It must be emphasized that the agreement around the maximum in the resistivity for Au-Sn, and indeed for all noble metal-Sn alloys is purely qualitative. The resistivity integrand in Eq. (7) for high noble metal concentrations is dominated almost entirely by the low angle behaviour of the $I_{ij}(K)$ (see Fig. 5), particularly those for Au-Au and Au-Sn for example, and accurate data in this region is extremely difficult to accumulate. In addition the pseudopotential elements $U_i(K)$ for the noble metals could be questionable because of the presence of the d bands in these metals. With these limitations in mind, however, any quantitative agreement obtained between theoretical and experimental resistivity values could be fortuitous.

On Non-Ideal Conditions in Plane Source Diffusion Experiments

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The concentration in bottom layer diffusion experiments with non-ideal initial conditions is expressed as an infinite series, the first term of which represents the ideal distribution. It is shown that it is always possible to define the zero time in such a way that the approximation of the diffusion process to an ideal one is optimized.

Introduction

It is often impossible in diffusion experiments to arrange initial conditions that agree with the theoretical conditions imposed in solving the diffusion equation. Strictly speaking, the "ideal" conditions are not necessary, since the diffusion equation has a solution for any known initial distribution. For the one-dimensional case this solution is [1].

$$c = \frac{1}{2\sqrt{\pi D t}} \cdot \int_{-\infty}^{\infty} \varrho(\xi) \cdot \exp[-(x-\xi)^2/4Dt] \, d\xi , \quad (1)$$

where the concentration c is expressed as a function of the time t and the position coordinate x. $\varrho(x)$ is the concentration distribution at $t=0$, and the diffusion coefficent D is assumed to be constant.

The present paper is concerned with plane source diffusion (or bottom layer diffusion) only, where the system is confined to the region $x \geqq 0$, the plane $x=0$ being impermeable. In this case Eq. (1) reduces to [1]

$$c = \alpha_0 (\pi D t)^{-1/2} \cdot \exp\{-x^2/4Dt\} , \quad (2)$$

where α_0 is the amount of diffusing substance per unit area. It is obviously impossible to attain the initial condition strictly in this case, since $c \to \infty$ as $x \to 0$, $t=0$.

We will treat three cases:

I. A controlled addition of diffusing substance takes place at $x=0$ during a finite time interval of length Θ.

II. The arbitrary initial distribution $\varrho(x)$ at a certain moment is determined empirically.

III. The initial distribution $\varrho(x)$ cannot be determined with sufficient accuracy, but the diffusion process can be observed during a certain period of time.

I. Description with Known Rate of Solute Addition

It is often an adequate description to assume that an amount of the diffusing substance is added at $x=0$ during a finite time interval of length Θ [2]. The solution of the diffusion equation is, for $t > t_0$,

$$c = \int_{t_0-\Theta}^{t_0} m(\tau - t_0) \cdot g(x, t-\tau) \, d\tau . \quad (3)$$

$m(\tau - t_0)$ dt is the source strength during the time interval $(\tau, \tau + d\tau)$ (the term $-t_0$ in the argument of the function m is introduced for convenience in what follows), and we have used the abbreviation

$$g(x,t) \equiv (\pi D t)^{-1/2} \cdot \exp\{-x^2/4Dt\} . \quad (4)$$

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[1] W. JOST, Diffusion in Solids, Liquids, Gases, Academic Press Inc., New York 1960, Chap. II, §§ IV, V, VIII.

[2] S. LJUNGGREN and O. LAMM, Acta Chem. Scand. **11**, 340 [1957].

We expand this function in a Taylor series:

$$g(x,t-\tau) = \sum_{n=0}^{\infty} [(1/n!)\,(-\tau)^n\,(\partial^n/\partial t^n)\,g(x,t)]\,. \tag{5}$$

A sufficient condition for the integrand to be uniformly convergent for $t > t_0$, when expressed by this series, is that $m(t)$ is bounded for all values of t. This must be the case for experimental reasons. Integration term by term is therefore permissible:

$$c = \sum_{n=0}^{\infty} [(1/n!)\,(\partial^n/\partial t^n)\,g(x,t)] \cdot \int_{t_0-\Theta}^{t_0} m(\tau-t_0)\,(-\tau)^n\,\mathrm{d}\tau\,. \tag{6}$$

We have

$$\int_{t_0-\Theta}^{t_0} m(\tau-t_0)\,(-\tau)^n\,\mathrm{d}\tau = \int_{-\Theta}^{0} m(\tau)\,(-\tau-t_0)^n\,\mathrm{d}\tau = \sum_{k=0}^{n} [\tbinom{n}{k}\,(-t_0)^{n-k}\,\alpha_k] \tag{7}$$

where we have defined

$$\alpha_k = (-1)^k \int_{-\Theta}^{0} m(\tau)\,\tau^k\,\mathrm{d}\tau = \int_{0}^{\Theta} m(-\tau)\,\tau^k\,\mathrm{d}\tau\,. \tag{8}$$

α_0, defined in this way, has evidently the same meaning as above. The last member of Eq. (8) shows that all the parameters $\alpha_k > 0$ if $m > 0$ for all values of t.

It can be shown by mathematical induction that

$$(\partial^n/\partial t^n)\,g(x,t) = g(x,t)\cdot P_n(y)/(2\,t)^n, \tag{9}$$

where $y \equiv x^2/2\,D\,t$, and P_n is a polynomial of degree n $(P_0 = 1)$.

Using (7) and (9) in Eq. (6), we get

$$c = g(x,t)\cdot\sum_{n=0}^{\infty}\left\{(1/n!)\cdot P_n(y)/(2\,t)^n \cdot \sum_{k=0}^{n}[\tbinom{n}{k}\,(-t_0)^{n-k}\cdot\alpha_k]\right\}. \tag{10}$$

II. Description with Arbitrary Initial Concentration Distribution

According to the assumptions made above, all material is added at $x = 0$, and has to be transported to regions $x > 0$ solely by diffusion. A more general treatment is possible if the concentration distribution at the start of the diffusion run is described by a function $\varrho(x)$. This distribution may be established in any way, such as by addition of material at $x > 0$ or by a transient convection process. The description above appears as a special case; we have at $t = t_0$:

$$\varrho(x) = \lim_{t\to t_0}\int_{t_0-\Theta}^{t_0} m(\tau-t_0)\cdot g(x,t-\tau)\,\mathrm{d}\tau\,. \tag{11}$$

With the conditions

$$\partial c/\partial x = 0, \qquad x = 0$$

and

$$c = \varrho(x), \qquad x \geqq 0, \qquad t = t_0,$$

where t_0 is a moment at or after the start of the undisturbed diffusion process, the concentration at time $t > t_0$ and position x may be derived from (1) by the method of images [1]:

$$c = \tfrac{1}{2}\int_{0}^{\infty}\varrho(\xi)\cdot[g(x-\xi,t-t_0)+g(x+\xi,t-t_0)]\,\mathrm{d}\xi\,. \tag{12}$$

We expand the integrand in two Taylor series:

$$\varrho(\xi)\cdot g(x\pm\xi,t-t_0) = \sum_{q=0}^{\infty}\{[\varrho(\xi)/q!]\cdot(\pm\xi\,\partial/\partial x - t_0\,\partial/\partial t)^q\,g(x,t)\}\,. \tag{13}$$

The series converge absolutely and uniformly for $t > t_0$, provided that $\varrho(x)$ is bounded for all values of x; this must be the case for experimental reasons.

$g(x,t)$ is a solution of Fick's second law, and we can therefore substitute the operator $(D\,\partial^2/\partial x^2)$ for $(\partial/\partial t)$ in Eq. (13). The absolute convergence makes possible a rearrangement of terms. The parenthesis of the integrand in Eq. (12) may thus be expressed as

$$\sum_{q=0}^{\infty}\sum_{p=0}^{q}\{[1+(-1)^p]\cdot[p!\,(q-p)!]^{-1}\cdot\xi^p\,(-D\,t_0)^{q-p}\,(\partial/\partial x)^{2q-p}\,g(x,t)\}\,.$$

We see that terms with odd powers of p vanish so we can set $p = 2\,k$. We also set $q - k = n$, and utilize again the equality of the operators

$$(\partial^2/\partial x^2) = (D^{-1}\,\partial/\partial t)\,.$$

According to the uniform convergence, we may perform the integration term by term, and we get

$$c = \sum_{n=0}^{\infty}\left\{(1/n!)\,(\partial^n/\partial t^n)\,g(x,t)\cdot\sum_{k=0}^{n}[\tbinom{n}{k}\,(-t_0)^{n-k}\cdot\beta_k]\right\} \tag{14}$$

where we have defined

$$\beta_k = [k!/(2\,k)!]\cdot\int_{0}^{\infty}\varrho(\xi)\,(\xi^2/D)^k\,\mathrm{d}\xi\,. \tag{15}$$

Finally, with the aid of Eq. (9), we get the following general expression for the concentration:

$$c = g(x,t) \cdot \sum_{n=0}^{\infty} \left\{ (1/n!) \cdot P_n(y)/(2\,t)^n \cdot \sum_{k=0}^{n} \left[\binom{n}{k} (-t_0)^{n-k} \cdot \beta_k \right] \right\}.$$

This equation is formally identical to Eq. (10), if we substitute α_k for β_k.

The following treatment is applicable to both case I and case II. For simplicity we neglect the distinction between α_k and β_k, it being understood that the definition (8) should be used for case I and (15) for case II.

We rewrite Eq. (10) in the following way:

$$c = \alpha_0 \cdot g(x,t) \cdot \sum_{n=0}^{\infty} \left[K_n(t_0) \cdot P_n(y)/(2\,t)^n \right], \quad (16)$$

where

$$K_n \equiv [1/(\alpha_0\, n!)] \cdot \sum_{k=0}^{n} \left[\binom{n}{k} (-t_0)^{n-k}\, \alpha_k \right]. \quad (17)$$

The series (16) is generally valid, irrespective of the choice of time scale. This characteristic will be utilized in section III. t_0, which specifies the moment when all diffusing material has been added (section I), or the moment when $\varrho(x)$ was determined (section II), can be considered a parameter, and the coefficients K_n depend on this parameter. This means that their values are determined by the choice of time scale, and by a suitable choice we can impose a condition on them, such as to make a certain $|K_j|$ a minimum.

We will now make such a specialization. It is often assumed à priori that the diffusion process in an experiment with non-ideal initial conditions can be described as an ideal one by introducing a "zero-time correction"[3, 4]. Eq. (16) shows that this is meaningful in the case of bottom layer diffusion:

The first order approximation is

$$c = \alpha_0 \cdot g(x,t) \cdot [1 + (\alpha_1/\alpha_0 - t_0) \cdot P_1(y)/(2\,t)]. \quad (18)$$

If we choose a new time scale t' so that

$$t' = t - (t_0 - \alpha_1/\alpha_0), \quad (19)$$

we get

$$t_0' = t_0 - (t_0 - \alpha_1/\alpha_0) = \alpha_1/\alpha_0 \quad (20)$$

and

$$K_1(t_0') = (\alpha_1/\alpha_0 - t_0') = 0. \quad (21)$$

Eq. (18) reduces to

$$c = \alpha_0 \cdot g(x, t') \quad (22)$$

where correction terms of second and higher order are neglected. In the following we will call the time scale defined by (19) the "ideal" scale.

It can be shown that

$$\frac{\mathrm{d}K_{n+1}}{\mathrm{d}t_0} = -K_n.$$

This implies that if $t_0' = \alpha_1/\alpha_0$ so that $K_1 = 0$, the next coefficient

$$K_2(t_0') = t_0'^2/2 - t_0'\,\alpha_1/\alpha_0 + \alpha_2/2\,\alpha_0 = \alpha_2/2\,\alpha_0 - \alpha_1^2/2\,\alpha_0^2 \quad (23)$$

will be a minimum. $|K_2|$ may be a minimum or a relative maximum, but in practical cases this extreme value is in general such as to make the second order term negligible within short time (see examples below).

It is to be noted that t_0', defined by Eq. (20), is a constant, independent of x and t. It seems intuitively plausible that a suitable definition of time scale should improve the approximation to the ideal equation also in the case of a plane boundary experiment[3] (initial conditions: $c = c_0$, $x < 0$; $c = 0$, $x > 0$). However, a well-defined t_0' can probably not be introduced as above (cf. Ref. [4]).

Although equations (16) through (23), and the reasoning accompanying them, are applicable to both case I and case II, there is a fundamental difference between the two cases regarding their practical usefulness. The definition (19) of the "ideal" time scale can be used in case I, or more generally, the constants α_k may be computed from (8). In case II, however, the computation of α_k from (15) requires the knowledge of the diffusion coefficient, which is normally to be determined in an experiment. For this reason either a "trial and error" or an iteration process[3] is required to find the "ideal" time scale for case II. The approach in Section III, however, is generally applicable, since it requires no explicit choice of time scale.

Example I

A concentrated solution is injected at constant rate at the bottom of a diffusion cell[2], i. e. $m(t - t_0) = m =$ constant in Eq. (3). By definition in Eq. (8) we have

$$\alpha_k = m \cdot \Theta^{k+1}/(k+1), \quad (24)$$

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[3] O. Bryngdahl, Acta Chem. Scand. **11**, 1017 [1957].

[4] O. Bryngdahl, Acta Chem. Scand. **12**, 684 [1958].

whence

$$\alpha_0 = m\,\Theta, \qquad \alpha_1 = \alpha_0\,\Theta/2, \qquad \alpha_2 = \alpha_0\,\Theta^2/3. \quad (25)$$

The constants (25) are used for computing $K_2(t_0')$ from (23). When this coefficient is introduced in Eq. (16), we get the second order approximation

$$c = \alpha_0 \cdot g(x, t') \cdot [1 + \Theta^2\,P_2(y')/96\,t'^2]\,, \quad (26)$$

where t' is the "ideal" time scale

$$t' = t - t_0 + \Theta/2$$

defined by (19),

$$y' \equiv x^2/2\,D\,t' \quad \text{and} \quad P_2(y') \equiv y'^2 - 6\,y' + 3.$$

In the interval $0 \leqq x \leqq 3.5\,(D\,t')^{1/2}$, which should cover the range of interest in an experiment, (26) deviates less than one per cent from the ideal equation as $t' \geqq 2.5\,\Theta$. With $\Theta \approx 4$ minutes as in Ref. [2], approximately 10 minutes from the middle of the interval of injection should be sufficient to attain this condition.

Example II

The following conditions

$$\left.\begin{array}{l} c = c_0\,, \quad x \leqq h \\ c = 0\,, \quad x > h \end{array}\right\} t = t_0\,, \qquad \partial c/\partial x = 0, \quad x = 0, \quad t \geqq t_0$$

give a well-known exact solution [1]:

$$c = (c_0/2) \cdot \left[\operatorname{erf} \frac{x+h}{2\,D\,(t-t_0)^{1/2}} - \operatorname{erf} \frac{x-h}{2\,D\,(t-t_0)^{1/2}}\right]. \quad (27)$$

Here again we want to find the best approximation (22) to the ideal equation. The constants α_k of (16) and (17) are given by (15):

$$\alpha_k = [k!/(2\,k+1)\,!] \cdot c_0\,h\,(h^2/D)^k, \quad (28)$$

and the first three of them are:

$$\alpha_0 = c_0\,h, \qquad \alpha_1 = (\alpha_0/3\,!) \cdot (h^2/D),$$
$$\alpha_2 = (2\,\alpha_0/5\,!) \cdot (h^2/\mathrm{D})^2. \quad (29)$$

The second order approximation, with the "ideal" time scale

$$t' = t - t_0 + h^2/6\,D \quad (30)$$

defined by (19), is obtained by using (23) and (29) in (16):

$$c = c_0\,h \cdot g(x, t') \cdot [1 - (h^2/D)^2 \cdot P_2(y')/720\,t'^2]. \quad (31)$$

(31) deviates less than one percent from the ideal plane source solution in the interval

$$0 \leqq x \leqq 3.5\,(D\,t')^{1/2}$$

as $t' \geqq .9/h^2/D$.

With the "common" time scale

$$t'' = t - t_0\,, \qquad t_0'' = 0\,, \quad (32)$$

Eq. (16) gives the first order approximation

$$c = c_0\,h\,g(x, t'') \cdot [1 + (h^2/D) \cdot P_1(y'')/12\,t''] \quad (33)$$

where $P_1(y'') \equiv y'' - 1$ and $y'' \equiv x^2/(2\,D\,t'')$.

This expression, which approximates the exact solution (27) in the time scale (32), requires $t'' \geqq 41\,h^2/D$ in order to deviate less than one per cent in the interval $0 \leqq x \leqq 3.5\,(D\,t'')^{1/2}$.

For diffusion in liquids, the $\varrho(x)$ assumed here is of the most unfavorable form. For hydrodynamic reasons, $\varrho(x)$ cannot possibly be an increasing function of x at any point, and a decreasing function gives lower values of α_k than those given above. In practice it is therefore likely that the deviation from ideality is less than in this example for a given h. In a solid, on the other hand, any $\varrho(x)$ is conceivable, but here it should be possible to control the initial distribution at will.

III. Description when the Initial Distribution is Unknown

The calculation of the constants α_k from (15) can be done only if we know the entire concentration distribution. This knowledge may be achieved by some optical methods, for instance, but very often the concentration or its derivative is recorded at a few points only. In such a case (with non-controlled addition of diffusing material) the parameter t_0 loses its experimental significance, and no special time scale can be associated with the diffusion process.

We can change the values of the constants K_n in Eq. (16) by changing the definition of time scale; and vice versa: by selecting a certain value for one of the constants, say $K_{j+1} = 0$, we tacitly define a special time scale

$$t' = t - T, \quad (34)$$

where t is the experimental time and T is an unknown constant.

We set $\qquad \sum\limits_{n=j+1}^{\infty} K_n\,P_n/(2\,t)^n = 0$

in Eq. (17). Sufficiently far from the start of the experiment, when the terms of order $(j+2)$ and higher orders may be neglected in comparison with that of order $(j+1)$, this means essentially $K_{j+1}=0$, and t' is thus a time scale for which this is true. In order to solve D, we need a set of $(j+2)$ of the resulting equations (if α_0 is assumed to be known):

$$c=\alpha_0\cdot g(x, t'+T)\cdot\sum_{n=0}^{j} K_n P_n/[2(t'+T)]^n, \quad (35)$$

where at least two different times must be used.

We may rewrite Eq. (35) in a more convenient form:

$$c=\alpha_0\cdot f(x, z)\cdot\sum_{n=0}^{j} L_n P_n/(2z)^n \quad (36)$$

where

$$z=D t'=D(t-T), \quad (37)$$

$$f(x, z) \equiv g(x, z/D), \quad (38)$$

$$L_n=K_n D^n, \quad (39)$$

and

$$P_n=P_n(x^2/2z). \quad (40)$$

If a sufficient amount of data is available, we may calculate z for a set of different times t. When the resulting z-values are plotted in a z versus t diagram, we expect a straight line with slope D for times where $\sum_{n=j+2}^{\infty} L_n P_n/(2z)^n$ is negligible in comparison with $L_j P_j/(2z)^j$, or to be exact: we expect the $z(t)$ curve to approach asymptotically the straight line with slope D and intercept T on the time axis.

If we retain only the ideal term [$j=0$ in Eq. (36)], the intercept is the "ideal" starting time. For the conditions in Example II, we get $T=t_0-h^2/6D$ for this case. With $j=1$ we get two different lines in this example since here $K_2(t_0)$ has two real roots.

Summing up, we find that the approach in Section III is generally valid for bottom layer diffusion, while that described in Section I may be convenient in special cases. A choice of "ideal" time scale by direct computation from (19) for the case in Section II is impossible in principle, but may be done if an approximate value of D is available.

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