LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA o LOS ALAMOS   NEW MEXICO

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FOR FISSION PRODUCTS

IN POWDERED OR SINTERED MATERIALS

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By

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ABSTRACT

It is pointed out that the diffusion of fission products out of irregularly shaped particles in which the initial concentration is uniform is approximately independent of particle shape during the early stages of the diffusion process. The concentration depends only on distance measured into the particle normal to the surface and on time; thus, the diffusion is initially one-dimensional.

The one dimensional diffusion equation with a time dependent diffusion coefficient is solved with appropriate boundary conditions and a brief discussion of the application of the solution to the experimental determination of diffusion coefficients is given.

INTRODUCTION

The study of the diffusion of fission products in various uranium compounds is greatly complicated by the fact that the material in which the diffusion occurs usually consists of a powder or of a sintered compact, i.e., a collection of microscopic particles (crystallites) of more or less random shape. A frequently used method of determining the diffusion coefficient, D, for some fission product in a sample of, for instance, UO_2 powder is to measure the fraction of the initial amount of fission product which diffuses out of the sample of UO_2 in a given time interval. One then assumes that the UO_2 powder consists entirely of crystallites of the same size and shape, usually spherical, and employs the solution of the diffusion equation for particles of the assumed shape to determine the diffusion coefficient. The error due to the assumption of a particular size and shape for the particles may be large and is, in any case, difficult to estimate.

It is the purpose of this report to discuss a way whereby the difficulty due to the unknown particle shape may be avoided. If the

diffusion proceeds for a sufficiently short time, only material near the surface of the crystallites will diffuse out of the sample; the concentration in the interior of the crystallites will remain unchanged. The amount of material which diffuses out will then depend only on the sum of the surface areas of the crystallites of the sample and not on the shape of the crystallites. Since the total surface area of a sample can be determined by the BET[1] method, the diffusion coefficient, as will be shown below, can be determined without any assumptions about the shape of the crystallites.

It should be emphasized at the start that this idea is not new. Solutions of the diffusion equation appropriate to the short time limit have been given by Inthoff and Zimen[2] and by Booth and Rymer[3]; and the experimental technique has been used by Booth and Rymer[3] as well as by Lindner and Matzke[4] in the study of the diffusion of Xe^{133} in various oxides of uranium.

In this report we will obtain a solution to the diffusion equation, for the case in which diffusion proceeds for only a short time, by a method which differs from those mentioned above and will briefly discuss its application to the interpretation of experiments designed to measure diffusion coefficients. Although our results are not essentially different from those obtained previously, it is hoped that this brief discussion will prove useful.

SOLUTION OF THE DIFFUSION EQUATION

If diffusion proceeds for only a short time the concentration, C, of diffusing substance within a crystallite will be a function only of time and distance measured into the crystallite in a direction normal to the surface; the meaning of "short time" will be specified below. Thus, we can treat the diffusion as a one-dimensional process. For the one-dimensional case the diffusion equation is

$$D \frac{\partial^2 C}{\partial x^2} - \frac{\partial C}{\partial t} = 0. \tag{1}$$

The x coordinate axis is taken normal to the crystallite surface with $x = 0$ at the surface and x positive inside the crystallite. We will define the zero of time to be that time when the concentration, C, is uniform throughout the crystallite. In practice this time is difficult to determine; some diffusion occurs as the sample is heated to the temperature at which the measurement is to be made. In order to properly consider this effect we will assume that the diffusion coefficient, D, is time dependent. We want a solution to (1) for positive values of x and t only. A solution may be written in the form

$$C(x,t) = \int_{-\infty}^{\infty} dk\ a(k)\ \exp\left(ikx - k^2 \int_0^t Ddt'\right) \tag{2}$$

as may be verified by direct substitution into (1). The integral in (2) is taken along the real k axis; the function, a(k), which is in general complex, is to be determined by the boundary conditions on $\dot{C}(x,t)$. The boundary conditions are that C be uniform for positive x for t = 0, and that C be zero at x = 0 for all times.

For t = 0 we have

$$C(x,0) = \int_{\infty}^{\infty} dk \, a(k) \, e^{ikx} = \begin{cases} C_0 & \text{for } x > 0 \\ 0 & \text{for } x = 0. \end{cases} \tag{3}$$

Here C_0 is the uniform initial value of the concentration. By the usual methods of contour integration we obtain the result that a term in a(k) equal to $\frac{C_0}{2\pi i} \frac{1}{k-i\epsilon}$, where it is understood that ϵ is positive but is to be allowed to approach zero, will give $C(x,0) = C_0$ for $x > 0$. Furthermore, it is clear that any pole in a(k) which lies below the real k axis will make no contribution to C(x,0) for x > 0. However, such a pole will contribute for t > 0. From (2) it is clear that if we choose a(k) to be an odd function of k then C = 0 at x = 0 for all times. Thus, we have

$$a(k) = \frac{C_0}{2\pi i} \left(\frac{1}{k-i\epsilon} + \frac{1}{k+i\epsilon} \right) = \frac{C_0}{\pi i} \frac{k}{k^2+\epsilon^2} \tag{4}$$

and

$$C(x,t) = \frac{C_0}{\pi} \int_{\infty}^{\infty} dk \, \frac{k \sin kx}{k^2+\epsilon^2} \exp \left(-k^2 \int_0^t D dt' \right). \tag{5}$$

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If we introduce a parameter ν defined by

$$\nu = \left(\frac{x^2}{4\int_0^t D\,dt'} \right)^{1/2} \qquad (6a)$$

and set $kx = y$ we can write (5) as

$$C(x,t) = \frac{C_0}{\pi} \int_{-\infty}^{\infty} dy\, \frac{y \sin y}{y^2 + x^2 \epsilon^2} \exp\left(-\frac{y^2}{4\nu^2} \right)$$

$$= \frac{C_0}{\pi} \int_{-\infty}^{\infty} dy\, \sum_n \frac{(-1)^n y^{2n}}{(2n+1)!} \exp\left(-\frac{y^2}{4\nu^2} \right)$$

where in the second integral we have taken the limit $\epsilon \to 0$. The series may be integrated term by term to give

$$C(x,t) = \frac{2C_0}{\sqrt{\pi}} \sum_n \frac{(-1)^n \nu^{2n+1}}{n!\,(2n+1)} = \frac{2C_0}{\sqrt{\pi}} \operatorname{erf}\nu. \qquad (6b)$$

Thus, $C(nt)$ depends on x and t only through the single parameter ν. The error function, $\operatorname{erf}\nu \equiv \int_0^\nu dy\, e^{-y^2}$, has been tabulated by Jahnke and Emde[5]. From the form of the solution we see that for $x \gg \left(\int_0^t D\,dt \right)^{1/2}$, which we will call the diffusion depth, the concentration approaches its initial value. Only within a distance of a few times the diffusion depth of the surface is the concentration different from its initial value. This point will be discussed more fully below.

APPLICATION TO EXPERIMENTS

For a sample composed of many crystallites the quantity of diffusing substance which at time t has been released from a layer of thickness x on the surface of all crystallites of the sample is

$$q(x,t) = \int da \int_0^x dx' \left[C_0 - C(x',t) \right] \qquad (7)$$

where the integral over a is over the total surface area of the sample. As our notation indicates, we consider the possibility that the initial concentration, C_0, may vary over the surface area of the sample. Such a variation, which may be over the surface of individual crystallites as well as from crystallite to crystallite, could be caused by self-shielding of the sample during the neutron irradiation which produces the initial concentration, C_0. We assume that the resulting gradient of C_0 is small enough to have only a negligible effect on diffusion. We substitute (6) for $C(x',t)$ in (7) and carry out the integral over x to obtain

$$q(x,t) = 2 \left(\int_0^t Ddt \right)^{1/2} g(v) \int da C_0 \qquad (8a)$$

where

$$g(v) = v - \frac{2v}{\sqrt{\pi}} \, erf\, v + \frac{1}{\sqrt{\pi}} \left(1 - e^{-v^2} \right) \qquad (8b)$$

with v defined, as before, by (6a).

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The function, $g(\nu)$, is plotted in Fig. 1; it is apparent that $g(\nu)$ approaches $\frac{1}{\sqrt{\pi}}$, its limiting value for large ν, to within a fraction of a per cent for $\nu \sim 2$. Therefore, if the diffusion depth, $\left(\int_o^t Ddt\right)^{1/2}$, is small compared to the dimensions of a crystallite, the total quantity of diffusing substance released by the sample in time, t, is given to good approximation by

$$\lim_{x \to \infty} q(x,t) = \frac{2}{\sqrt{\pi}} \left(\int_o^t Ddt \right)^{1/2} \int da C_o \qquad (9)$$

The fraction, $f(t)$, of diffusing substance released by the entire sample in time, t, is

$$f(t) = \frac{2}{Q_o \sqrt{\pi}} \left(\int_o^t Ddt \right)^{1/2} A \overline{C_o} \qquad (10)$$

where A is the total surface area of the sample, Q_o is the initial quantity of diffusing substance contained in the sample, and $\overline{C_o}$ is the initial concentration averaged over the surface area of the sample. If we assume $\overline{C_o}$ to be the same as the volume average of C_o, we obtain

$$f(t) = \frac{2}{\sqrt{\pi}} \left(\int_o^t Ddt \right)^{1/2} \frac{A}{V} \qquad (11)$$

where V is the total volume of the sample.

Thus, a measurement of $f(t)$, A, and V allows a determination of $\int_o^t Ddt$. If the measurement is done in such a manner that for $t > t_o$
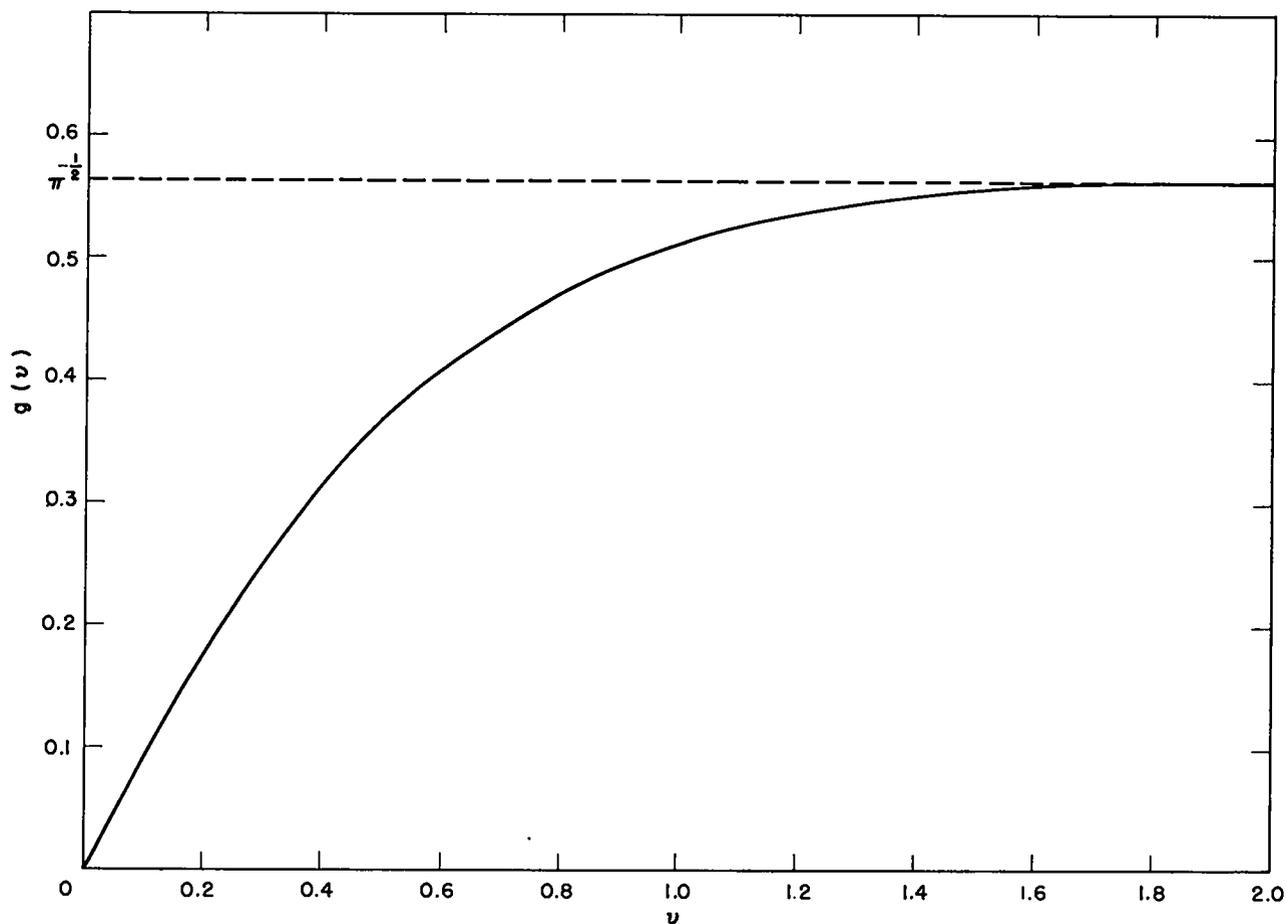
Fig. 1 - Plot of the function $g(\nu) = \nu - \dfrac{2\nu}{\sqrt{\pi}}\,\text{erf}\,\nu + \dfrac{1-e^{-\nu^2}}{\sqrt{\pi}}$ vs ν. The parameter ν is $\left(\dfrac{x^2}{4\int_{o}^{t}Ddt}\right)^{1/2}$.

The quantity, $q(x,t)$, of substance which at time t has been released from a layer of thickness x on the surface of the sample depends on x only through being proportional to $g(\nu)$. It is clear that $q(x,t)$ approaches a limiting value for x only a few times the diffusion depth, $(\int_{o}^{t}Ddt)^{1/2}$.

the temperature and therefore D are held constant, we have

$$f(t) = \frac{2}{\sqrt{\pi}} \left(I + (t-t_0)D \right)^{1/2} \frac{A}{V} \qquad (12a)$$

with
$$I = \int_0^{t_0} D \, dt. \qquad (12b)$$

For $(t-t_0)D \gg I$, this is approximately

$$f(t) \cong \frac{2}{\sqrt{\pi}} \frac{A}{V} \left[(t-t_0)D \right]^{1/2}. \qquad (13)$$

Equation (13) or equivalent expressions have been obtained previously[2,3] and used in the determination of diffusion coefficients[3,4]. In these experiments the sample was heated as rapidly as possible in order to reduce the effect of the diffusion which occurred before the sample temperature reached the value at which the measurement was to be made. The measured values of $f(t)$ were plotted against $\sqrt{t_0-t}$; to within the experimental error the plots were linear. However, it was observed by Booth and Rymer[3] that, for $t = t_0$, the plot of $f(t)$ did not pass through zero. This may indicate that diffusion which occurred during the heating up time, represented by I in equation (12), was not negligible. If I is important, the plot of $f(t)$ vs $\sqrt{t-t_0}$ should also curve upward slightly, but such a curvature could easily be masked by the experimental error.

A way of avoiding this difficulty is to plot $f^2(t)$ vs $t-t_0$. By squaring equation (12a) we get

$$f^2(t) = \frac{4}{\pi} \frac{A^2}{V^2} \left[I + (t-t_0)D \right].$$ (14)

Thus, the diffusion coefficient, D, may be determined from the slope, $\frac{4}{\pi} \frac{A^2}{V^2} D$, of this plot; no special precautions need be taken to keep I small compared to $(t-t_0)D$ provided the total diffusion depth remains small.

The main requirement for the validity of this method is that the diffusion depth, $\left(\int_0^t D dt' \right)^{1/2}$, be small compared to crystallite dimensions. As is seen from equation (11), this implies that $f(t)$ be small compared to one. As soon as the diffusion depth becomes comparable to the dimensions of the smaller crystallites of the sample, the plot of $f^2(t)$ vs $t-t_0$ will begin to curve downward due to depletion of the smaller particles. It is apparent that if this technique is to be used successfully there must be a rather definite lower limit to the range of particle sizes in the sample.

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