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A MATHEMATICAL INTERPRETATION OF LIMITED DIFFUSION PROCESSES*

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1. Introduction. Recently T. G. Giallorenzi et al. obtained an abnormal experimental result in a diffusion process of silver ions into a glass plate [1]. The result indicated that a maximum in silver concentration, and accordingly a refractive-index maximum, too, were found in the glass interior when the bath of fused silver-nitrate was not stirred. The limited diffusion process is noteworthy in the sense that it provides a simple experimental means of producing low-loss optical waveguides. They suggested that this phenomenon might result from the depletion of silver ions in the diffusion source near the glass surface. However, the interpretation cannot be considered to be a persuasive one, for it is not evident that the depletion produces the interior maxima. Furthermore, a similar phenomenon, not yet sufficiently explained, in the diffusion process of copper ions into lithium tantalate crystal was found only recently by J. Noda et al. [2]. It is the purpose of this note to give an explicit interpretation of the diffusion processes on the supposition of interface reactions which obey the law of kinetic mass action.

2. Statement of the limited diffusion processes and solutions. Let t be the diffusion process time, z the coordinate chosen perpendicular to the surface of the glass or crystal plate, and $C = C(t, z)$ the concentration of diffusing ions. Let us assume that the surface concentration $F(t)$ decreases with increasing process time; for example, in Giallorenzi's experiment, this is ascribed to the depletion of silver ions in the liquid phase adjacent to the glass surface. Consider the case in which the initial concentration is zero within the substrate. Then we can write down the limited diffusion processes as

$$\begin{aligned} \partial C / \partial t &= D \cdot \partial^2 C / \partial z^2, \\ C &= 0, & z > 0 \quad \text{and} \quad t = 0, \\ C &= F(t), & z = 0 \quad \text{and} \quad t > 0. \end{aligned} \tag{1}$$

Here D is the diffusion coefficient of diffusing ion and $dF/dt \leq 0$. According to the text by Carslaw and Jaeger [3], the solution of Eqs. (1) is given in the form

$$C = \frac{z}{2(\pi D)^{1/2}} \cdot \int_0^t F(s) \cdot (t-s)^{-3/2} \cdot \exp \left[-\frac{z^2}{4D(t-s)} \right] \cdot ds. \tag{2}$$

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Let us consider whether or not the function $C(t, z)$ has a maximum value for $z > 0$. On differentiating both sides of Eq. (2) with respect to z , we obtain

$$\frac{\partial C}{\partial z} = -\frac{F(0)}{(\pi Dt)^{1/2}} \cdot \exp\left(-\frac{z^2}{4Dt}\right) - \int_0^t \frac{dF/ds}{[\pi D(t-s)]^{1/2}} \cdot \exp\left[-\frac{z^2}{4D(t-s)}\right] \cdot ds. \quad (3)$$

It is seen from this equation that if dF/ds has sufficiently large negative values in $0 \leq s \leq t$ or in some part of the interval, then the function $C(t, z)$ will have a maximum value. When phase-boundary reactions are fast and reversible, this is physically obvious; at any time the surface concentration could be rapidly dropped to zero (or some other value) which is less than the concentration inside (which is not zero). The total amount M of diffusing substance in the substrate per unit cross-sectional area is given by

$$M = \int_0^\infty C \cdot dz. \quad (4)$$

Inserting Eq. (2) into Eq. (4) and carrying out the integration with respect to z , we have

$$M = 2\left(\frac{Dt}{\pi}\right)^{1/2} \cdot F(0) + \lim_{z \rightarrow 0} \left(\frac{1}{\pi}\right)^{1/2} \int_0^t F'(s) [4D(t-s)]^{1/2} \exp\left[-\frac{z^2}{4D(t-s)}\right] ds. \quad (5)$$

From Eqs. (1) and (4) we get the well-known relation

$$dM/dt = \lim_{z \rightarrow 0} (-D \cdot \partial C / \partial z). \quad (6)$$

We see from this that the presence of an interior concentration maximum can be examined indirectly from the time dependence of internal diffusing ions M instead of from the concentration distribution.

Now let us consider three particular cases for $F(t)$ in order to see more explicitly the limited diffusion phenomenon.

Case 1: first-order surface reaction type.

$$-dF(t)/dt = kF(t),$$

hence

$$F(t) = C_0 \exp(-kt). \quad (7)$$

Here k is a rate constant and C_0 is the initial surface concentration. Substitution of Eq. (7) into Eq. (2) yields

$$C = \frac{2}{(\pi)^{1/2}} \cdot C_0 \exp(-kt) \int_u^\infty \exp(-s^2 + u^2 \cdot kt/s^2) ds, \quad (8)$$

with

$$u = z/2(Dt)^{1/2}. \quad (9)$$

Eq. (8) may be reduced to the form easy to calculate, namely

$$C/C_0 = \cos[2(kt)^{1/2}u] \cdot [\exp(-kt) - EX] + \sin[2(kt)^{1/2}u] \cdot EY, \quad (10)$$

where

$$\begin{aligned}
EX &= \frac{2}{(\pi)^{1/2}} \cdot \int_0^u \exp(-x^2) \cdot \cos[2(kt)^{1/2}x] \cdot dx, \\
&\doteq (\pi)^{-1} \cdot \sum_{i=1}^{15} w_i \cdot \{ \sin[2(x_i + \sqrt{kt})u]/(x_i + \sqrt{kt}) \\
&\quad + \sin[2(x_i - \sqrt{kt})u]/(x_i - \sqrt{kt}) \}, \quad (11)
\end{aligned}$$

and

$$\begin{aligned}
EY &= \frac{2}{(\pi)^{1/2}} \cdot \int_u^\infty \exp(-x^2) \cdot \sin[2(kt)^{1/2}x] \cdot dx, \\
&\doteq (\pi)^{-1} \cdot \sum_{i=1}^{15} w_i \cdot \{ -\cos[6(x_i + \sqrt{kt})]/(x_i + \sqrt{kt}) \\
&\quad + \cos[6(x_i - \sqrt{kt})]/(x_i - \sqrt{kt}) \\
&\quad + \cos[2(x_i + \sqrt{kt})u]/(x_i + \sqrt{kt}) \\
&\quad - \cos[2(x_i - \sqrt{kt})u]/(x_i - \sqrt{kt}) \}, \quad \text{for } u \leq 3.0, \\
&\doteq 0, \quad \text{for } u > 3.0. \quad (12)
\end{aligned}$$

Here $\{w_i\}$ and $\{x_i\}$ are the Christoffel weight factors and the zeros of Hermite polynomials, respectively [4]. Figs. 1 show the form of C/C_0 . We see from the figure that a concentration maximum is present inside the substrate for comparatively large kt . This is in agreement with the experimental results by T. G. Giallorenzi et al. and J. Noda et al. The total amount M is given by

$$\begin{aligned}
M &= 2\left(\frac{Dt}{\pi}\right)^{1/2} \cdot C_0, \quad k = 0, \\
&= \left(\frac{D}{k}\right)^{1/2} \cdot C_0 \cdot EY(u = 0), \quad k > 0. \quad (13)
\end{aligned}$$

Fig. 2 shows the form of M/C_0 . It is seen that $M(t)$ has a maximum value when $(kt)^{1/2} \doteq 0.92$, and for $(kt)^{1/2} > 0.92$ it has negative gradients; namely, diffusing substances flow towards the substrate surface.

Case 2: second-order surface reaction type.

$$-dF(t)/dt = k \cdot F^2(t),$$

hence

$$F(t) = C_0 \cdot (1 + C_0 kt)^{-1}. \quad (14)$$

Here k is a rate constant and C_0 the initial surface concentration. Substituting Eq. (14) into Eq. (2), we obtain

$$C = 2(\pi)^{-1/2} \cdot C_0 \cdot \int_u^\infty [1 + C_0 kt(1 - u^2/s^2)]^{-1} \cdot \exp(-s^2) \cdot ds. \quad (15)$$

The form of the function C is shown in Fig. 3. We see from the figure that a concentration maximum is present at the substrate interior in this case, too. The total amount M is given by

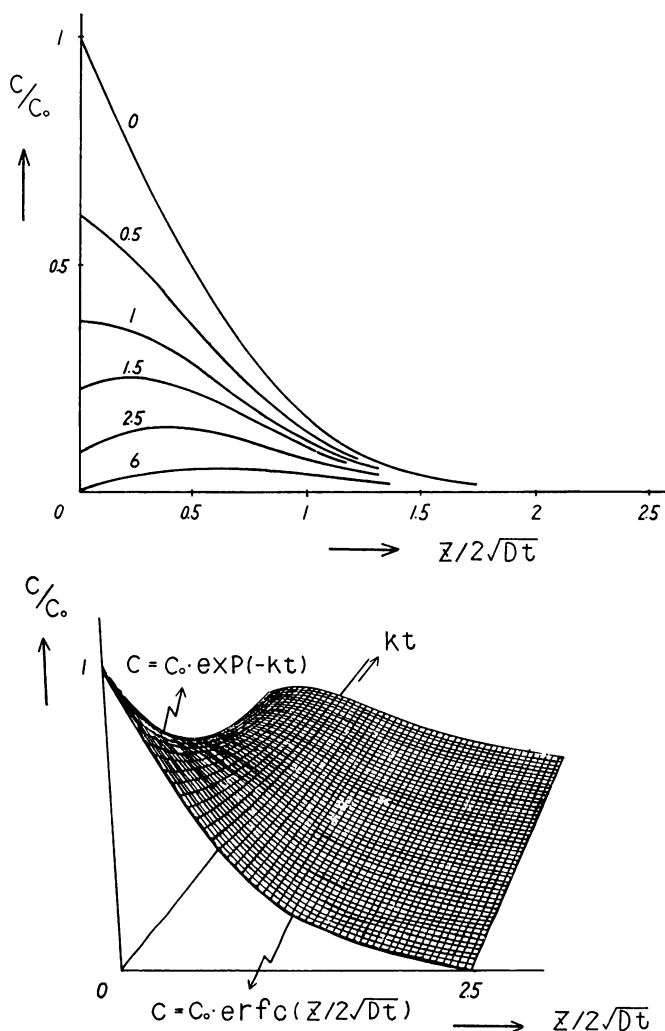


FIG. 1. Diffusion accompanied by the first-order surface reaction. Numbers on curves are values of kt .

$$\begin{aligned}
 M &= 2(Dt/\pi)^{1/2} \cdot C_0, & k &= 0, \\
 &= (\pi)^{-1/2} C_0 \frac{D/C_0 k}{(Dt + D/C_0 k)^{1/2}} \cdot \ln \frac{(Dt + D/C_0 k)^{1/2} + (Dt)^{1/2}}{(Dt + D/C_0 k)^{1/2} - (Dt)^{1/2}}, & k &> 0.
 \end{aligned} \quad (16)$$

The function $M(t)$ has a maximum value when $C_0 kt \doteq 2.3$. Fig. 4 shows the form.

Case 3: half-order surface reaction type.

$$-dF(t)/dt = k \cdot F^{1/2}(t),$$

hence

$$F(t) = C_0 \cdot (1 - kt/2C_0^{1/2})^2, \quad 0 < t \leq 2C_0^{1/2}/k. \quad (17)$$

Here k and C_0 are a rate constant and the initial surface concentration, respectively. This surface reaction becomes a physically meaningless one after a finite time $t_1 = 2C_0^{1/2}/k$. Therefore, we shall discuss this diffusion problem under the condition of time less than t_1 .

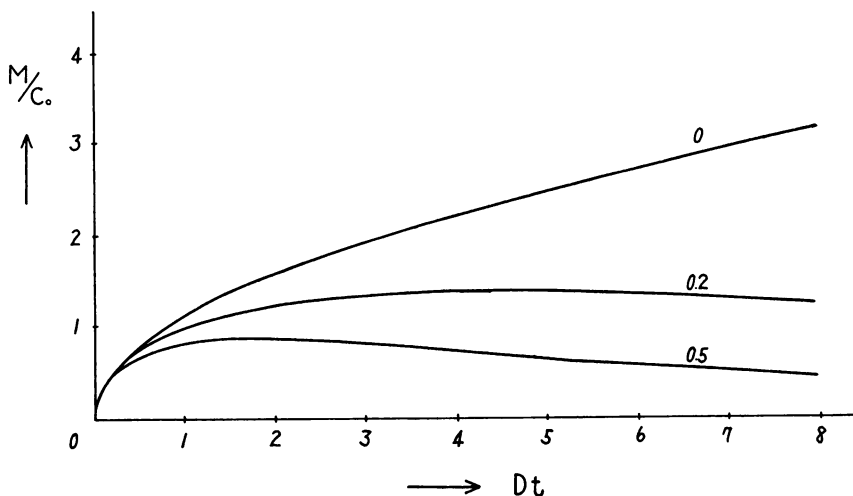


FIG. 2. Total amount of diffusing substance in the case of first order type. Numbers on curves are values of k/D .

Substituting Eq. (17) into Eq. (2), we have

$$C = 2(\pi)^{-1/2} \cdot C_0 \cdot \int_u^{\infty} (1 - kt/2C_0^{1/2} + u^2 kt/2C_0^{1/2} s^2)^2 \exp(-s^2) ds. \quad (18)$$

Eq. (18) might be reduced to the form easy to calculate, the Laplace transform method being used, namely

$$C = C_0 \cdot \{ \operatorname{erfc} u \cdot [1 - y(1 + 2u^2) + (y^2/12) \cdot (3 + 12u^2 + 4u^4)] + \exp(-u^2) [2(\pi)^{-1/2} \cdot yu - (y^2/6) \cdot (\pi)^{-1/2} \cdot (5u + 2u^3)] \}, \quad (19)$$

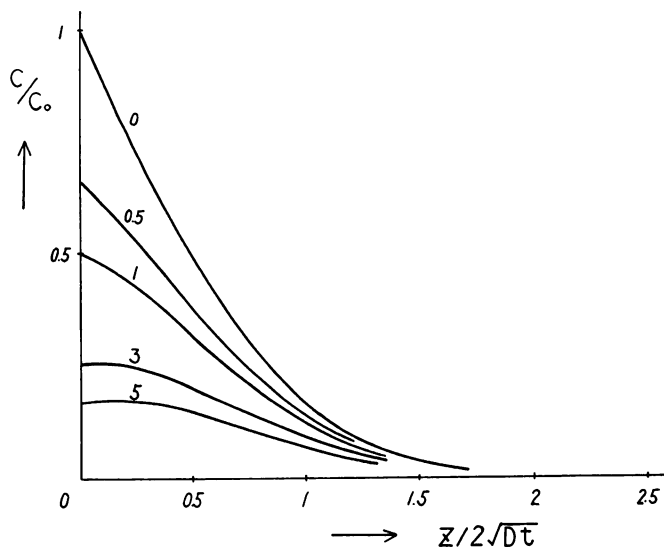


FIG. 3. Diffusion accompanied by the second-order surface reaction. Numbers on curves are values of $C_0 kt$.

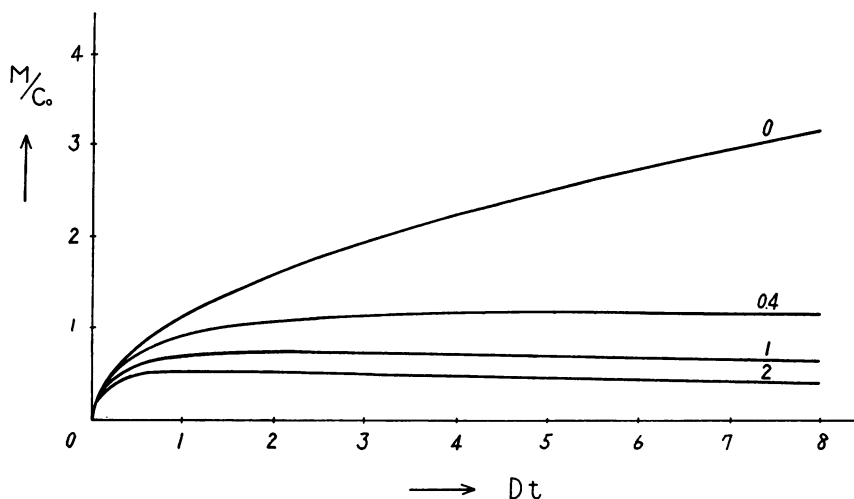


FIG. 4. Total amount of diffusing substance in the case of second-order type. Numbers on curves are values of $C_0 k/D$.

with

$$y = kt(C_0)^{-1/2}, \quad (20)$$

and $\operatorname{erfc} u$ is the complementary error function. The total amount of diffusing substance is given by

$$M = 2(Dt/\pi)^{1/2} \cdot C_0 \cdot (1 - 2y/3 + 2y^2/15). \quad (21)$$

The forms of the functions $C(t, z)$ and $M(t)$ are shown in Figs. 5 and 6, respectively. The quantity $M(t)$ has a maximum value when $y \doteq 0.63$.

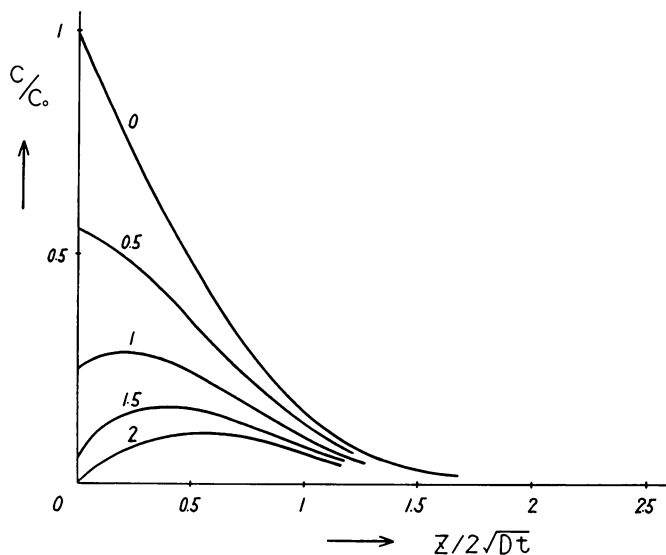


FIG. 5. Diffusion accompanied by the half-order surface reaction. Numbers on curves are values of $kt/\sqrt{C_0}$.

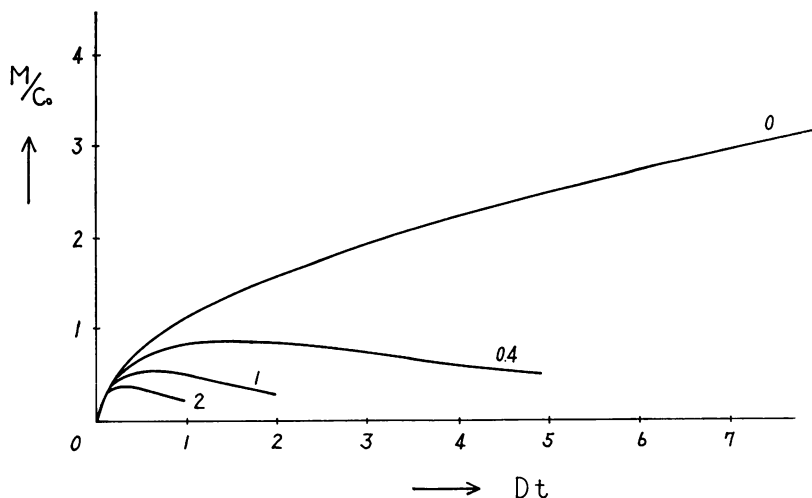


FIG. 6. Total amount of diffusing substance in the case of half-order type. Numbers on curves are values of $k/D\sqrt{C_0}$. ($Dt \leq 2D\sqrt{C_0}/k$.)

3. Concluding remarks. The problems of 'limited' diffusion have been solved and the numerical solutions obtained for three particular cases have been graphically shown. The solutions suggest that the positions of interior concentration maxima are generally dependent on time and that the peak heights are always less than the initial surface concentration. This latter fact is in contrast with that in the one-step field method [5], where the peak height is not always less than the initial surface concentration.

Whether the mass balance at the substrate-diffusion source interface in the limited diffusion processes remarked by T. G. Giallorenzi et al. and J. Noda et al. are of first-order type, of second-order, of half-order, or of the other may be determined from the measurement of time dependence of the surface concentration $F(t)$.

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