SOLUTION OF THE DIFFUSION EQUATION OF MATERIAL IN A SPHERICAL GRAIN WITH AN ARBITRARY FUNCTION OF CHANGE IN ADSORBATE CONCENTRATION

S. P. Grekov, A. E. Kalyusskii,
N. A. Rodimova, and B. P. Pyasetskii

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A mathematical model of isothermal adsorption in boundary conditions of the third kind, with an arbitrary function expressing the change in adsorbate concentration, is developed. An analytical solution of the problem is presented.

In [1], a solution of the diffusion equation of gas in a sphere with constant adsorbate concentration at its surface and the absence of "sinks" was presented. In [2], sorption of material in the sphere was taken into account by introducing a mass-transfer coefficient β in the boundary condition, while in the initial equation the diffusion coefficient was replaced by some reduced value including the Henry coefficient.

It is suggested in the present work that the physical model of the adsorption of material by the sphere may be more expediently considered as follows. The model of the system consists of adsorbent in the form of a porous particle of radius R, which is placed in a flux of adsorbate. Initially ($\tau = 0$), the adsorbate concentration outside the particle is equal to the concentration inside the pore of the particle, c_0 (in the particular case $c_0 = 0$). When $\tau = 0$ and $c_0 \neq 0$, some of the material is adsorbed at the surface of pores of the particle, and is in equilibrium with the adsorbate inside the pore; the relation between the adsorbed material and that in the free state is taken in accordance with the dependence $a_0 = \gamma c_0$.

Starting at $\tau > 0$, the adsorbate concentration in the flux varies arbitrarily: $c_0(\tau) = f(\tau)$. The adsorbate concentration in the pores of the particle also varies, because of diffusion of material into the sphere from the flux (or, conversely, from the sphere into the flux), and also in connection with sorption (or desorption) of material by the pore surface of the sorbent. Mass transfer at the boundary of the flux with the sphere surface occurs according to Newton's law.

The mathematical formulation of the proposed physical model of the sorption process takes the form

$$\frac{\partial c}{\partial \tau} = \frac{1}{r^2}\psi\frac{\partial c}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right) - \beta(\gamma c - a), \tag{1}$$

$$\frac{\partial a}{\partial \tau} = \beta(\gamma c - a), \tag{2}$$

$$-\frac{\partial c}{\partial r} + H(c_0(\tau) - c(R,\ \tau))|_{r=R} = 0, \tag{3}$$

$$\left.\frac{\partial c}{\partial r}\right|_{r=0} = 0, \tag{4}$$

$$\gamma c(r,\ 0) = a(r,\ 0) = a_0. \tag{5}$$

Laplace transformation of Eqs. (1) and (2), taking the condition in Eq. (5) into account, yields the system of equations

$$(p + \beta\gamma)c^* = \frac{\psi}{r^2}\frac{d}{dr}\left(r^2\frac{dc^*}{dr}\right) + \beta a^* + c_0, \tag{6}$$

$$pa^* - a_0 = \gamma\beta c^* - \beta a^* \tag{7}$$

with the conditions

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$$-\frac{dc^*}{dr}+H(c_0^*-c^*)|_{r=R}=0, \tag{8}$$

$$\left.\frac{dc^*}{dr}\right|_{r=0}=0. \tag{9}$$

Eliminating a^* from Eqs. (6) and (7) gives

$$a^*=\frac{\gamma\beta c^*+a_0}{p+\beta}. \tag{10}$$

$$\frac{\psi}{r^2}\frac{d}{dr}\left(r^2\frac{dc^*}{dr}\right)-p\left(1+\frac{\gamma\beta}{p+\beta}\right)c^*=-c_0\left(1+\frac{\beta\gamma}{p+\beta}\right). \tag{11}$$

The solution of Eq. (11), taking Eq. (9) into account, takes the form

$$c^*=\frac{A\,\mathrm{sh}\,\lambda r}{r}+\frac{c_0}{p}, \tag{12}$$

where

$$\lambda=\sqrt{\frac{p}{\psi}\left(1+\frac{\beta\gamma}{p+\beta}\right)}. \tag{13}$$

Satisfying Eq. (8), the value of A is obtained

$$A=\frac{HR^2\left(c_0^*-\frac{c_0}{p}\right)}{\lambda R\,\mathrm{ch}\,\lambda R+(HR-1)\,\mathrm{sh}\,\lambda R}. \tag{14}$$

Thus, the solution for c* is obtained in the form

$$c^*=\frac{HR^2\left(c_0^*-\frac{c_0}{p}\right)}{\lambda R\,\mathrm{ch}\,\lambda R+(HR-1)\,\mathrm{sh}\,\lambda R}\,\frac{\mathrm{sh}\,\lambda r}{r}+\frac{c_0}{p}. \tag{15}$$

It may be shown, analogously to the proof in [1], that c* is a meromorphic function of p with simple poles at the points where

$$\lambda R\,\mathrm{ch}\,\lambda R+(HR-1)\,\mathrm{sh}\,\lambda R=0, \tag{16}$$

as well as the point $\lambda = 0$.

At the point p = 0, there is no pole. Since Eq. (16) has purely imaginary roots, the following notation is adopted

$$\lambda R=i\mu. \tag{17}$$

Then, the characteristic Eq. (16) takes the form

$$\mu\cos\mu+(HR-1)\sin\mu=0, \tag{18}$$

and the solution in Eq. (15) becomes

$$c^*=\frac{HR^2\left(c_0^*-\frac{c_0}{p}\right)}{S_\mu}\,\frac{\sin\mu\frac{r}{R}}{r}+\frac{c_0}{p}, \tag{19}$$

where

$$S_\mu=\mu\cos\mu+(HR-1)\sin\mu. \tag{20}$$

Let μ_k be the positive roots of Eq. (20). Then it follows from Eq. (13) that

$$p_k(p_k+\beta+\gamma\beta)=-\frac{\psi\mu_k^2}{R^2}(p_k+\beta),$$

$$(p_k+\beta)^2+\left(\gamma\beta-\beta+\frac{\psi\mu_k^2}{R^2}\right)(p_k+\beta)+\beta^2\gamma=0, \tag{21}$$

$$p_k^{(1)} + \beta = -\frac{\gamma\beta - \beta + \frac{\psi\mu_k^2}{R^2}}{2} - \sqrt{\frac{\left(\frac{\psi\mu_k^2}{R^2} + \gamma\beta - \beta\right)^2}{4} + \beta^2\gamma}, \tag{22}$$

$$p_k^{(2)} + \beta = -\frac{\beta\gamma - \beta + \frac{\psi\mu_k^2}{R^2}}{2} + \sqrt{\frac{\left(\frac{\psi\mu_k^2}{R^2} + \beta\gamma - \beta\right)^2}{4} + \beta^2\gamma}. \tag{23}$$

Introducing the notation

$$\sigma_k = \frac{\beta - \gamma\beta - \frac{\psi\mu_k^2}{R^2}}{2}, \tag{24}$$

$$\nu_k = \sqrt{\sigma_k^2 + \beta^2\gamma}, \tag{25}$$

the roots of Eq. (21) may be written in the form

$$p_k^{(1)} = \sigma_k - \nu_k - \beta, \tag{26}$$

$$p_k^{(2)} = \sigma_k + \nu_k - \beta. \tag{27}$$

Adopting the Cauchy residue theorem for the transformation, as shown in [1], it is found that

$$c(r, \tau) = \frac{\psi}{2rR} \sum_{k=1}^{\infty} A_k \frac{\mu_k}{\nu_k} \sin \mu_k \frac{r}{R} \left[(\nu_k - \sigma_k) \left(c_k^{(1)} - \frac{c_0}{p_k^{(1)}} \right) e^{p_k^{(1)}\tau} + (\nu_k + \sigma_k) \left(c_k^{(2)} - \frac{c_0}{p_k^{(2)}} \right) e^{p_k^{(2)}\tau} \right], \tag{28}$$

where

$$c_k^i = \int_0^{\tau} c_0(t)\, e^{-p_k^{(i)} t}\, dt; \tag{29}$$

$$A_k = (-1)^{k+1} \frac{2\mathrm{Bi}\sqrt{(\mathrm{Bi} - 1)^2 + \mu_k^2}}{\mathrm{Bi}^2 - \mathrm{Bi} + \mu_k^2}. \tag{30}$$

Averaging c(r, τ) with respect to r according to the formula

$$\bar{c} = \frac{3}{R^3} \int_0^R c(r, \tau)\, r^2 dr, \tag{31}$$

it is found that

$$\bar{c}(\tau) = \frac{\psi}{2R^2} \sum_{k=1}^{\infty} \frac{\mu_k^2}{\nu_k} B_k \left[(\nu_k - \sigma_k) \left(c_k^{(1)} - \frac{c_0}{p_k^{(1)}} \right) e^{p_k^{(1)}\tau} + (\nu_k + \sigma_k) \left(c_k^{(2)} - \frac{c_0}{p_k^{(2)}} \right) e^{p_k^{(2)}\tau} \right]. \tag{32}$$

The value of $a(\tau)$ is calculated from the formula

$$a(r, \tau) = \left[a_0 + \gamma\beta \int_0^{\tau} c(r, t)\, e^{\beta t} dt \right] e^{-\beta\tau}. \tag{33}$$

Consider the sorption of nitrogen by sandstone. The change in nitrogen concentration in the mixture enclosing the rock sample is taken in accordance with the dependence

$$c_0(\tau) = c_0 + (c_c - c_0)(1 - e^{-\alpha\tau}). \tag{34}$$

Then the solution in Eq. (31) takes the form

$$\begin{aligned} \bar{c}(\tau) = {} & \frac{\psi}{2R^2} \sum_{k=1}^{\infty} \frac{\mu_k^2}{\nu_k} B_k (\nu_k - \sigma_k) \left[\frac{(c_c - c_0)\, e^{p_k^{(1)}\tau}}{p_k^{(1)}} - \frac{c_c}{p_k^{(1)}} + \right. \\ & \left. + \frac{c_c - c_0}{\alpha + p_k^{(1)}} \left(e^{-\alpha\tau} - e^{p_k^{(1)}\tau} \right) \right] + \frac{\psi}{2R^2} \sum_{k=1}^{\infty} \frac{\mu_k^2}{\nu_k} B_k (\nu_k + \sigma_k) \left[\frac{(c_c - c_0)\, e^{p_k^{(2)}\tau}}{p_k^{(2)}} - \frac{c_c}{p_k^{(2)}} + \frac{c_c - c_0}{\alpha + p_k^{(2)}} \left(e^{-\alpha\tau} - e^{p_k^{(2)}\tau} \right) \right], \end{aligned} \tag{35}$$

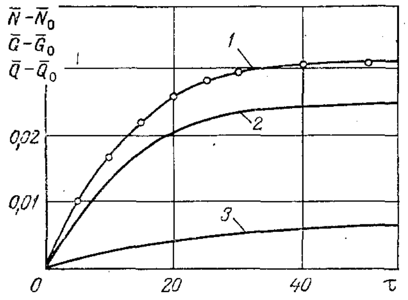

Fig. 1

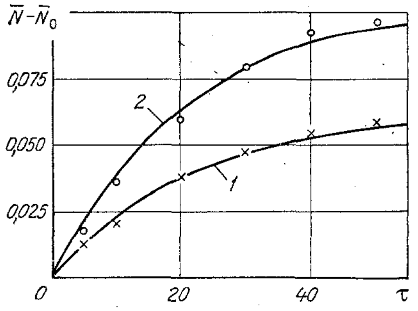

Fig. 2

Fig. 1. Theoretical curves (1-3) of the total amount of absorbed nitrogen, adsorbed gas, and gas filling the pore space, respectively, and experimental data (points) on the total amount of adsorbed nitrogen. τ, h; $\bar{N}-\bar{N}_0$, $\bar{G}-\bar{G}_0$, $\bar{Q}-\bar{Q}_0$, ml/g.

Fig. 2. Theoretical dependence of the total amount of absorbed nitrogen (curves) and experimental results (points) on the sorption of nitrogen by sandstone shale (1) and clay shale (2). τ, h; $\bar{N}-\bar{N}_0$, ml/g.

and the solution in Eq. (33) is written as follows

$$\bar{a}(\tau) = a_0 e^{-\beta\tau} + \gamma\beta \frac{\psi}{2R^2} \sum_{k=1}^{\infty} \frac{\mu_k^2}{\nu_k} B_k \frac{\nu_k - \sigma_k}{p_k^{(1)} + \beta} \left[\frac{e^{p_k^{(1)}\tau}}{p_k^{(1)}} (c_e - c_0) - \right.$$
$$- \frac{c_c}{p_k^{(1)}} + \frac{c_c - c_0}{\alpha + p_k^{(1)}} (e^{-\alpha\tau} - e^{p_k^{(1)}\tau}) + \frac{c_c}{\beta}(e^{-\beta\tau} - 1) - \frac{c_c - c_0}{\alpha - \beta}(e^{-\alpha\tau} - e^{-\beta\tau}) +$$
$$\left. + \frac{c_0}{p_k^{(1)}} e^{-\beta\tau} \right] + \gamma\beta \frac{\psi}{2R^2} \sum_{k=1}^{\infty} \frac{\mu_k^2}{\nu_k} B_k \frac{\nu_k + \sigma_k}{p_k^{(2)} + \beta} \left[\frac{e^{p_k^{(2)}\tau}}{p_k^{(2)}} (c_c - c_0) - \frac{c_c}{p_k^{(2)}} + \right.$$
$$\left. + \frac{c_c - c_0}{\alpha + p_k^{(2)}} (e^{-\alpha\tau} - e^{p_k^{(2)}\tau}) + \frac{c_c}{\beta}(e^{-\beta\tau} - 1) - \frac{c_c - c_0}{\alpha - \beta}(e^{-\alpha\tau} - e^{-\beta\tau}) + \frac{c_0}{p_k^{(2)}} e^{-\beta\tau} \right]. \tag{36}$$

The experimental data of [3] on the sorption kinetics of nitrogen by sandstone are used. Before the experiment, the rock samples were kept in air, and therefore, it may be assumed that the N_2 concentration in the sorbent process was the same as in the surrounding air, i.e., $987.5 \cdot 10^3$ mg/m^3. According to the data of [3], c_c was $1120 \cdot 10^3$ mg/m^3.

It is assumed here, as in the formulation of the physical model, that loss of nitrogen from the mixture surrounding the sorbent occurs as a result of filling of the pore space and its adsorption at the surface of the pore walls. Then the relative amount of N_2 filling the rock pores is

$$\bar{Q} = \frac{V^{\varepsilon}}{\gamma_D} \bar{c}(\tau), \tag{37}$$

and the amount of adsorbed N_2 is

$$\bar{G} = \frac{V^{\varepsilon}}{\gamma_D} \bar{a}(\tau). \tag{38}$$

Theoretical curves of $\bar{Q}$, $\bar{G}$, and the total amount of absorbed nitrogen $\bar{N}$ are shown in Fig. 1, together with the experimental data of [3]. In the calculations, the following parameter values were assumed: $H = 15$ m^{-1}; $\psi = 2.5 \cdot 10^{-9}$ m^2/sec; $\beta = 3 \cdot 10^{-4}$ sec^{-1}; $R = 0.009$ m; $\varepsilon = 0.15$; $\gamma_D = 2.6$ ton/m^3; $\alpha = 5.2 \cdot 10^{-4}$ sec^{-1}; $\gamma = 4.6$; $\gamma_V = 0.8 \cdot 10^{-6}$ m^3/mg.

The mean-square deviation of the experimental data from the theoretical results over the entire sorption period was 0.0006 ml/g, and the variation coefficient was 0.23%. From this it may be concluded that the agreement of the proposed dependences with the experimental data is good.

The given mathematical model of the absorption of material by a sphere was also used in the analysis of experiments on the sorption of nitrogen by other rocks – sandstone and clay shales. The theoretical curves reflecting the dependence of the total amount of nitrogen absorbed on the sorption time and the experimental data of [3] are shown in Fig. 2. In the calculations, the parameter values assumed for sandstone shale were: $R = 0.009$ m; $\varepsilon = 0.15$; $\gamma_V = 0.8 \cdot 10^{-6}$ m^3/mg; $\gamma_D = 2.6$ tons/m^3; $\alpha = 5.2 \cdot 10^{-4}$ sec^{-1}; $H = 15$ m^{-1}; $\psi = 4 \cdot 10^{-9}$ m^2/sec; $\beta = 1.8 \cdot 10^{-4}$ sec^{-1}; $\gamma = 8.8$; those assumed for the clay shale were; $R = 0.009$ m; $\varepsilon = 0.1$; $\gamma_V = 0.8 \cdot 10^{-6}$ m^3/mg; $\gamma_D = 1.9$ ton/m^3; $\alpha = 5.2 \cdot 10^{-4}$ sec^{-1}; $H = 15$ m^{-1}; $\psi = 6.7 \cdot 10^{-9}$ m^2/sec; $\beta = 2.6 \cdot 10^{-4}$ sec^{-1}; $\gamma = 16.4$.

The mean-square deviation of the experimental data from the theoretical results after the sorption period and the variation coefficient for sandstone shale were 0.0019 ml/g and 0.4%, while those for clay shale were 0.0053 ml/g and 0.66%.

NOTATION

c, adsorbate concentration, mg/m^3; ψ, diffusion coefficient, m^2/sec; R, radius of sorbent particle, m; β, adsorption coefficient, sec^{-1}; γ, Henry coefficient; a, amount of sorbed material, referred to sorbent mass, mg/m^3; ε, sorbent porosity; Bi = HR, Biot number; $c_0(\tau)$, function expressing change in adsorbate concentration, mg/m^3; γ_V, specific volume of sorbate, m^3/mg; γ_D, density of sorbent, ton/m^3; τ, time, sec.

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SORPTION ON HYDROPHILIC SWELLING MATERIALS

N. I. Gamayunov and A. V. Tvardovskii

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A sorption equation for swelling, colloidal, capillary-porous bodies is obtained by the methods of statistical physics. The results of the calculations are in good agreement with experiment.

Vapor and gas absorption by swelling materials may be regarded as a process of mixing of active centers of the sorbent with sorbate molecules [1]. It is assumed that each such center comprises several molecules. In considering pair interactions in solutions, only the nearest neighbors of the active centers need be taken into account. The change in sorbate enthalpy on sorption may be expressed as the product [2]

$$\Delta H \approx -\Delta\omega_{12}p_{12}. \tag{1}$$

The number of contacts averaged over the sorbent volume is

$$p_{12} \approx z_0 n_2 U_1 \approx z_0 n_1 U_2. \tag{2}$$

Each active center may interact locally with some number of sorbate molecules differing from z_0, but on average over the volume the number of interactions is z_0. In addition, the probability of a reaction between sorbate molecules and the active centers of the sorbent depends on the volume fraction of the sorbent U_2 in the sorbate–sorbent system.

Substition of Eq. (2) into Eq. (1) yields

$$\Delta H \approx -\Delta\omega_{12}z_0 n_1 U_2. \tag{3}$$

If the total number of molecules n_1 is replaced in Eq. (3) by Avogadro's number N_a, then the change in enthalpy ΔH_1 per mole of sorbate is obtained:

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