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### Publication Date

1968-07-01

UCRL-18345

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UCRL-18345  
UC-4 Chemistry  
TID-4500 (52nd Ed.)

UNIVERSITY OF CALIFORNIA  
Lawrence Radiation Laboratory  
Berkeley, California  
AEC Contract No. W-7405-eng-48

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A CHEMICAL SECTIONING METHOD FOR THE MEASUREMENT OF  
SMALL DIFFUSION COEFFICIENTS IN SOLIDS

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ABSTRACT

A mathematical analysis of diffusion measurements in silver bromide, obtained by a chemical sectioning method, may lead to a more general application of this simple experimental technique for the determination of small ( $10^{-10}$  -  $10^{-14}$   $\text{cm}^2 \text{s}^{-1}$ ) diffusion coefficients in solids. The mathematical treatment which involves the exact solution of Fick's law can be used to establish optimal experimental procedures for the measurement of small diffusion coefficients within a relatively short period of time.

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## II. EXPERIMENTAL\*

Large crystals of pure AgBr, obtained by the Kyropoulos method,<sup>3</sup> were shaped into cylinders (2-3 cm diameter, 1-2 cm thickness) and their plane faces chemically polished by wrapping the crystal on a soft velvet cloth impregnated with a solution of KCN 1M. The crystallographic orientation of the surface to be studied was determined by chemical development as described in Ref. 4. For diffusion measurements, a polished glass ring ( $\phi$  1.5 cm) was firmly held against one of the polished plane surfaces of the crystal. A volume of a radioactive AgNO<sub>3</sub> solution,\*\* sufficient to cover the entire portion of the surface enclosed by the glass ring, was then introduced into the latter and left in contact with the crystal surface until it reached a state of homogeneous\*\*\* radioactivity (by the exchange of part of its surface silver ions) of ca.  $10^4$  c/min (time of exchange  $t_0$  ca. 24 hr or less).

The radioactive AgNO<sub>3</sub> solution was then removed and the crystal left at constant temperature for  $t_1$  hours (total diffusion time  $t = t_0 + t_1$ ). The residual activity in the crystal has been determined by successive dissolution of thin (2-5 $\mu$ ) layers of AgBr. This chemical sectioning was obtained by wrapping the activated crystal surface on a velvet cloth impregnated with a 0.1 M solution of KCN, and the thickness  $x$  of the dissolved layers was determined by weight ( $\Delta x = \pm 0.1\mu$ ). The

\* For further details see reference 1.

\*\* AgNO<sub>3</sub> 1M, containing 1 mC Ag<sup>110m</sup> per liter ( $t_{1/2} = 253d$ ,  $\bar{E}_\gamma = 0.66$  MeV)

\*\*\* Equally distributed as controlled by autoradiography of the activated surface

radioactivity remaining in the AgBr crystal after the dissolution of each layer was measured with a KI-Tl scintillation counter under constant geometric conditions (statistical error 1%). No reactivation of the crystal has been observed during the chemical sectioning procedure.

## III. THEORY AND RESULTS

Fick,<sup>5</sup> in his theoretical study of diffusion, drew an analogy between the diffusion process in gases and the phenomenon of a solute dissolving in a solvent. By comparing the latter with the diffusion of heat through a conductor, he asserted that the concentration of solute in a solvent was governed by Fourier's law of heat conduction with concentration substituted for temperature. This hypothesis has become known as Fick's law. Many more sophisticated theories of diffusion, applicable to mixtures of general continua - fluid-solid, solid-solid, mixtures of fluids etc., have since been developed by numerous authors.<sup>6-10</sup> However, Fick's law [Equation (1)] suffices when the diffusion coefficients are small as in the experiments under consideration in this paper.

Solving

$$-\frac{\partial c}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2} \quad (1)$$

for the linear diffusion (in the x-direction only) into a semi-infinite cylinder of arbitrary shape, having at its plane surface an infinitely thin layer of radioactive ions, we obtain the following equation (since activities are proportional to concentrations:

$$A(x,t) = \frac{A_0}{\sqrt{\pi Dt}} \exp - (x^2/4Dt) \quad (2)$$

where  $A_0 = \int_0^{\infty} A(x,0) dx$  is the total radioactivity of the solid at  $t = 0$ ,  $D$  is the diffusion coefficient and  $t$  the diffusion time.



We define

$$R(x,t) = A_0 - \int_0^x A(y,t) dy = \int_x^\infty A(y,t) dy \quad (3)$$

where  $R(x,t)$  is the activity measured in the solid after dissolution of a thickness  $x$  and a total diffusion time  $t$ .

From (2) and (3) we find that

$$R(x,t) = \frac{A_0}{\sqrt{\pi Dt}} \int_x^\infty \exp(-y^2/4Dt) dy \quad (4)$$

which, after substitution of

$$\operatorname{erfc}(u) = 1 - \frac{2}{\sqrt{\pi}} \int_0^u \exp(-z^2) dz$$

leads to

$$R(x,t) = A_0 \operatorname{erfc} \frac{x}{2\sqrt{Dt}} = A_0 - A_0 \operatorname{erf} \frac{x}{2\sqrt{Dt}} \quad (5)$$

which can also be written as

$$\operatorname{erf} \frac{x}{2\sqrt{Dt}} = \operatorname{erf} \frac{1}{\sqrt{D}} \frac{x}{2\sqrt{t}} = \frac{A_0 - R(x,t)}{A_0} \quad (6)$$

By using the inverse error function  $G$  defined by

$$G\{\operatorname{erf}(u)\} = u$$

and substituting into (6) we find

$$\frac{1}{\sqrt{D}} \frac{x}{2\sqrt{t}} = G\left\{ \frac{A_0 - R(x,t)}{A_0} \right\} \quad (7)$$

Thus, by plotting  $G$  as a function of  $x/2\sqrt{t}$  we should find a straight line with the slope  $1/\sqrt{D}$  (see Figs. 1 and 3). Steiger,<sup>1</sup> in a previous

From (10) and (11), therefore, we see that for small values of  $x/\sqrt{Dt}$ ,

$$\frac{1}{\frac{d(\log R)}{d(x^2)}} = -4Dt \left\{ \frac{\sqrt{\pi}}{2} \frac{x}{\sqrt{Dt}} e^{x^2/4Dt} - \left[ \frac{x^2}{2Dt} + \frac{1}{1.3} \left( \frac{x^2}{2Dt} \right)^2 + \frac{1}{1.3.5} \left( \frac{x^2}{2Dt} \right)^3 + \dots \right] \right\} \quad (12)$$

which accounts for the deviation from  $-4Dt$  observed for small values of  $x$ .

Similarly, by repeated integration by parts of the integral  $\int_u^\infty \exp(-z^2) dz$ , it can be shown\* that for large values of  $x/\sqrt{Dt}$

$$\operatorname{erfc} \frac{x}{2\sqrt{Dt}} = \frac{2}{\sqrt{\pi}} e^{-x^2/4Dt} \left[ \frac{\sqrt{Dt}}{x} - 2 \left( \frac{\sqrt{Dt}}{x} \right)^3 + 1.3.2^2 \left( \frac{\sqrt{Dt}}{x} \right)^5 - \dots - 1.3.5.2^3 \left( \frac{\sqrt{Dt}}{x} \right)^7 + \dots \right], \quad (13)$$

where the error involved in terminating the series at any stage is less than the next term in the series.

Hence, for large values of  $\frac{x}{\sqrt{Dt}}$ ,

$$\frac{1}{\frac{d(\log R)}{d(x^2)}} = -4 Dt \left[ 1 - \frac{2Dt}{x^2} + 1.3 \left( \frac{2Dt}{x^2} \right)^2 - 1.3.5 \left( \frac{2Dt}{x^2} \right)^3 + \dots \right] \quad (14)$$

and clearly this tends to a constant value of  $-4Dt$  as  $x \rightarrow \infty$ . This explains why the graph in Fig. 1 tended to a straight line of slope

\* See reference 11.

$-\frac{1}{2.30 \times 4Dt}$  for larger values of  $x$ .

The error involved in the calculated value of  $D$  when one assumes that the slope of the graph of  $\log R(x,t)$  against  $x^2$ , at the point  $x$ , is equal to  $-\frac{1}{4Dt}$ , is given by

$$D - D \cdot \frac{\frac{x}{\sqrt{Dt}} \operatorname{erfc} \frac{x}{2\sqrt{Dt}}}{\frac{2}{\sqrt{\pi}} e^{-x^2/4Dt}} = \text{error},$$

using Eq. (10).

Hence,

$$\text{error} = D \left( 1 - \frac{2u(1-\operatorname{erf}(u))}{\frac{2}{\sqrt{\pi}} e^{-u^2}} \right) \quad (15)$$

where

$$u = \frac{x}{2\sqrt{Dt}} \quad (16)$$

The order of the error can therefore be calculated for different values of  $x$  and  $t$  if the order of magnitude of the diffusion coefficient is known. The results are given for two different orders of magnitude of  $Dt$  in Fig. 4.

## IV. CONCLUSIONS

A. Experimental Results on AgBr

A diffusion coefficient of magnitude  $D = 1.0 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  has been calculated with the previously discussed<sup>1</sup> approximation (see Fig. 2), while, on the basis of the same experimental results\* (Fig. 1) but using the exact solution of Fick's law [Eq. (7)], a value of  $D = 1.2 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  was obtained (Fig. 3). The discrepancy between these two values of  $D$  is of the order of the experimental error on  $D$  which is expected when measuring very small diffusion coefficients by sectioning methods. The discussion of errors mentioned above (section III) as applied to our experimental results ( $Dt \approx 10^{-6} \text{ cm}^2$ ,  $D \approx 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ ,  $t \approx 10^6 \text{ s}$ ) shows that the observed discrepancy between the two theoretical treatments is in agreement with the calculated error (Fig. 4, curve A). A comparison between the two calculated curves (Figs. 2 and 3) and the error curve (Fig. 4a) confirms our observation (section III) that the logarithmic approximation (Fig. 2) can be used for  $x \geq 10^{-3} \text{ cm}$  ( $10\mu$ ) where our experimental values of  $\log_{10} R(x,t)$  obey a linear law when plotted against  $x^2$ . As, however, such good agreement between the proposed theoretical treatments is not generally true, it was necessary to discuss the diffusion equations in order to apply our experimental technique in the general case.

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Other results which agree with the ones discussed here within the limits of experimental error are presented in Ref. (1).

### B. Diffusion Measurements in Other Systems

The preceding analysis of the experimental results on AgBr crystals suggests the application of this chemical sectioning method for diffusion measurements in other solids by using either the exact solution of Fick's law [Eq. (7)] or the logarithmic approximation previously used<sup>1</sup> (which is more easily plotted since no inverse error function must be calculated) and gives results lying within the limits of experimental error. It is possible (see Fig. 1) to dissolve very thin successive layers ( $2\mu$ ) with a good precision ( $\pm 0.1\mu$ ), and hence, diffusion coefficients as low as  $10^{-13}$  to  $10^{-14}$   $\text{cm}^2 \text{ s}^{-1}$  may be measured within a reasonable total diffusion time. This procedure involves small experimental errors\* and difficulties. Such difficulties generally arise when the activity must be determined in the removed layers instead of the activity remaining in the crystal. In order to reduce the self-absorption of radiation by the crystal to a minimum, it is advisable to use energetic gamma emitters as tracers, and the activation period  $t_0$  can be minimized by the application of higher radioactivities in the tracer-solution. The optimum experimental conditions, using the proposed technique for the measurement of diffusion coefficients in similar systems to ours, will finally be such that a minimum error is obtained within the smallest total diffusion time  $t$  for which the diffusion distance  $x$  can be split into a sufficient number of sections for accurate measurements.

\* Following Fig. 4b, one sees for example that the average value of  $D$  using the logarithmic approximation would be of the order  $1.3 \times 10^{-14}$   $\text{cm}^2 \text{ s}^{-1}$  instead of  $1.0 \times 10^{-14}$   $\text{cm}^2 \text{ s}^{-1}$  as calculated by Eq. (7) if five experimental points 2 microns apart are measured after a total diffusion time  $t = 5.0 \times 10^6$  s.

ACKNOWLEDGEMENTS

This work was supported in part by the United States Atomic Energy Commission.

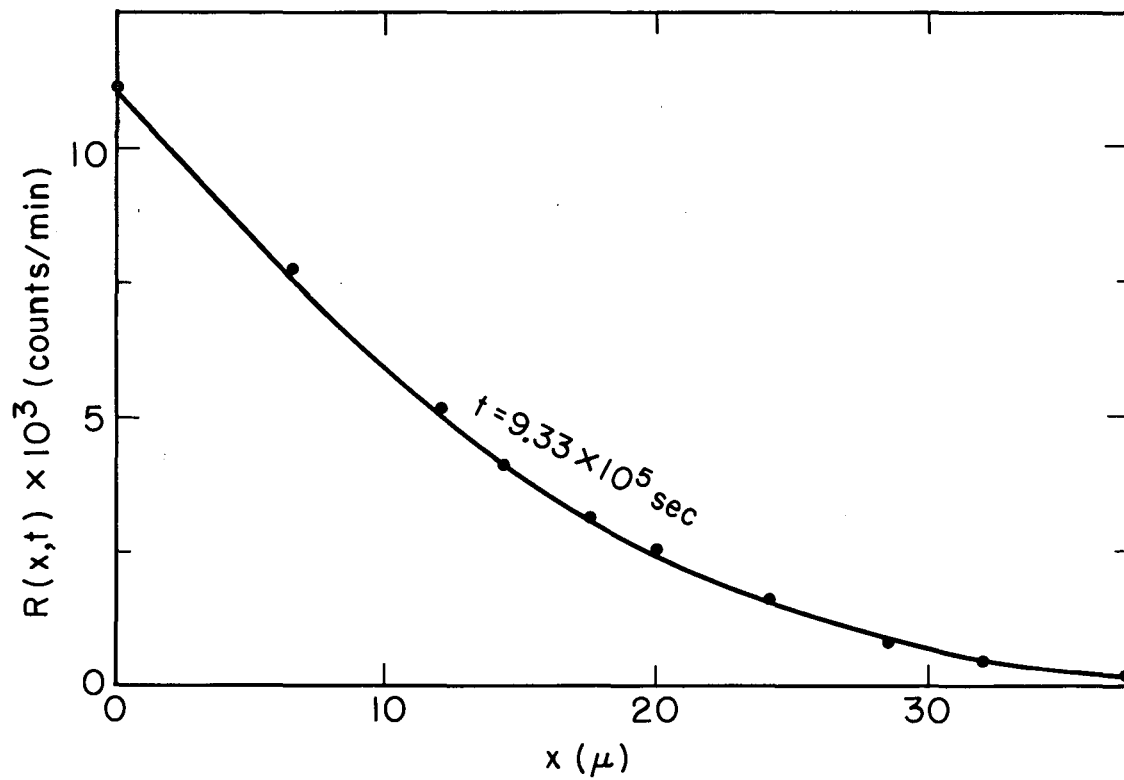
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FIGURE CAPTIONS

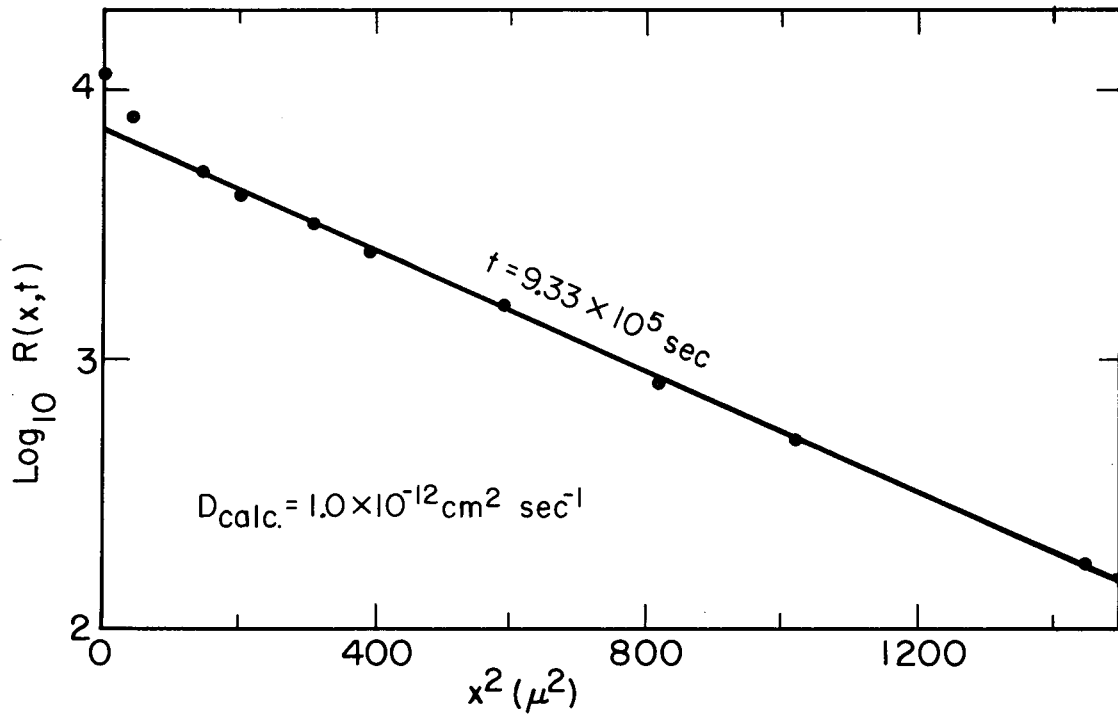
- Fig. 1 Measured values of  $R(x,t)$  versus  $x$ , where  $R(x,t)$  is the residual radioactivity in the AgBr crystal after dissolution of a section of thickness  $x$ . Total diffusion time: 259 hours.
- Fig. 2 Logarithmic approximation  $\log_{10} R(x,t)$  versus  $x^2$  as calculated from the measured values of Fig. 1.
- Fig. 3 Inverse error function  $G$  versus  $x/2\sqrt{t}$ , as calculated from the measured values of Fig. 1 by means of equation (7).
- Fig. 4 Error on  $Dt$  versus distance  $x$  as obtained if the logarithmic approximation (Fig. 2) is used instead of the exact solution of Fick's law represented by equation (7). Curves a and b have been calculated for two different values of  $Dt$  by means of equation (15).





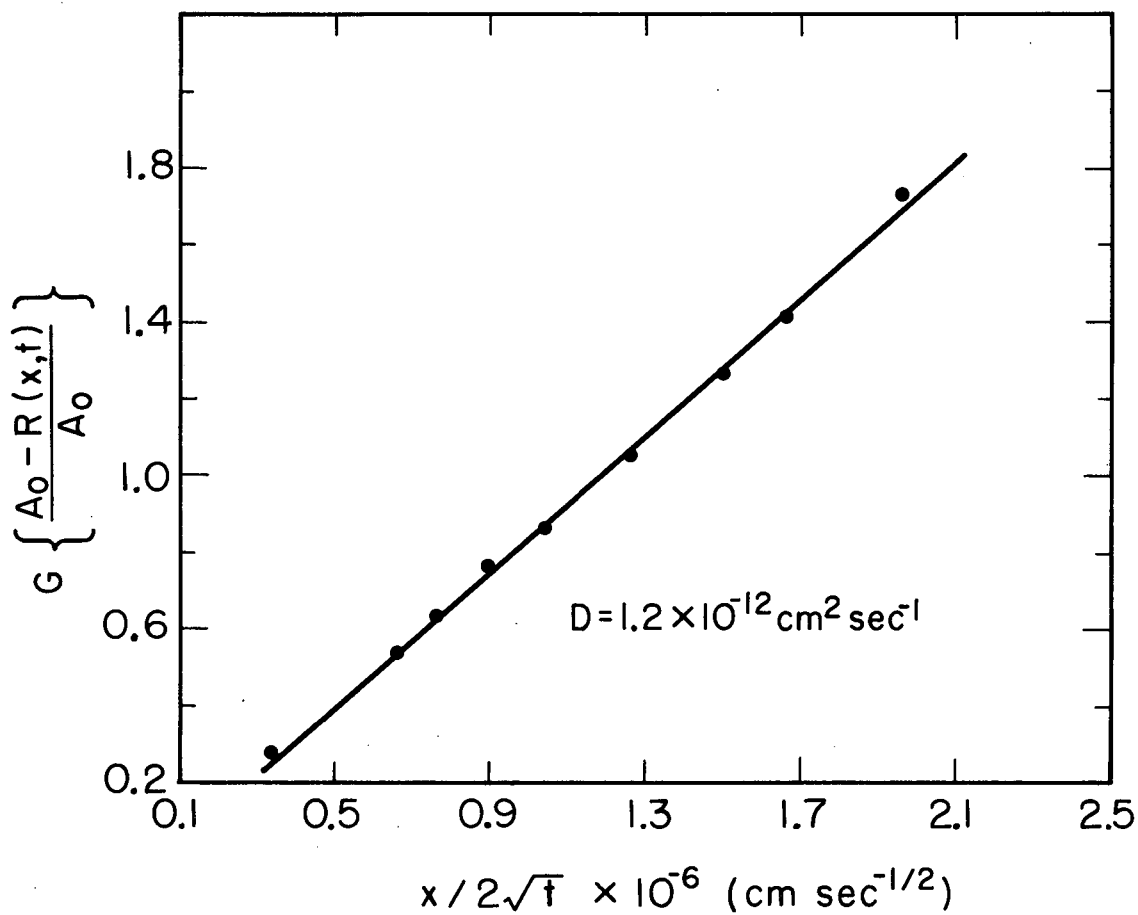
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Fig. 1



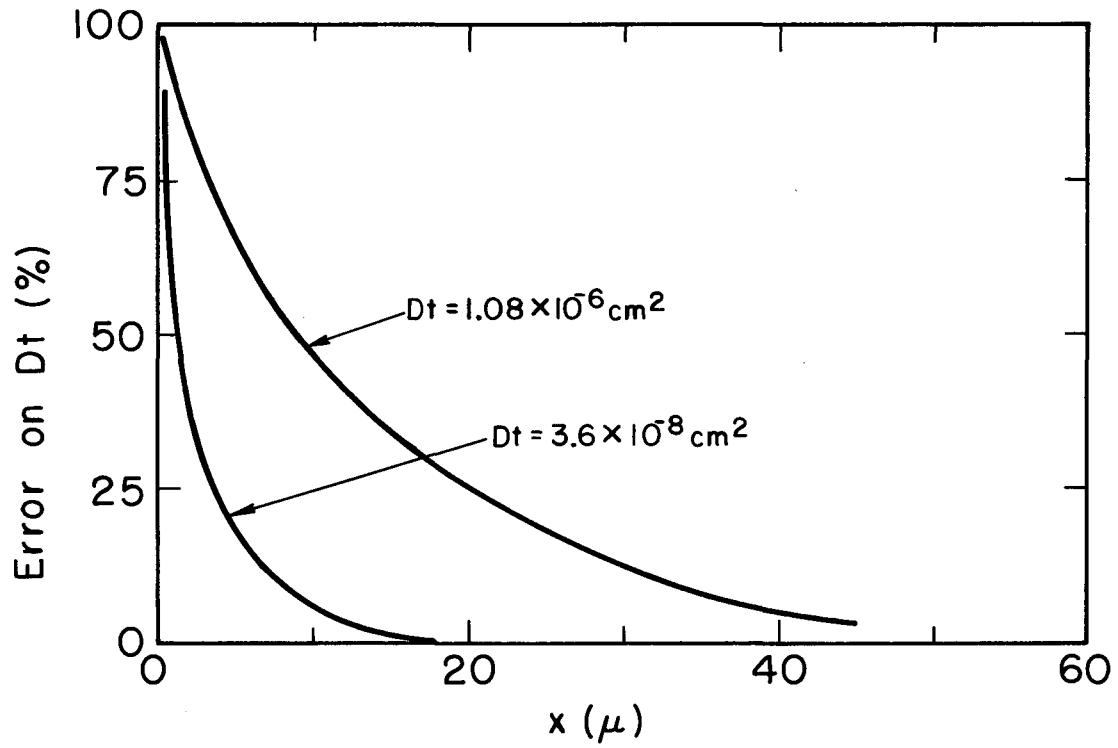
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Fig. 2



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Fig. 3



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Fig. 4

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