

Numerical Method for Determining the Diffusion Coefficient of a Gas-Forming Impurity in a Solid Using the Results of the Integral Penetrability Method

V. N. Lobko*^a and I. N. Bekman^b

^a Vladimir State University, ul. Gor'kogo 87, Vladimir, 600000 Russia

^b Moscow State University, Moscow, 119991 Russia

*e-mail: lobko_vn@laser-2.vpti.vladimir.ru

Received January 13, 2010

Abstract—A numerical method is proposed for determining the diffusion coefficient of a gas in a solid upon its isothermal penetration through a plane-parallel plate and accumulation in a closed receiving volume. The method is tested with the use of mathematical modeling as well as on a specific experimental material.

DOI: 10.1134/S1063784210090124

INTRODUCTION

The penetrability method is one of the basic methods for studying gas diffusion in solids. In practice, various versions of this method are used: integral, differential, pulse, concentration wave methods, etc. Among them, the integral version is the most sensitive method. In this version, the experiment is carried out on a diffusion cell separated by a membrane being tested into a reservoir and a receiver. At the initial instant, a gas (penetrant) is delivered to the reservoir and its passage into the closed receiver is studied (from the variation of its partial pressure with time in the receiver) [1]. If the results of nonstationary penetrability of plane membranes are analyzed by a traditional method, it is usually assumed that both a reservoir and a receiver have an “unlimited” capacity, so that the partial pressure of the penetrant at the membrane input remains constant during the entire diffusion experiment, while the effect of partial pressure on the kinetics of penetrability can be disregarded. In real experiments, this approximation is usually valid for a reservoir but is not valid for a receiver: to increase the sensitivity of the receiver, its volume is chosen as small as possible, so that the increase of the partial pressure of the penetrant in the receiver at the last stage may substantially distort the shape of the kinetic curve.

Mathematical processing of the results of the experiments on nonstationary penetrability of membranes carried out in a diffusion cell with a limited volume is a complicated and not yet solved problem which requires graphical solution of transcendental equations. The aim of this study is to develop a simple computational technique for the coefficient of diffusion of monoatomic and diatomic (nondissociating as well as dissociating) gases through a plane solid membrane using the data of nonstationary experiments car-

ried out under the conditions of a limited capacity of the receiver. The technique is based on the numerical solution of the initial diffusion equations. The technique was verified by the integral version of the penetrability method both on the arrays obtained by the method of mathematical modeling and on the experimental curves of nitrogen penetrability through a plate of microporous material (modified graphite) and hydrogen penetrability through a nickel membrane.

THEORY OF THE METHOD

Diffusion coefficient D in the approximation $D = \text{const}$ is determined at the zero initial condition and the following boundary conditions: $c(0, t) = c_0 = \text{const}$ and $c(l, t) = f(t)$ (where c is the concentration and t is the time). The values of plate thickness l and $c_0 = \text{const}$, as well as the time dependences of output concentration $c_{\text{out}} = f(t)$ and output flux $J_{\text{out}} = f(t)$ are used in the technique. The $c_{\text{out}} = f(t)$ dependence can be obtained from the experimental curve of output pressure $p_{\text{out}} = f(t)$ if the boundary conditions of the first kind are fulfilled according to the Henry law for a non-dissociating diatomic or monoatomic gas or according to the Sieverts law for a dissociating gas. In this case, the Henry and Sieverts constants must be known. Output concentration $c_0 = \text{const}$ is determined analogously from $p_0 = \text{const}$. The $J_{\text{out}} = f(t)$ dependence can be obtained by numerical differentiation of $p_{\text{out}} = f(t)$; in this case, it is better to use the Tikhonov regularization.

In our case, the diffusion problem can be formulated as follows:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}, \quad c(0, t) = c_0 = \text{const}, \quad c(l, t) = f(t). \quad (1)$$

Let us integrate the second Fick law

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} \quad (2)$$

with separation of variables:

$$\int_{J_x}^{J_{out}} dJ = -\int_x^l \frac{\partial c}{\partial t} dx, \quad J_x = \int_x^l \frac{\partial c}{\partial t} dx + J_{out}. \quad (3)$$

Combining it with the first Fick law

$$J_x = -D \frac{\partial c}{\partial x}, \quad (4)$$

$$D = -\frac{\int_x^l \frac{\partial c}{\partial t} dx + J_{out}}{\frac{\partial c}{\partial x}} \quad (5)$$

and substituting the resultant expression into the differential diffusion equation

$$\frac{\partial c}{\partial t} = -\frac{\int_x^l \frac{\partial c}{\partial t} dx + J_{out}}{\frac{\partial c}{\partial x}} \frac{\partial^2 c}{\partial x^2}, \quad (6)$$

we get the integro-differential equation which does not contain the diffusion coefficient, but contains the output flux. Thus, the inverse problem can be solved if information (experimental) about the time dependence of J_{out} is available.

Let us introduce an analytic grid along the x axis: $i = 0, 1, \dots, n$, and along the t axis: $j = 0, 1, \dots, m$. We denote by h a step along the x axis and by τ a step along

the t axis. Then, J_{out} will be denoted as $J_{n,j}$. We apply the finite difference method:

$$\frac{\partial c}{\partial t} = \frac{c_{i,j} - c_{i,j-1}}{\tau}; \quad (7)$$

$$\frac{\partial c}{\partial x} = \frac{c_{i+1,j} - c_{i-1,j}}{2h}; \quad (8)$$

$$\frac{\partial^2 c}{\partial x^2} = \frac{c_{i-1,j} - 2c_{i,j} + c_{i+1,j}}{h^2}. \quad (9)$$

We replace the integral in (6) according to the trapezium rule:

$$\begin{aligned} \int_x^l \frac{\partial c}{\partial t} dx &= \frac{h}{2} \left[\left(\frac{\partial c}{\partial t} \right)_i + \left(\frac{\partial c}{\partial t} \right)_n + 2 \sum_{k=i+1}^{n-1} \left(\frac{\partial c}{\partial t} \right)_k \right] \\ &= \frac{h}{\tau} \left[\frac{c_{i,j} - c_{i,j} + c_{i,j} - c_{i,j}}{2} \right. \\ &\quad \left. + \sum_{k=i+1}^{n-1} (c_{k,j} - c_{k,j-1}) \right], \quad i = 0, \dots, n-1 \end{aligned} \quad (10)$$

for

$$i = n \int_x^l \frac{\partial c}{\partial t} dx = 0.$$

Writing expression (5) in terms of (10) and (8), we obtain:

$$D = -\frac{2h^2 \left[\frac{c_{i,j} - c_{i,j} + c_{i,j} - c_{i,j}}{2} + \sum_{k=i+1}^{n-1} (c_{k,j} - c_{k,j-1}) + \frac{\tau}{h} J_{n,j} \right]}{\tau (c_{i+1,j} - c_{i-1,j})}, \quad (11)$$

$$i = 1, 2, \dots, n-1.$$

Substituting relations (11), (7), and (9) into (6), we get the following difference scheme:

$$\begin{aligned} &2(c_{i-1,j} - 2c_{i,j} + c_{i+1,j}) \left[\frac{c_{i,j} - c_{i,j-1} + c_{n,j} - c_{n,j-1}}{2} \right. \\ &+ \sum_{k=i+1}^{n-1} (c_{k,j} - c_{k,j-1}) + \frac{\tau}{h} J_{n,j} \left. \right] + (c_{i,j} - c_{i,j-1}) \\ &\times (c_{i+1,j} - c_{i-1,j}) = 0, \quad i = 1, 2, \dots, n-1. \end{aligned} \quad (12)$$

Scheme (12) is a system of nonlinear equations, which can be solved by Newton's method. We denote each of these equations by F_i and calculate the Jacobian of the system:

$$\begin{aligned} \frac{\partial F_i}{\partial c_{i-1,j}} &= 2 \left[\frac{c_{i,j} - c_{i,j-1} + c_{n,j} - c_{n,j-1}}{2} \right. \\ &+ \sum_{k=i+1}^{n-1} (c_{k,j} - c_{k,j-1}) + \frac{\tau}{h} J_{n,j} \left. \right] - (c_{i,j} - c_{i,j-1}), \end{aligned} \quad (13)$$

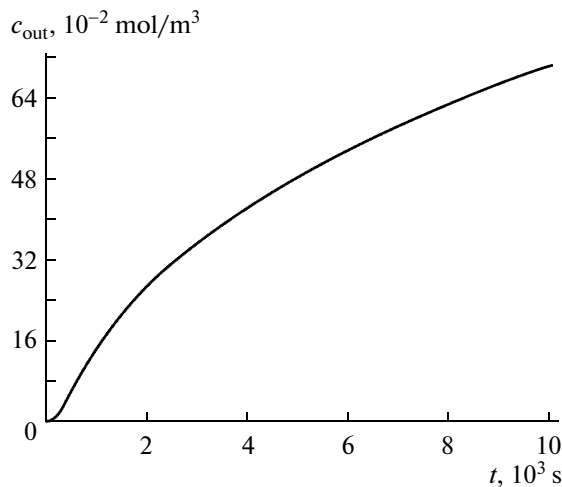


Fig. 1. Modeling of penetrability of a plane-parallel plate. The time dependence of the output concentration.

$$\frac{\partial F_i}{\partial c_{i,j}} = 2 \left\{ \frac{(c_{i-1,j} - 2c_{i,j} + c_{i+1,j})}{2} - 2 \left[\frac{c_{i,j} - c_{i,j-1} + c_{n,j} - c_{n,j-1}}{2} \right] \right\} \quad (14)$$

$$+ \sum_{k=i+1}^{n-1} (c_{k,j} - c_{k,j-1}) + \frac{\tau}{h} J_{n,j} \left. \right\} + (c_{i+1,j} - c_{i-1,j}),$$

$$\frac{\partial F_i}{\partial c_{i+1,j}} = 2 \left\{ (c_{i-1,j} - 2c_{i,j} + c_{i+1,j}) + \left[\frac{c_{i,j} - c_{i,j-1} + c_{n,j} - c_{n,j-1}}{2} \right] \right\} \quad (15)$$

$$+ \sum_{k=i+1}^{n-1} (c_{k,j} - c_{k,j-1}) + \frac{\tau}{h} J_{n,j} \left. \right\} + (c_{i,j} - c_{i,j-1}),$$

$$\frac{\partial F_i}{\partial c_{k,j}} \Big|_{k=i+2, \dots, n-1} = 2(c_{i-1,j} - 2c_{i,j} + c_{i+1,j}). \quad (16)$$

For the number of partitions $n = 6$ along the x axis, the system of Newton's method has the form (k is the number of iteration):

$$\frac{\partial F_1^{(k-1)}}{\partial c_{1,j}} X_1 + \frac{\partial F_1^{(k-1)}}{\partial c_{2,j}} X_2 + \frac{\partial F_1^{(k-1)}}{\partial c_{3,j}} X_3 + \frac{\partial F_1^{(k-1)}}{\partial c_{4,j}} X_4 + \frac{\partial F_1^{(k-1)}}{\partial c_{5,j}} X_5 = -F_1^{(k-1)},$$

$$\frac{\partial F_2^{(k-1)}}{\partial c_{1,j}} X_1 + \frac{\partial F_2^{(k-1)}}{\partial c_{2,j}} X_2 + \frac{\partial F_2^{(k-1)}}{\partial c_{3,j}} X_3 + \frac{\partial F_2^{(k-1)}}{\partial c_{4,j}} X_4$$

$$+ \frac{\partial F_2^{(k-1)}}{\partial c_{5,j}} X_5 = -F_2^{(k-1)}, \quad (17)$$

$$\frac{\partial F_3^{(k-1)}}{\partial c_{2,j}} X_2 + \frac{\partial F_3^{(k-1)}}{\partial c_{3,j}} X_3 + \frac{\partial F_3^{(k-1)}}{\partial c_{4,j}} X_4 + \frac{\partial F_3^{(k-1)}}{\partial c_{5,j}} X_5 = -F_3^{(k-1)},$$

$$\frac{\partial F_4^{(k-1)}}{\partial c_{3,j}} X_3 + \frac{\partial F_4^{(k-1)}}{\partial c_{4,j}} X_4 + \frac{\partial F_4^{(k-1)}}{\partial c_{5,j}} X_5 = -F_4^{(k-1)},$$

$$\frac{\partial F_5^{(k-1)}}{\partial c_{4,j}} X_4 + \frac{\partial F_5^{(k-1)}}{\partial c_{5,j}} X_5 = -F_5^{(k-1)}$$

(the value of concentration in the zeroth ($i = 0$) and n th layers for $i = n$ is known from the boundary conditions).

As it is clear from relations (17), the difference scheme has a nontrivial form with a variable pattern. The system can be solved, for example, by the Gauss method (or its modification taking into account a special form of the system) with respect to corrections:

$$X_i = c_{i,j}^{(k)} - c_{i,j}^{(k-1)}. \quad (18)$$

In this formula, $c_{i,j}^{(k)}$ are the required concentrations of the next iteration. Thus, the concentration profiles over the plate thickness can be constructed for each time layer. From these profiles, we can easily determine the concentration gradients on the output side of the plate (layer $i = n$), and the output fluxes are known from the experiment; thus, using the first Fick law, we can calculate diffusion coefficient D for different concentrations. Ideally, it should be the same in all the time layers.

APPROBATION OF THE METHOD. NUMERICAL EXPERIMENT

To demonstrate the potentialities of the method, we used the results of simulation of diatomic gas diffusion into a small receiving volume for the parameters given in Appendix 1.

Diffusion coefficient D was now assumed to be unknown, the input concentration was $c_0 = 7.38 \text{ mol/m}^3$, the output concentration as a function of time (Fig. 1), and output flux as a function of time (Fig. 2) were considered as the experimental results (they are measured not directly but are determined from the values of the input and output pressure, as shown above). The calculations also require the value of the plate thickness. In addition, to realize Newton's method, it is necessary to specify the initial rough approximation of diffusion coefficient D , so we took the value $5 \times 10^{-9} \text{ m}^2/\text{s}$.

By using this method, the concentration profiles over the plate thickness were constructed for each time layer. From these profiles, the concentration gradients were computed for the output (right) side of the plate,

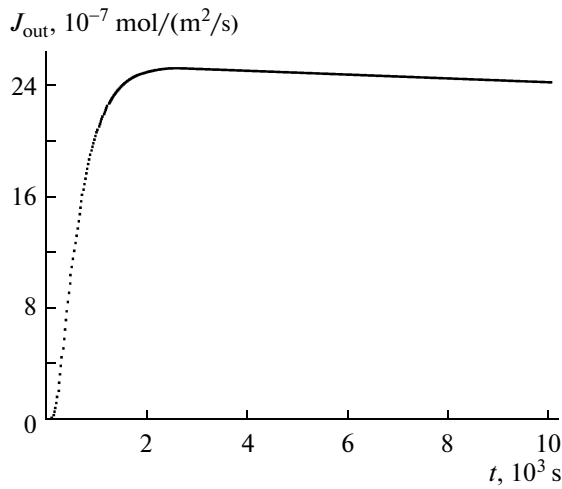


Fig. 2. Modeling of penetrability of a plane-parallel plate. The time dependence of the output flux.

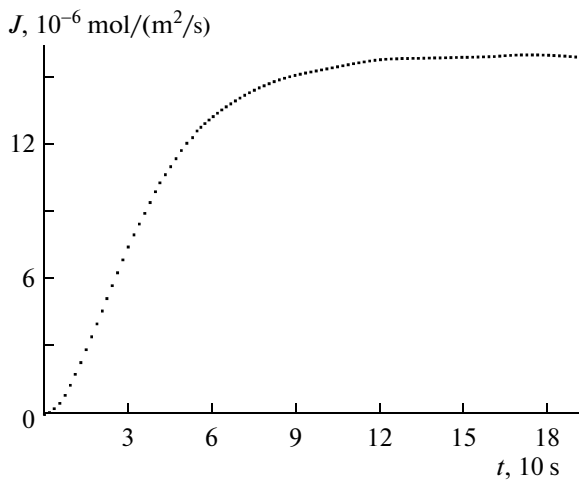


Fig. 4. Diffusion of nitrogen through a graphite material. The time dependence of the output flux. The curve is obtained by differentiating the experimental integral curve.

and the diffusion coefficients for each time layer were computed by the first Fick law for the known output fluxes. Thus, the values of D were obtained for different concentrations, namely, from zero to the maximum output concentration. The values of D from the maximum output to the input concentrations were determined from the last concentration profile. The results are shown in Fig. 3. Exact value $5.66 \times 10^{-10} \text{ m}^2/\text{s}$ was obtained. Then, the computations were repeated with the initial value $5.66 \times 10^{-10} \text{ m}^2/\text{s}$, and the same value was again obtained at the output.

**APPROBATION OF THE METHOD.
PROCESSING OF THE EXPERIMENTAL DATA**

The method was tested for two cases using specific experimental data. Differentiation of experimental curve $p_{out} = f(t)$ for nitrogen diffusion through graphite

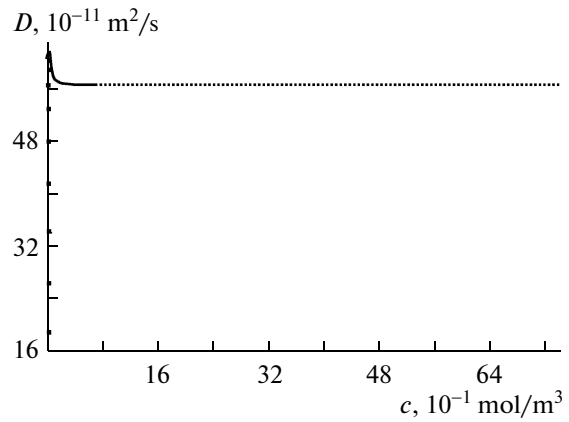


Fig. 3. Results of calculation of the diffusion coefficient for the initial approximation $D = 5 \times 10^{-9} \text{ m}^2/\text{s}$ (for different concentrations).

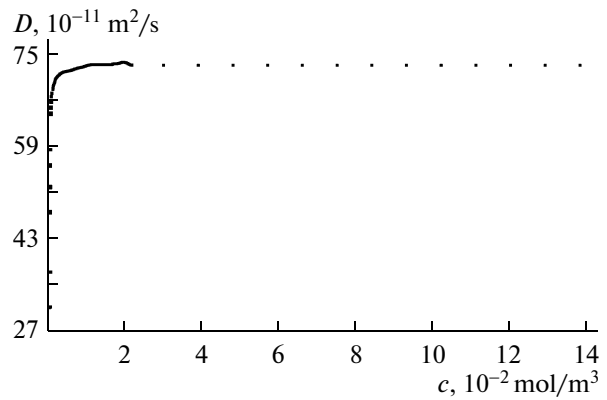


Fig. 5. Diffusion of nitrogen through a graphite material. The diffusion coefficient for different concentrations at the initial approximation $D = 5 \times 10^{-9} \text{ m}^2/\text{s}$.

materials [1] leads to the conventional time dependence of output flux for the integral method (Fig. 4). Here, the receiving volume is sufficiently large unlike in the case given in Fig. 2.

For our computations, we used the parameters given in Appendix 2.

The results are given in Fig. 5 on an enlarged scale. The value of the coefficient of diffusion of gaseous nitrogen in a graphitized material was $7.31 \times 10^{-10} \text{ m}^2/\text{s}$, and the calculation by classical methods yielded $7.32 \times 10^{-10} \text{ m}^2/\text{s}$.

Hydrogen diffusion in pure nickel [2] was carried out under the conditions that slow down the output flow of hydrogen at the final stage of the experiment (i.e., we obtained a curve of the form given in Fig. 2). Strictly speaking, the calculation of the diffusion coefficient with the use of classical methods is unacceptable in this case and is permissible only for estimation. The calculation according to the proposed technique for the parameters given in Appendix 3 yielded the following result: $5.76 \times 10^{-10} \text{ m}^2/\text{s}$

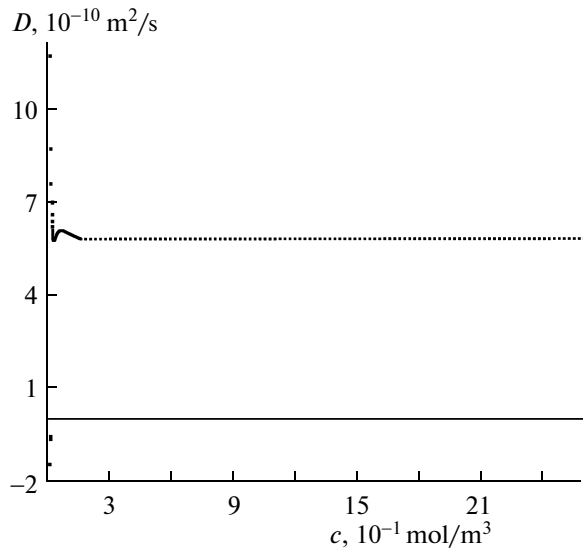


Fig. 6. Diffusion of hydrogen in pure nickel. The diffusion coefficient for different concentrations at the initial approximation $D = 5 \times 10^{-9} \text{ m}^2/\text{s}$.

(Fig. 6); the estimate obtained by classical methods amounts to $5.79 \times 10^{-10} \text{ m}^2/\text{s}$. These values are in good agreement with the tabular data (4.99×10^{-10} and $6.41 \times 10^{-10} \text{ m}^2/\text{s}$) given in [3].

CONCLUSIONS

The stability of the proposed difference scheme was tested empirically in each case. The initial rough approximation of the diffusion coefficient should be taken deliberately overestimated; otherwise, the scheme sometimes loses stability since at the initial period of time the concentration profiles are close to zero in the middle of the plate and on the right side, and mistakes may occur in the solutions.

The advantages of the method are: the use of information over all experimental points, multiple calculation of the diffusion coefficient in full compliance with the concentration profiles, and the possibility to process nonclassical curves with the decreasing output flux (see, for example, Fig. 2). The need for additional information on the solubility coefficient can be considered as a disadvantage of the method. On the other hand, however, the latter can become a direction for the development of the method, when it will be possible to determine both parameters in one experiment.

This method can also be improved by taking into account slow surface processes and possible dependence $D = f(c)$.

APPENDIX 1

The parameters of modeling of diffusion of a diatomic gas into a closed small receiving volume are as follows: the plate thickness is $1.5 \times 10^{-3} \text{ m}$; the temperature is 680.5 K; the plate area is $3.14 \times 10^{-4} \text{ m}^2$; the diffusion coefficient is $5.66 \times 10^{-10} \text{ m}^2/\text{s}$; the Sieverts constant is $2.45 \times 10^{-2} \text{ mol}/(\text{m}^3/\text{Pa}^{1/2})$; the input volume is 0.05 m^3 ; the output volume is $5 \times 10^{-5} \text{ m}^3$; the input pressure is 680 Torr; the output pressure is 0; the initial concentration in the plate is $10^{-12} \text{ mol}/\text{m}^3$; the number of partitions along the x axis is 100; the final time is 10 000 s; and the number of partitions along the t axis is 500.

APPENDIX 2

The parameters of diffusion of nitrogen through a graphite material are as follows: the plate thickness is $4.1 \times 10^{-4} \text{ m}$; the temperature is 298 K; the plate area is $1.3 \times 10^{-3} \text{ m}^2$; the Henry constant is $1.17 \times 10^{-4} \text{ mol}/(\text{m}^3/\text{Pa})$; the output volume is $4.18 \times 10^{-5} \text{ m}^3$; the input pressure is 769.4 Torr; the input concentration is $9.00 \text{ mol}/\text{m}^3$; and the final time is 190 s.

APPENDIX 3

The parameters of diffusion of hydrogen in pure nickel are as follows: the plate thickness is $1.542 \times 10^{-3} \text{ m}$; the temperature is 680.5 K; the plate area is $3.14 \times 10^{-4} \text{ m}^2$; the Sieverts constant is $0.87 \times 10^{-2} \text{ mol}/(\text{m}^3/\text{Pa}^{1/2})$; the output volume is $4.96 \times 10^{-5} \text{ m}^3$; the input pressure is 680 Torr; the input concentration is $2.6 \text{ mol}/\text{m}^3$; and the final time is 11 000 s.

REFERENCES

1. I. N. Beckman, *Polymeric Gas Separation Membranes*, Ed. by D. R. Paul and Y. P. Yampolskii (CRC, Boca Raton, 1994), pp. 301–352.
2. V. N. Lobko, *Zh. Alternat. Energ. Ekolog.*, No. 4, 40 (2002).
3. *Hydrogen-Metal Interaction*, Ed. by A. P. Zakharov (Nauka, Moscow, 1987) [in Russian].

Translated by N. Wadhwa