ON A PROCEDURE FOR DETERMINING PARAMETERS OF DIFFUSION SATURATION IN SOLIDS

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A method for determining diffusivity, the constants of the phase-boundary reaction, and the maximum attainable concentration level on the surface, in diffusional saturation of solids, is proposed.

A mathematical description of diffusion saturation processes in solids taking up foreign atoms from a vapor phase is usually based on the concept that the rate of advance of the material from the surroundings is much greater than the diffusional mobility of the diffusant material through the solid phase. It is assumed that the limiting concentration of the diffusing element, for the conditions specified, is established practically instantaneously on the interface separating the phases, and that it is maintained subsequently. In that case the distribution of the concentration in the diffusion zone can be described by the Gaussian error function [1], in the event of saturation of an isotropic material.

However, investigation of some systems featuring increasing contact times discloses a monotonic increase in the concentration on the surface of the object being saturated, thereby reflecting the influence of processes taking place on the phase interface on saturation kinetics. Analysis of diffusion in systems of that type has been carried out [2-4] under the assumption that the flow of material across the interface varies in proportion to the difference between the limiting concentration and the instantaneous value of the surface concentration at each instant of time. From that point of departure, the description of the distribution of the diffusant is aided by an expression similar to the known solution of the heat conduction equation for a semi-infinite body under boundary conditions of the third kind [5]:

$$\frac{C(x,\ \tau)}{C_0} = \operatorname{erfc}\left(\frac{1}{2\sqrt{\mathrm{Fo}}}\right) - \exp\left[\frac{\mathrm{Ti}}{\sqrt{\mathrm{Fo}}} + \mathrm{Ti}^2\right] \operatorname{erfc}\left(\frac{1}{2\sqrt{\mathrm{Fo}}} + \mathrm{Ti}\right), \tag{1}$$

where

$$\mathrm{Fo} = \frac{D\tau}{x^2}; \quad \mathrm{Ti} = \frac{\alpha}{\sqrt{D}}\sqrt{\tau};$$

$$\operatorname{erfc} z = \frac{2}{\sqrt{\pi}} \int\limits_u^\infty \exp(-u^2)\, du.$$

Methods for determining the kinetic parameters of the process experimentally may be found in [6, 7].

The present authors earlier proposed a method [6] for calculating the constants D and α from experimentally derived values of the concentration on the surface and of the amount of material diffusing through a unit surface area, for different instants of time, which are related to the unknown values by the expressions

$$\frac{C(0,\ \tau)}{C_0} = 1 - \exp(\mathrm{Ti}^2) \operatorname{erfc} \mathrm{Ti} \tag{2}$$

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*Deceased.

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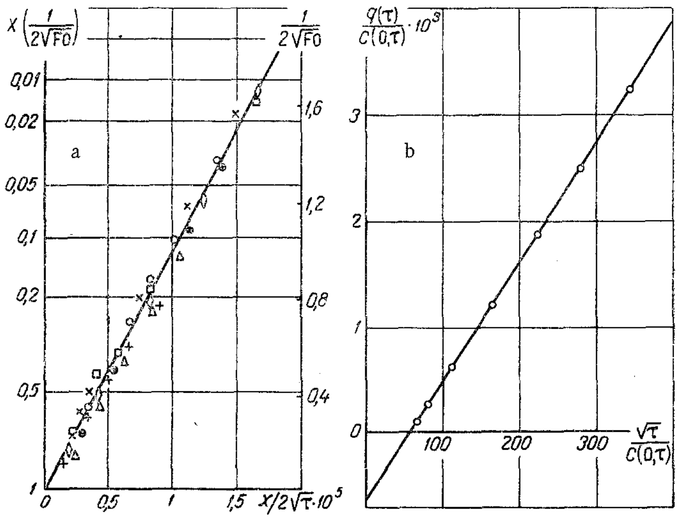

Fig. 1. Illustration of procedure for calculating constants D, α, and C_0. Data points on the graph were taken from [6].

and

$$q(\tau) = \frac{C_0 D}{\alpha}\left[\frac{2}{\sqrt{\pi}}\,\mathrm{Ti} - \frac{C(0,\,\tau)}{C_0}\right]. \tag{3}$$

Formula (1) has been represented [7] as a product of two functions

$$\frac{C(x,\,\tau)}{C_0} \cong Y(\mathrm{Ti})\,X\left(\frac{1}{2\sqrt{\mathrm{Fo}}}\right).$$

Values of the functions Y(Ti) and $X(1/2\sqrt{\mathrm{Fo}})$ have been tabulated. Curves of the distribution of concentration with respect to the depth of the diffusion zone are employed in calculating the kinetic parameters of the process. In both cases, the limiting concentration C_0 must be known in order to calculate the coefficients α and D. Emphasis is placed [7] on the fact that this concentration does not coincide, as a general rule, with the solubility limit, or with any other curves on the phase diagram. It can be determined in principle experimentally as the limit toward which the concentration on the surface of the specimen tends when the contact time in the particular medium is sufficiently long. Under certain conditions, however, the processes progress so slowly on the phase interface that extremely laborious experiments have to be staged in order to arrive at the limiting concentration on the surface. The constant C_0 must be known not only in order to determine the kinetic constants of the saturation process, but are also of independent interest in their own light, specifically for estimating the viability of the material under conditions of long-term service of products in gaseous media.

All three constants of the saturation process, α, D, and C_0, can be calculated from a single series of experiments, if a single procedure is devised for the calculation of the parameters α and D, as suggested in [6] and in [7].

Let us construct a uniform scale of values $1/2\sqrt{\mathrm{Fo}}$ and a matching scale of corresponding values of the function $X(1/2\sqrt{\mathrm{Fo}})$ from [7]. If we now plot the experimental ratios $C(x,\,\tau)/C(0,\,\tau)$ on the $X(1/2\sqrt{\mathrm{Fo}})$ scale for the corresponding $x/\sqrt{\tau}$ values, we obtain a straight line passing through the origin of corrdinates (Fig. 1a) in the system of coordinates $1/2\sqrt{\mathrm{Fo}} = \varphi(x/2\sqrt{\tau})$. The slope of that straight line $k_1 = 1/\sqrt{D}$ can be used to determine the diffusivity D. We then proceed to construct the dependence of $q(\tau)/C(0,\,\tau)$ on $\sqrt{\tau}/C(0,\,\tau)$ in a cartesian frame of reference. We learn from Eqs. (2) and (3) that this dependence must also be depicted graphically by a straight line (Fig. 1b). The values of α and C_0 are calculated* from the slope $k_2 = (2/\sqrt{\pi})(C_0\sqrt{D})$ of the straight line and from the initial ordinate $b = -D/\alpha$. The amount of material diffused over a time τ can be determined either from the weight gain of the specimen, or by calculating the area under the concentration curve $C(x,\,\tau)$.

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*If C_0 is known, one diagram, Fig. 1b, will be sufficient for calculating D and α.

Figure 1 illustrates this procedure, using the example of treating data on changes in the concentration on the surface $C(0, \tau)$ and in the depth of the diffusion zone $C(x, \tau)$, as well as data on changes in the amount of material diffused $q(\tau)$, for different contact times τ, plotted in Fig. 1 and Fig. 2 of reference [6].

NOTATION

$q(\tau)$	is the amount of material diffused through unit surface, g/cm^2;
τ	is the saturation time, sec;
x	is the distance from surface, cm;
D	is the diffusivity, cm^2/sec;
α	is the constant of phase-boundary reaction, cm/sec;
$C(x, \tau)$	is the instantaneous value of concentration, g/cm^3;
$C(0, \tau)$	is the instantaneous value of concentration on surface, g/cm^3;
C_0	is the limiting concentration on surface, g/cm^3;
Fo	is the diffusion Fourier ratio;
Ti	is the diffusion Tikhonov ratio.

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