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## Abstract

## Full Text

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D. P. TIMOFEEV

# STUDY OF THE DEPENDENCE OF THE DIFFUSION COEFFICIENT ON LOADING IN SORBENT GRAINS OF ARBITRARY SHAPE

*(Presented by Academician M. M. Dubinin, 20 X 1959)*

The diffusion coefficients of adsorbing gases in porous bodies are not constant in different regions of loading (1-3). The study of this dependence, which is of considerable interest for elucidating the mechanism of mass transfer, is usually carried out on grains of regular geometric shape, for which solutions of the differential diffusion equation are available. Such grains are prepared by pressing powders—for example, carbon black, silica gel, etc.—or by grinding sorbent grains of larger size. The disadvantage of the first method is that the pressed grains are only a model, and one that does not always reproduce sufficiently well the structure of real porous bodies; in the second case, the possibility is not excluded that large pores may be clogged by small sorbent particles during the treatment of the grain, which to some extent leads to distortion of the results. In order to avoid these uncertainties associated with the preparation of the objects of investigation, the possibility of studying the dependence of the diffusion coefficient on loading in real sorbent grains is considered below.

Let us assume that a grain of arbitrary shape, with an equilibrium adsorption value corresponding to concentration $c_1$, is placed in a gas medium whose concentration is maintained constant and equal to $c_2$. Let us further assume that the experiment is carried out in a narrow concentration interval within which the diffusion coefficient $D$ and the Henry coefficient $\Gamma = da/dc$ are approximately constant ($a$ is the adsorption value, $c$ is the concentration).

In this case the equation of the nonstationary diffusion process in a homogeneous medium can be written in the form

$$\frac{\partial\gamma}{\partial t} = \frac{D}{1+\Gamma}\Delta\gamma, \tag{1}$$

where $\gamma = \dfrac{c-c_2}{c_1-c_2}$ is the relative concentration; $c$ is the concentration in the grain (a function of coordinates and time); $\Delta$ is an operator whose expression depends on the chosen coordinate system.

The additional condition for desorption will be $\gamma = 1$ at $t = 0$.

In most cases $1 \ll \Gamma$ (although this assumption is not necessary for the subsequent exposition), and, consequently,

$$\frac{\partial\gamma}{\partial t} = \frac{D}{\Gamma}\Delta\gamma. \tag{2}$$

A particular solution of equation (2) by Fourier' s method can be represented as the product of two functions, one of which, $v$, depends on time, the other, $u$, on the coordinates, i.e.

$$\gamma = Avu; \tag{3}$$

$A$ is an arbitrary constant.

The functions $v$ and $u$ are related by the equation

$$\frac{\Gamma}{D}\frac{v'}{v} = \frac{\Delta u}{u} = -k^2, \tag{4}$$

where $k$ is an arbitrary constant.

It follows directly from (4) that

$$v = e^{-k^2\tau}, \tag{5}$$

where $\tau = Dt/\Gamma$. The constant of integration is not written, since it can be taken into account by the coefficient $A$.

Substituting (5) into (3), we have

$$\gamma = Aue^{-k^2\tau}. \tag{6}$$

The general solution is expressed as the sum of particular solutions, i.e.,

$$\gamma = \sum_n A_n u_n e^{-k_n^2\tau}, \tag{7}$$

where the coefficients $A_n$ and $k_n$ are chosen so as to satisfy the specified conditions. The form of the function $u_n$ is determined by condition (4).

In what follows we shall be interested in the amount of adsorption; therefore we pass to the mean relative concentration $\overline{\gamma}$, which is found by integrating $\gamma$ over the volume of the grain $W$:

$$\overline{\gamma} = \frac{1}{W}\int_W \sum_n A_n u_n e^{-k_n^2\tau}\,dW = \sum_n e^{-k_n^2\tau}\frac{1}{W}\int_W A_{nu} n\,dW = \sum_n e^{-k_n^2\tau} B_n, \tag{8}$$

where the quantity

$$B_n = \frac{1}{W}\int_W A_{nu} n\,dW$$

does not depend on time.

It was assumed above that $a = \Gamma c$ and, consequently,

$$\overline{\gamma} = \frac{a - a_2}{a_1 - a_2} = \sum_n B_n e^{-k_n^2\tau}, \tag{9}$$

where $a$ is the amount of adsorption at the given instant of time; $a_1$ and $a_2$ are the equilibrium amounts of adsorption, respectively, at concentrations $c_1$, $c_2$.

Equation (9) corresponds to the case of desorption. For adsorption ($a_2 > a_1$) the equation takes the form

$$\frac{a - a_1}{a_2 - a_1} = 1 - \sum_n B_n e^{-k_n^2\tau}. \tag{10}$$

It follows from equations (9) and (10) that, for a specified amount of adsorption (desorption) $a = a_\xi$,

$$\tau_\xi = \frac{D t_\xi}{\Gamma} = \text{const}, \tag{11}$$

and, consequently, for different regions of the isotherm the relation

$$\frac{D_2}{D_1} = \frac{\Gamma_2}{\Gamma_1}\frac{t'_\xi}{t''_\xi} \tag{12}$$

holds.

Quantities with subscript 1 refer to one concentration interval, and those with subscript 2 to another.

Equation (12) makes it possible to find the dependence of $D$ on filling for sorbent grains of any shape. The Henry constants for different concentration intervals are found from adsorption isotherms, and the time $t_\xi$ directly from kinetic measurements.

Institute of Physical Chemistry
Academy of Sciences of the USSR

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*Note: Figure translations are in progress. See original paper for figures.*