voids between particles with liquid. As is well known [9], this moisture content corresponds to the critical level of potential P_{cr}. When N = 6, the condition $U < U_{cr}$ corresponds to angles $\varphi < 45°$. For a quartz–water system $U_{cr} \approx 0.031$ g/g. Thus our calculations apply to low moisture contents in the porous space.

According to Fig. 2a, the capillary pressure rises as U drops and, at equal moisture contents, the absolute pressure P is higher in systems with smaller size particles. The presence of film moisture causes pressure P in the porous body to rise sharply as the specific surface enlarges. This can also be recognized on the graph of relation $c_m(U) = dU/dP$. The specific mass capacity becomes lower with smaller particle diameters. As in real porous bodies, c_m becomes lower at lower moisture contents.

The second part of the problem, namely determining the mass transfer coefficient K for the same model, is more difficult to solve. It requires that the mass transfer rate be calculated with the simultaneously occurring vapor diffusion and liquid film flow along the particle surfaces taken into account. The total moisture current can be expressed as

$$q = -\frac{\rho D v_m n_*}{RT}\bar{\nabla} p - \frac{\rho f h^2}{3\eta}\nabla P = -K\overline{\nabla P}, \tag{6}$$

with $n_* = n - \rho_0 U(1-n)(1/\rho)$ denoting the porosity which corresponds to the volume of air-filled pores and f denoting the section area covered with liquid film as a fraction of the total specimen section:

$$f = \frac{6h}{d}C = \frac{6h}{d}\left[1 - \frac{N}{2}(1-\cos\varphi)\right]. \tag{7}$$

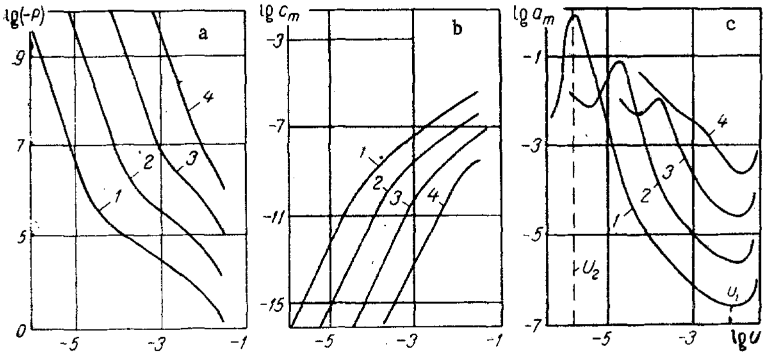

Fig. 2. Capillary pressure P (a), specific mass capacity c_m (b), and liquid diffusivity a_m (c) as functions of the moisture content U in the model system: d = 0.1 cm (1), 0.01 cm (2), 0.001 cm (3), 0.0001 cm (4).

Assuming that the vapor and the liquid in the porous body are in thermodynamic equilibrium, i.e., that $P = (RT/v_m)\ln(p/p_s)$, we find expressions relating the mean gradients of vapor and liquid pressure:

$$\overline{\nabla p} = \frac{p_s v_m \overline{\nabla P}}{RT} \exp\left(\frac{P v_m}{RT}\right). \tag{8}$$

We will consider here that the local gradients of liquid pressure (analogous to the local temperature gradients in [16]) may be higher than the mean gradients, because the hydraulic drag is much higher in the film regions than in the capillary interstices. This is valid, to the first approximation,*, inasmuch as the ratio of mean to local gradient is equal to the ratio of the shortest distance between capillary interstices l at a particle surface (Fig. 1) to the distance between adjacent particle contact points. Then, for N = 6

$$\nabla P/\overline{\nabla P} = 1/[1-(4\varphi/\pi)]. \tag{9}$$

With this correction, we have

$$K = \rho D n p_s \left(\frac{v_m}{RT}\right)^2 \exp\left(\frac{v_m P}{RT}\right) \frac{2\rho A\,[1-3(1-\cos\varphi)]}{\eta P d\,[1-(4\varphi/\pi)]}. \tag{10}$$

This expression follows from (6) after f, h, $\overline{\nabla}$p, and ∇P have been replaced by their respective values from (7), (4), (8), and (9).

Since to every value of φ correspond values of P and U, according to Eqs. (2) and (3) respectively, hence from (10) one can easily calculate K as a function of the moisture content U in the system. It appears also feasible, using expression (5) for the specific mass capacity, to obtain an expression for the diffusivity of liquid as well:

$$a_m = K/c_m\gamma_0 = K/c_m\rho_0(1-n). \tag{11}$$

The diffusivity a_m as a function of the moisture content and of the particle diameter is shown in Fig. 2c for the model quartz–water system. As in real porous bodies [17-19], the function a_m(U)has two extrema: a minimum at some value U_1 and a maximum at $U = U_2 < U_1$. At $U > U_1$ both K and a_m increase fast. This is due to the rising liquid level in the interstices after a merger of capillary channels, which rapidly increases the mobility of liquid in the system. Thus, the minimum value of a_m should correspond to the critical moisture potential P_{cr}, at which the capillary moisture becomes interspersed with film moisture [9]. As has been mentioned earlier, $U_{cr} \sim 0.03$ g/g, which agrees closely with the values for U_1 in Fig. 2c.

We note that in a random packing of particles (unlike in a regular packing) the pores will fill with liquid not under a very definite pressure P_{cr} but within a range of pressures P. First the narrowest pores (regions of closest packing), where the transition occurs earlier, will fill up and then the wider pores. For this reason, the mass conductivity K of real materials increases monotonically as the porous space is filled with liquid, until it reaches its maximum value equal to the filtration coefficient. In order to

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*We also do not consider here the deviation from a linear drop in vapor pressure. In order to take this effect into account, it would be necessary to solve the two-dimensional problem of vapor diffusion.

extend the calculation of c_m and a_m to this range of moisture contents, it becomes necessary (as in [12, 13]) to introduce the size distribution function of porous volumes.

The peaking of the $a_m(U)$ curve within the range of low moisture contents has been noted in many experimental studies [13, 17, 18, 20-22]. According to calculations, the physical cause of this trend is the weaker vapor diffusion current at lower moisture contents. This, in turn, is due to the reduced partial vapor pressure following a strengthened bond between the liquid and the solid phase. We will illustrate this on the $a_m(U)$ relation for small values of U, with no meniscal vapor present and with a negligible effect of film transport.* In that case only the second term is retained in Eq. (2), which yields for a (4)-type isotherm:

$$P = -\frac{A}{U^3}\left(\frac{6\rho}{\rho_0 d}\right)^3; \tag{12}$$

$$c_m = \frac{U^4}{3A}\left(\frac{\rho_0 d}{6\rho}\right)^3; \tag{13}$$

$$a_m = \frac{3A\rho D p_s n}{\rho_0 U^4(1-n)}\left(\frac{v_m}{RT}\right)^2\left(\frac{6\rho}{\rho_0 d}\right)^3 \exp\left[-\frac{v_m A}{RTU^3}\left(\frac{6\rho}{\rho_0 d}\right)^3\right]. \tag{14}$$

The exponential factor in (14) characterizes the decrease in partial vapor pressure above the adsorbed moisture. As the moisture content decreases, a_m first increases with $1/U^4$ and then begins to decrease because of the faster decreasing exponential factor.

The moisture content U_2 corresponding to the maximum diffusivity will be found from the condition that $da_m/dU = 0$:

$$U_2 = \frac{3\rho}{\rho_0 d}\left(\frac{3v_m A}{RT}\right)^{1/3}. \tag{15}$$

As the size of particles decreases, according to (15), the value of U_2 should shift toward higher moisture contents (Fig. 2c). Inserting the value of U_2 from (15) into (12), we obtain $P_2 = -4/(RT/v_m)$ and this yields $p_2/p_s = 0.263$ for water. At such a water pressure, which corresponds to a $\theta \sim 1.3$ fill in a monolayer of water molecules on the quartz surface [23], the diffusivity becomes maximum beyond the range where it depends on the particle size.

These calculations are approximate (especially within the $U \to 0$ range) however, inasmuch as the adsorption of water on the surface of quartz particles cannot be described by a single isotherm (4). The applicability of this isotherm is limited to the range of relatively thick films. At some pressure level Π_* or p_* the wetting film becomes instantly thinner and this indicates a transition to a different kind of adsorption isotherm [9, 24]. For water on quartz, therefore, one can use an isotherm of polymolecular adsorption according to Deryagin and Zorin [25, 26] within the pressure range $p_*/p_s > 0.95$ but isotherms of monomolecular adsorption [23, 27] within the range of lower pressures. Preliminary estimates indicate that, as $U \to 0$, a_m remains constant in the case of a linear Henry isotherm, but increases in the case of a bending isotherm (e.g., a Langmuir isotherm). Only in the case of a bending Kiselev isotherm [27] accounting for the adsorbate–adsorbent interaction does a_m decrease when $U \to 0$, as usually noted in practice. The trend of the $a_m(U)$ relation within the range of very low moisture contents is determined by the specific shape of the adsorption isotherms.

The proposed method yields analytical expressions for the coefficients of isothermal mass transfer in systems composed of identical spherical particles. It may be extended also to polydisperse systems.

Analogous calculations were made earlier by Lykov for a simpler model of a porous body: nonintersecting cylindrical capillaries of diverse radii [12, 13]. Those calculations were most successfully applied to the range of high liquid levels in the threshold space. Our solutions yield analytical expressions for the transfer coefficients for disperse (granular) bodies with moderate moisture contents. They make it possible to theoretically analyze the structural characteristics of a system (size of particles, mode of packing) as well as the nature of interaction between the liquid and the solid phase. This again makes it feasible, in principle, to predict the optimum structural characteristics and mass transfer modes in various technological processes.

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* An almost stationary adsorption film remains on the particle surfaces.

NOTATION

P	is the capillary pressure, dyn/cm^2;
U	is the moisture content, g/g solid phase;
v	is the volume of contact interstice, cm^3;
d	is the diameter of particle, cm;
d_n	is the diameter of an elementary volume in the porous body;
σ	is the surface tension of liquid, dyn/cm;
φ	is the angle between a line connecting the centers of two particles and a radius pointing toward the capillary contact between capillary moisture and surface film;
ρ	is the density of liquid, g/cm^3;
ρ_0	is the density of solid phase, g/cm^3;
h	is the film thickness, cm;
Π	is the film breakdown pressure, dyn/cm^2;
A	is the constant in the breakdown-pressure isotherm, erg;
q	is the moisture current, $g/cm^2 \cdot sec$;
D	is the vapor diffusivity, cm^2/sec;
p	is the vapour pressure, dyn/cm^2;
R	is the gas constant, $erg/mole \cdot {}^\circ K$;
T	is the absolute temperature;
η	is the kinematic viscosity of liquid, $dyn \cdot sec/cm^2$;
K	is the mass conductivity, sec;
v_m	is the molar volume of liquid, $cm^3/mole$;
p_s	is the saturated-vapor pressure, dyn/cm^2;
c_m	is the specific mass capacity, cm^2/dyn;
a_m	is the liquid diffusivity, cm^2/sec;
$\overline{\nabla P}$	is the mean gradient of liquid pressure, dyn/cm^3;
∇p	is the local gradient of liquid pressure, dyn/cm^3;
γ_0	is the mass of solid phase per unit volume, g/cm^3.

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