THE DETERMINATION OF DIFFUSION COEFFICIENTS BY THE METHOD OF INTEGRAL ANALOGS

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A new method is discussed for determining diffusion coefficients – the method of integral analogs. This method makes it possible to calculate diffusion coefficients from experimental results to higher accuracy than existing methods.

1. Analysis of Known Methods for Determining Diffusion Coefficients

The basis for the determination of diffusion coefficients is the partial differential equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}. \tag{1}$$

The overwhelming majority of methods involve the determination of the concentration as a function of the coordinates and the time, i.e., c(x, t) depending on the initial and boundary conditions in the actual problem; if c(x, t) is known it is easy to determine the diffusion coefficient D from the diffusion equation.

A very large number of papers have been devoted to the development of methods based on using solutions of the above equation [1, 2]. But all these methods have serious inherent deficiencies: low accuracy of the determined parameters, difficulty in processing experimental results, need of a special scheme for experiments, etc. The most important of these deficiencies is the low accuracy of the determined diffusion coefficient.

Computational formulae are deduced from an idealized model and do not cover complex cases of diffusion.

Occasionally it is completely impossible to determine the diffusion parameters. Thus, for example, there are no satisfactory methods of determining variable diffusion coefficients.

A general method has been developed [3] for determining the parameters of systems which can be described by differential equations, the essence of which is as follows. The original differential equation is replaced by its equivalent integral equation for the function itself (and not the leading derivative, as in the general theory of integral equations). The terms due to the nonzero initial and boundary values of the functions and their derivatives are eliminated algebraically. In the equations of the simplest type these terms may be the initial and boundary values of the functions and their derivatives themselves. A particular case of the general method [3] is the method of modulating functions [4]. The method of modulating functions is the most highly developed of those now known and is of greatest interest to us.

2. The One-Dimensional Diffusion Equation with Constant Coefficients

We consider the simplest case of one-dimensional diffusion, described by Eq. (1), and to determine D from (1) we use the method of modulating functions. From the variables in (1) we choose the modulating functions f(x) and φ(t) so that they satisfy the conditions:

$$f(0) = f(L) = f_x'(0) = f_x'(L) = 0, \tag{2}$$

$$\varphi(0) = \varphi(T) = 0, \tag{3}$$

where (0, L) is the interval of observation for the x coordinate; (0, T) is the interval of observation for the time.

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We multipy both sides of (1) by the modulating functions f(x) and φ(t) and by dx, dt

$$\int_0^L f(x)\,dx \int_0^T \frac{\partial c}{\partial t}\varphi(t)\,dt = D \int_0^T \varphi(t)\,dt \int_0^L \frac{\partial^2 c}{\partial x^2} f(x)\,dx. \tag{4}$$

If we make the necessary integrations, we obtain an equation for D

$$D = -\frac{\int_0^L\int_0^T c\,f(x)\,\varphi_t'(t)\,dxdt}{\int_0^L\int_0^T c\,f_x''(x)\,\varphi(t)\,dxdt}. \tag{5}$$

To determine the diffusion coefficient from (5) we have to find the concentration of the diffusing element c(x, t). When the diffusion parameters are determined experimentally the concentration c(x) is usually obtained as a function of the coordinate at some moment of time. From these data and Newton's interpolating polynomial [5] we can determine the concentration as a function of the coordinate and the time in (5). For example, the function can be written as

$$c(x,\ t) = a_0 + a_1x + a_2t + a_3xt + a_4x^2 + a_5t^2, \tag{6}$$

where the a_i $(0 \le i \le 5)$ are constants determined by the actual experimental functions c(x, t_0) for fixed values of the time t_0 = const.

The modulating functions in (5) can be chosen arbitrarily; it is only necessary that they satisfy (2) and (3). The simplest modulating functions are

$$\begin{aligned} f_1(x) &= \sin^2\left(\frac{\pi}{L}x\right), \\ \varphi_1(t) &= \sin\frac{\pi}{T}t, \end{aligned} \tag{7}$$

$$\begin{aligned} f_2(x) &= x^2(x-L)^2, \\ \varphi_2(t) &= t(t-T), \end{aligned} \tag{8}$$

where T and L are some fixed values of the time t and the coordinate x, called the upper limits of observation of the coordinate and the time.

If we take, for example, (8) as the modulating functions, then using (6) again, we can obtain a simple expression for the constant diffusion coefficient from (5)

$$D = \frac{a_2}{2a_4} + \frac{a_3L}{4a_4} + \frac{a_5T}{2a_4}. \tag{9}$$

We still have to solve the problem of the appropriateness of using integral analogs of the diffusion equation to determine the diffusion coefficient D. In fact, from (6), it is easy to determine the partial derivatives

$$\frac{\partial c}{\partial t} = \sum_{i,\ j=0}^{2} ja_{ij}\,x^it^{j-1}, \tag{10}$$

$$\frac{\partial^2 c}{\partial x^2} = \sum_{i,\ j=0}^{2} i(i-1)\,a_{ij}\,x^{i-2}t^j, \tag{11}$$

substitution of which in the simplest diffusion equation (1) yields

$$D = \frac{\sum_{i,j=0}^{2} i(i-1)\,a_{ij}\,x^{i-2}t^j}{\sum_{i,j=0}^{2} ja_{ij}\,x^it^{j-1}}, \tag{12}$$

and the problem can be considered as solved without any integration of (1) or the use of (5). If, thus, we know the function $c(x_1, \ldots, x_n, t)$, we can determine D not only without solving a boundary value problem, but also without forming integral analogs of the form (5). But the known function $c(x_1, \ldots, x_n, t)$ is approximate. Equations (5) and (12), referring to the same diffusion process are not equivalent, because in one of them the diffusion coefficient is determined by integrating approximate functions, while in the other, it is found by differentiation. In the first case the error is far less than in the second.

Thus, the very approach to the formation of the concentration as a function of the independent variables, which assumes use of experimental data, and hence is approximate, automatically prevents these approaches being identical for determining D, and from the point of view of the accuracy of the solution of the problem, yields a decisive advantage to the method of forming integral analogs corresponding to the diffusion equation.

3. Determination of a Variable Diffusion Coefficient

We now show that the method of forming the integral analog of the corresponding diffusion equation makes it possible to solve the problem of determining the diffusion coefficient when the condition D = const does not hold. We consider the equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x} \right) \tag{13}$$

and, multiplying both sides of (13) by the modulating functions f(x) and $\varphi(t)$, satisfying (2) and (3), and also by dx, dt, we integrate with respect to x and t from 0 to L and 0 to I respectively

$$\int_0^L \int_0^T \frac{\partial c}{\partial t} f(x)\, \varphi(t)\, dxdt = \int_0^L \int_0^T \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x} \right) f(x)\, \varphi(t)\, dxdt. \tag{14}$$

After some calculations we obtain

$$-\int_0^L \int_0^T c(x,\ t)\, f(x)\, \varphi(t)\, dxdt = \int_0^L \int_0^T c(x,\ t) \frac{\partial}{\partial x}[D\, f'(x)]\, \varphi(t)\, dxdt. \tag{15}$$

Equation (15) is an integral equation for D, since D occurs under the sign for double integration.

The direct solution of (15) is a complex problem even when we know the concentration as a function of the independent variables, i.e., c(x, t).

Because of their complexity and the approximate nature of c(x, t), the solution of integral equations of the type (15) for D have to be sought approximately, for example, using an approximation for D(x, t). Here, however, the problem is of quite a different kind from that of the approximate function c(x, t), for which we had information from experiment. In the case when the function D(x, t) is approximate, the problem is different in that in this approximation the variables are unknown, so that, for example, if we approximate using polynomials in x and t, the constant coefficients of these polynomials are unknown. Having calculated an approximate expression for D in (15) and evaluated the integrals, we can obtain an algebraic equation for the unknown coefficients in the expansion of D. Subsequently the aim is to obtain a system of equations for these coefficients. This system can be obtained by an arbitrary choice of the modulating functions f(x) and $\varphi(t)$, and also by choosing the intervals of observation with suitable L and T. Indeed, we can choose any functions satisfying the conditions by requiring that they and their first $n - 1$ derivatives are zero at the ends of the intervals of observation, which, on substitution in (15), will give, in conjunction with the approximate concentration functions with known expansion coefficients and diffusion coefficient with unknown expansion coefficients, algebraic equations for the expansion coefficients of D. There are as many algebraic equations as unknowns. Similarly we can obtain a system of algebraic equations for the unknown expansion coefficients of D by varying the numerical values of the definite integrals as functions of the upper limits L and T of integration, i.e., by choosing appropriate intervals of observation for the coordinate and the time.

We still have to explain which variables we have to approximate in the diffusion coefficient. It is generally accepted in the literature (see, e.g., [2, 6]) that D is a function of the concentration c.

At the same time, both the concentration and the diffusion coefficient are functions of independent variables – the spatial coordinates and the time (this follows from the diffusion equation). Under certain conditions, which we shall assume to hold, the functions

$$D = D(c), \tag{16}$$

$$D = D(x,\ t) \tag{17}$$

are related in such a way that if we know (16), we can obtain (17) for $c = c(x, t)$, and conversely. Then it is formally a matter of indifference which variables we choose as independent for D; either the concentration in the one case or the spatial coordinates and the time in the other. Hence, we shall assume the following representations possible:

$$D = D(c) = \sum_{k=0}^{n} b_k c^k, \tag{18}$$

$$D = D(x,\ t) = \sum_{k,i=0}^{m} a_{ki} t^i x^k, \tag{19}$$

where the a_{ki}, b_k are unknown expansion coefficients and the choice of the approximation (18) or (19) is dictated by considerations of simplicity in calculating the defining integrals in the integral analogs.

We give an expression for the diffusion coefficient as a function of the coordinate (D can be assumed to be a function only of the coordinate if the diffusion annealing is at constant temperature) [7].

We start from the diffusion equation (13) and write the concentration and diffusion coefficient as

$$c(x,\ t) = a_0 + a_1 x + a_2 t + a_3 xt + a_4 x^2 + a_5 t^2, \tag{20}$$

$$D(x) = b_0 + b_1 x + b_2 x^2. \tag{21}$$

Computing as above, we obtain the final expression

$$D(x) = \frac{a_2 + a_5 T}{2a_4} - \frac{a_3}{16a_4^2}(2a_1 + a_3 T) + \frac{a_3}{4a_4} x. \tag{22}$$

NOTATION

D	is the diffusion coefficient;
c	is the concentration;
x	is the space coordinate;
t	is the time;
L	is the interval of observation of coordinate;
T	is the interval of observation of time;
a_{ki}, b_k	are the expansion coefficients;
$a_0, a_1, \ldots, a_5$	are the coefficients in the expansion of the concentration in x and t.

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