INTERNAL DIFFUSION IN A BIPOROUS SORBENT IN THE CASE OF A RECTANGULAR SORPTION ISOTHERM

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Sorption in a sorbent of biporous structure is considered in the case of a limiting convex – "rectangular" – isotherm. An accurate integral equation for the sorption wave front is obtained. Asymptotic laws of front motion are found for small and large times.

Media of biporous structure consist of randomly distributed particles, the spaces between which form a porous system, while the particles themselves are also porous; such media are often encountered, both naturally and in engineering. In the first approximation soils may be regarded as materials of this type, as may many building materials, sorbents, catalysts, etc. It is of considerable practical interest to investigate diffusion and sorption in these materials. The principles by which equations of mass and heat transfer may be constructed for sorption in such media were outlined in [1, 2].

The equations of internal diffusion in sorbents of biporous structure containing micro- and macropores (granular zeolites, active charcoal) were considered in [3-5]. The analogous equations derived in [3] describe the sorption of dyes on fibers [6] and sorption in composite two-phase polymer materials [7]. The method of moments (see [4, 8], for example) may be used to determine the internal-diffusion coefficients in microporous regions (the porous system within the particles) and transport pores (the porous system within the particles) from experimental kinetic curves in the case of linear sorption isotherms. Sorption in these materials in the case of nonlinear and, in particular, sharply convex sorption isotherms is very important for both practical and research purposes. Such isotherms are characteristic, for example, of the sorption of many materials on sorbents that are widely used in practice, such as granular zeolites and microporous charcoal.

In [9, 10] internal diffusion in a sorbent of biporous structure was considered in the case of a limiting convex – "rectangular" – sorption isotherm, and for real sorbents of large capacity an approximate solution was obtained on the basis of a modified integral-relation method.

Below, an accurate integral equation is obtained for the sorption wave front in the case of a rectangular sorption isotherm and an arbitrary sorbent capacity, together with asymptotic laws of front motion for small and large times. These results are of interest, in particular, for the quantitative interpretation of experiments on the x-ray transmission of zeolite and active-charcoal granules in the sorption of x-ray-contrast materials [11, 12].

Consider a semiinfinite cylindrical sorbent grain with an isolated side surface. In this case, the equation of internal diffusion in a biporous sorbent may be written as follows [3, 9]

$$\frac{\partial a}{\partial t}+\frac{\partial c}{\partial t}=D\,\frac{\partial^2 c}{\partial x^2},\quad 0<x<\infty, \tag{1}$$

$$a=\int_0^t f\,[c\,(x,\ \tau)]\,\varphi'\,(t-\tau)\,d\tau. \tag{2}$$

Here $a(x, t)$ and $c(x, t)$ are the local concentrations of the material being sorbed in the unmoving and moving phases, respectively; $f(c)$, sorption isotherm in the microporous structures (for simplicity, it is assumed here that sorption on the transport-pore walls is small in comparison with sorption in the micropores, which

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is correct in the overwhelming majority of cases); D, diffusion coefficient in the transport pores; $\varphi(t)$, kinetic function of the microporous structures [9], specifying the relative quantity of material being sorbed which is absorbed by the microporous structure under the condition that the concentration of the material on its surface is constant.

Consideration will now be restricted to an approximate function $\varphi(t)$ of the form [9]

$$\varphi(t) = 1 - \exp(-\beta t), \tag{3}$$

where $1/\beta$ is the characteristic relaxation time in the microporous structures (regions), and a rectangular sorption isotherm

$$f(c) = a_0 \chi(c), \tag{4}$$

where $\chi(c)$ is the Heaviside function.

In addition, it is assumed that, initially, the sorbent is free of the material which is to be sorbed, and at the grain boundary, $c = c_0 = \text{const}$.

It is known [9] that for the rectangular isotherm in Eq. (4) at each time $t > 0$ there is a finite region in which $c > 0$. Suppose that $x = h(t)$ is the law governing the motion of the boundaries of this region, i.e., $c > 0$ when $0 \leq x < h(t)$ and $c = 0$ when $x \geq h(t)$. Then

$$c(0, t) = c_0, \; c(x, 0) = a(x, 0) = c[h(t), t] = 0, \; \left(\frac{\partial c}{\partial x}\right)_{x=h(t)} = 0. \tag{5}$$

Essentially, Eqs. (1)-(5) may be regarded as solved after the function $h(t)$ has been determined, since $c(x, t)$ and $a(x, t)$ are easily determined in this case [9]. An integral equation for the function $h(c)$ may be obtained using the approach developed in [13] for the Stofan problem of heat-conduction theory.

The function $\bar{c}(p, t)$ is now defined by the relation

$$\bar{c}(p, t) = \int_0^{h(t)} c(x, t) \operatorname{sh} px dx, \tag{6}$$

where p is a parameter, $p > 0$.

Multiplying Eq. (1) by sinh px, integrating with respect to x from 0 to $h(t)$, and taking account of Eq. (5), the following result is obtained

$$\frac{d\bar{c}}{dt} - Dp^2\bar{c} = Dpc_0 - \int_0^{h(t)} \frac{\partial a}{\partial t} \operatorname{sh} px dx, \; \bar{c}(p, 0) = 0. \tag{7}$$

Hence

$$\bar{c} \exp(-Dp^2 t) = \int_0^t \left[Dpc_0 - \int_0^{h(\tau)} \frac{\partial a}{\partial \tau} \operatorname{sh} px \right] \exp(-Dp^2 \tau) \, d\tau. \tag{8}$$

Passing to the limit as $t \to \infty$ in Eq. (8) gives

$$\int_0^{\infty} \exp(-Dp^2\tau) \, d\tau \int_0^{h(\tau)} \frac{\partial a}{\partial \tau} \operatorname{sh} px dx = \frac{c_0}{p}. \tag{9}$$

At the same time, it follows from Eqs. (2)-(4) that

$$a(x, t) = \beta a_0 \int_0^t \chi[h(\tau) - x] \exp[-\beta(t - \tau)] \, d\tau. \tag{10}$$

Substituting Eq. (10) into Eq. (9), the following equation is obtained for the function $\tau = \tau(x)$ inverse to $h(t)$

$$\int_0^{\infty} \operatorname{sh} xp \exp[-Dp^2 \tau(x)] \, dx = \frac{(\beta + Dp^2) c_0}{\beta p a_0}. \tag{11}$$

Note that setting $\beta = \infty$ in Eq. (11) (the case of a homogeneous porous sorbent) yields the well-known solution $\tau = \alpha x^2$, where α is the root of the algebraic equation

$$\frac{\sqrt{\pi}\, a_0}{2c_0 \sqrt{\alpha D}} \exp\left(\frac{1}{4\alpha D}\right) \operatorname{erf}\left(\frac{1}{2\sqrt{\alpha D}}\right) = 1. \quad (12)$$

The asymptote of $h(t)$ for large t may be found using Eq. (11). Set $\tau(x) = \alpha x^2 + \gamma + g(1/x)$ in Eq. (11), where α is the root of Eq. (12) and the constant γ and the finite function $g(1/x)$ remain to be determined.

Substituting this expression for $\tau(x)$ into Eq. (11) and taking account of Eq. (12), an equation is obtained for $g(1/x)$

$$\int_0^\infty \operatorname{sh} px \exp(-\alpha D p^2 x^2) [1 - \exp(-\gamma D p^2 - D p^2 g)]\, dx = -\frac{D p c_0}{\beta a_0}. \quad (13)$$

To find the value of γ and the asymptote of $g(1/x)$ as $x \to \infty$, suppose that $p \to 0$ in Eq. (13). Expanding $[1 - \exp(-\gamma D p^2 - D p^2 g)]$ in series, the result is substituted into Eq. (13) to give

$$\int_0^\infty \operatorname{sh} xg(p/x) \exp(-\alpha D x^2)\, dx = -\left(\gamma + \frac{1}{\beta}\right)\frac{c_0}{a_0} + \frac{\gamma^2 D p^2 c_0}{2a_0} + o(p^2), \quad p \to 0. \quad (14)$$

Hence it is evident that $\gamma = -1/\beta$, so that Eq. (14) takes the form

$$\int_0^\infty \operatorname{sh} x \exp(-\alpha D x^2)\, g(p/x)\, dx = \frac{D p^2 c_0}{2\beta^2 a_0} + o(p^2), \quad p \to 0. \quad (15)$$

Applying the Mellin transform to Eq. (15) gives

$$M_s[x \operatorname{sh} x \exp(-\alpha D x^2)]\, M_s[g] = F(s), \quad (16)$$

where $M_s[f]$ is the Mellin transform of the function f with the parameter s; $F(s)$ is the Mellin transform of the right-hand side of Eq. (16). According to [15], the following relation holds

$$M_s[x \operatorname{sh} x \exp(-\alpha D x^2)] = \frac{1}{4}(\alpha D)^{-1-\frac{s}{2}}\, \Gamma\left(1 + \frac{s}{2}\right) \Phi\left(1 + \frac{s}{2}, \frac{3}{2}; \frac{1}{4\alpha D}\right),$$

where $\Phi(1 + s/2, 3/2; 1/4\alpha D)$ is a degenerate hypergeometric function. Therefore

$$M_s[g] = 4F(s)(\alpha D)^{1+\frac{s}{2}} / \Gamma\left(1 + \frac{s}{2}\right) \Phi\left(1 + \frac{s}{2}, \frac{3}{2}; \frac{1}{4\alpha D}\right). \quad (17)$$

It is known [14] that the asymptote of the function is determined by the properties of its Mellin transform. Accordingly, if $\nu = \nu(1/4\alpha D)$ is the rightmost root of the function $\Phi(1 + \nu/2, 3/2; 1/4\alpha D)$, then $g \sim Ct^{-\nu}$ as $t \to 0$, where C is the residue of the function $M_s[g]$ at the point $s = \nu$. Analysis of the zero function $\Phi(1 + s/2, 3/2; 1/4\alpha D)$ shows that $\nu < -2$, while $\nu \to -2$ as $(1/4\alpha D) \to \infty$ and $|\nu| \to \infty$ as $(1/4\alpha D) \to 0$. Thus

$$\tau(x) \sim \alpha x^2 - \frac{1}{\beta} + O(x^\nu), \quad x \to \infty. \quad (18)$$

Passing to the function $h(t)$ and confining attention to the first two terms, the following result is obtained as $t \to \infty$

$$h(t) \sim \sqrt{\frac{t}{\alpha}}\left(1 + \frac{1}{2\beta t}\right). \quad (19)$$

Equation (19) allows the time for $h(t)$ to reach the steady value $h_\infty(t) = \sqrt{t/\alpha}$ to be estimated

$$\left|\frac{h(t_0) - h_\infty(t_0)}{h_\infty(t_0)}\right| = \varepsilon, \quad t_0 = \frac{1}{2\beta\varepsilon}.$$

Note that when $a_0 \gg c_0$ Eq. (19) is practically the same as the corresponding expression for $h(t)$ obtained in [9] by the modified integral-relation method. The difference is that in Eq. (19) α is the root of Eq. (12), whereas in [9] $\alpha = a_0/2Dc_0$, i.e., a sufficiently good approximation to the root of Eq. (12) when $a_0 \gg c_0$. The condition $a_0 \gg c_0$ is satisfied for real engineering sorbents, in which the sorption capacity is large. However, this condition is violated in diffusion processes in a number of porous materials where sorption is a second-order accompanying process.

Using Eq. (11), the asymptote of $h(t)$ as $t \to 0$ may now be found. First, Eq. (11) is rewritten in the form

$$\int_0^\infty \operatorname{sh}\left[\sqrt{\frac{s}{D}}\, h(t)\right] \exp(-st)\, h'(t)\, dt = \frac{(\beta+s)\sqrt{D}c_0}{\beta a_0 \sqrt{s}}, \tag{20}$$

where $s = Dp^2$.

Expanding $\sinh[\sqrt{(s/D)}h(t)]$ in a series in powers of its argument, substitution of the result into Eq. (20) gives

$$\sum_{k=1}^\infty \frac{s^k}{(2k)!} \int_0^\infty \left[\frac{h^2(t)}{D}\right]^k \exp(-st)\, dt = \frac{(\beta+s)c_0}{\beta s a_0}. \tag{21}$$

It is assumed that in Eq. (21) the parameter s increases without limit, remaining real. Then, using the inequality $h^2/D < Bt$ when $t > t_1$ (B = const), which follows from Eq. (19), it is not difficult to show that

$$\sum_{k=1}^\infty \frac{s^k}{(2k)!} \int_{t_1}^\infty (h^2/D)^k \exp(-st)\, dt < \frac{1}{s} \exp\left(-\frac{s}{2}\right)$$

when $s \to \infty$, so that Eq. (21) may be written in the form

$$\sum_{k=1}^\infty \frac{s^k}{(2k)!} I_k(s) = \frac{(\beta+s)c_0}{\beta s a_0} + O\left(\frac{1}{s}\exp\left(-\frac{s}{2}\right)\right), \quad s \to \infty,$$
$$I_k(s) = \int_0^{t_1} \left[\frac{h^2(t)}{D}\right]^k \exp(-st)\, dt. \tag{22}$$

Suppose that $h^2(t)/D \sim tQ(\ln 1/t)$ as $t \to 0$, where Q is a growth function of no more than exponential minimum type. Q is found by means of a Mellin transformation with parameter λ:

$$M_\lambda[I_k(s)] = \Gamma(\lambda) \int_0^{t_1} \left[\frac{h^2(t)}{D}\right]^k t^{-\lambda}\, dt,$$

where $\Gamma(\lambda)$ is a gamma function.

In view of the proposed asymptote of $h^2(t)/D$ as $t \to 0$, the function $\int_0^{t_1} (h^2/D)^k t^{-\lambda}\, dt$ is analytic in the region $\operatorname{Re}\lambda < k + 1$ and is analytically continued to the right, meeting the first singularity at the point $\lambda = k + 1$ of the form $BQ^k(1 + k - \lambda)$; BQ^k is a function associated according to Borel with the function Q^k [14]. Hence

$$I_k(s) \sim \frac{k!}{s^{k+1}} Q^k(\ln s), \quad s \to \infty \tag{23}$$

and since

$$\sum_{k=1}^\infty \frac{k!}{(2k)!} x^k = \frac{\sqrt{\pi x}}{2} \exp\left(\frac{x}{4}\right) \operatorname{erf}\left(\frac{\sqrt{x}}{2}\right),$$

Eq. (22) takes the form

$$\frac{\sqrt{\pi Q(\ln s)}}{2} \exp\left[\frac{Q(\ln s)}{4}\right] \operatorname{erf}\left[\frac{\sqrt{Q(\ln s)}}{2}\right] = \frac{c_0 s}{\beta a_0} + \frac{c_0}{a_0} + o(1), \quad s \to \infty. \tag{24}$$

The cases $\beta = \infty$ and $\beta < \infty$ are possible here. When $\beta = \infty$, Eq. (24) is satisfied on setting Q = const, so that Q satisfies the algebraic equation

$$\sqrt{Q} \exp\left(\frac{Q}{4}\right) \operatorname{erf}\left(\frac{\sqrt{Q}}{2}\right) = \frac{2c_0}{\sqrt{\pi} a_0}$$

in accurate agreement with the earlier proposal – Eq. (12).

When $\beta < \infty$, the function $Q(\ln s)$ must satisfy a relation deriving from Eq. (24)

$$Q \exp\left(\frac{Q}{2}\right) = 2A^2s^2[1+o(1)], \quad s \to \infty \quad \left(A^2 = \frac{2c_0^2}{\pi\beta^2 a_0^2}\right).$$

Hence

$$Q(\ln s) = \ln(A^4s^4) - \ln\ln^2(A^2s^2) + o(1), \quad s \to \infty$$

and finally

$$Q\left(\ln \frac{1}{t}\right) = \ln\left[\frac{A^4}{t^4 \ln^2(A^2/t^2)}\right] + o(1), \quad t \to 0. \quad (25)$$

Thus, the asymptote of h(t) for small times takes the form

$$h(t) \sim \left\{2Dt \ln\left[\frac{A^2}{t^2 \ln(A^2/t^2)}\right]\right\}^{\frac{1}{2}}. \quad (26)$$

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