ABSTRACT

A computer least squares technique has been developed to compute values of the activation energy, Q, the frequency factor, D0, and their standard deviations by using data obtained from semi-infinite diffusion couples and where Grube's solution of Fick's equation is appropriate. The Gauss iteration method is employed to overcome the problems associated with non-linear functions. A FORTRAN code is available to compute the results. However, initial estimates are necessary. Methods of finding the initial estimates are given.

* Work done under the auspices of the U. S. Atomic Energy Commission.
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
The phenomenological laws describing diffusion were first formulated by Fick by analogy to the equations of heat conduction derived earlier by Fourier. Most diffusion experiments are designed so that diffusion occurs as the result of a concentration gradient along one direction only, and it is appropriate to state Fick's law to express the time dependent change of concentration due to diffusion as

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) \quad [1]
\]

where \( C \) represents the concentration of the diffusing species at a distance \( x \) from the interface after a time interval \( t \), and \( D \) is the diffusion coefficient.

If \( D \) is independent of concentration, equation [1] may be rewritten as

\[
\frac{\partial C}{\partial x} = D \frac{\partial^2 C}{\partial x^2} \quad [2]
\]

and \( D \) may be determined by the method of Grube. The use of probability paper, introduced by Johnson, allows evaluation of the assumption that \( D \) is independent of concentration, and also provides a graphical method of determining \( D \). If \( D \) is dependent upon concentration, as would be indicated by a non-linear probability plot of the concentration-penetration data, then it must be estimated by using the more complicated Boltzman-Matano method. This method includes graphical integration to satisfy the Matano assumptions and determination of \( \partial C/\partial x \) by a tangent construction. Very recently a computer program was developed for the Boltzman-Matano method.
It is the intent of this article to present a computer least squares technique for estimating diffusion parameters and their precision when use of the Grube method is appropriate. A specific example of this least squares technique is its application to the self-diffusion of plutonium.

STATEMENT OF THE PROBLEM

A common experimental geometry for evaluating the diffusion coefficient, \( D \), in binary metallic systems is the semi-infinite diffusion couple. In this geometry two pieces of metal, the thicknesses of which are large in comparison with the distance over which diffusion will occur, are bonded together with a planar interface. After a diffusion anneal for an appropriate time, \( t \), at a temperature, \( T \), the couple may be sectioned and analyzed to obtain a concentration-penetration profile. For this geometry and typical boundary conditions* the appropriate solution of equation [2] is

\[
\frac{C - C_1}{C_0 - C_1} = \frac{1}{2} \left[ 1 + \frac{2}{\sqrt{\pi}} \int_0^{2\sqrt{Dt}} e^{-\lambda^2} d\lambda \right]
\]

The left hand side of equation [3] is the normalized concentration where

- \( C_1 = \) initial concentration of the diffusing species on the side of low concentration, and
- \( C_0 = \) the initial concentration of the diffusing species on the side of high concentration.

---

* (1) \( C = C_0 \) for \( x > 0 \), and \( C = c_1 \) for \( x < 0 \) when \( t = 0 \).
The right hand side of this equation may be rewritten in terms of the error function

\[
\frac{C - c_1}{C_0 - c_1} = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{x}{2 \sqrt{Dt}} \right) \right]
\]  

[3a]

to allow use of error function tables in computation. It is assumed that the interface coincides with the plane where \( \frac{C - c_1}{C_0 - c_1} = 0.5 \).

Experimentally, it may be easier to measure distances from a reference plane at an edge of the diffusion couple rather than from the interface. Denoting the experimentally measured distances as \( y \), the relationship \( x = (y - \mu) \) may be used for computation, \( \mu \) being the true distance from the reference plane to the interface of the diffusion couple.

Experience shows that an Arrhenius-type equation usually may be employed to describe the relationship between \( D \) and absolute temperature \( T \)

\[
D = D_0 \exp \left( -\frac{Q}{RT} \right)
\]

[4]

where \( R = \) universal gas constant

\( D_0 = \) Frequency Factor

\( Q = \) Activation Energy

Values of \( D_0 \) and \( Q \) have theoretical significance in interpreting diffusion behavior and are usually the values sought in a diffusion experiment.

By making appropriate substitutions, the general relationship between the measured variables and the desired parameters can be stated in the form

\[
\frac{C_{i1} - c_{i1}}{C_{i0} - c_{i0}} = \frac{1}{2} \left[ 1 + \frac{2}{\sqrt{\pi}} \int_0^{(y_{ij} - \mu_j)} \left[ \frac{4D_0 t_j e^{-Q/RT_j}}{4D_0 t_j e^{-Q/RT_j}} \right]^{1/2} e^{-\lambda^2} d\lambda \right]
\]

[5]
Generally a number of observations \((i = 1, 2, 3, \ldots, n_j)\) of \(y_{ij}\) and \(C_{ij}\) are made for each sample which has been annealed, and there are a number of samples \((j = 1, 2, 3, \ldots, k)\) annealed at various times \(t_j\) and temperatures \(T_j\). \(y_{ij}\), \(t_j\) and \(T_j\) are independent variables assumed to be known exactly (i.e., they are free from error). The problem is to estimate \(\mu_j\), \(D_0\), and \(Q\).

In the determination of the self diffusion coefficient for plutonium, concentrations, \(C_{ij}\), of the diffusing isotope \(^{238}\text{Pu}\) were obtained by alpha pulse-height counting techniques. \(\gamma_1\) is the number of counts assignable to \(^{238}\text{Pu}\), and \(\gamma_2\) is the number of counts assignable to \(^{239}\text{Pu}\) and \(^{240}\text{Pu}\). The independently observed counts, \(\gamma\), the specific alpha activities, \(S\), and concentrations, \(C\), are related by

\[
\frac{\gamma_{1ij}}{\gamma_{1ij} + \gamma_{2ij}} = \frac{S_{238} C_{ij}}{S_{238} C_{ij} + S_{239} C_{239} + S_{240} C_{240}} \tag{6}
\]

The concentrations \(C_{239}\) and \(C_{240}\) are known from analysis of the starting material. The specific activity \(S\) (disintegrations per minute per gram) of each isotope may be computed from the half life, \(t_{1/2}\), by the relation

\[
S = \frac{-dN}{dt} = \frac{\ln 2}{t_{1/2}} \cdot N \tag{7}
\]

where \(N\) is the number of atoms per gram of the isotope.

**SOLUTION**

The parameters in equation (5) are estimated by the method of least squares. To obtain the most significant information from the data it is desirable to weight the value of each point by an appropriate factor \(W_{ij}\). Weighting of points by the reciprocals of the estimated variances of the observed points is common practice. 7
In the determination of the self-diffusion coefficient for plutonium, the concentrations $C_{ij}$ are computed by equation [6], from the numbers of counts $\gamma_{1ij}$ and $\gamma_{2ij}$; each number of counts is assumed to be distributed as independent Poisson distributions. This distribution implies that the estimate of the variance of $\gamma_{1ij}$, for instance, is $\gamma_{1ij}$. It can be shown by propagation of error that the estimate of the variance of $C_{ij}$ in equation [6] is

$$\hat{\sigma}^2_{C_{ij}} = \left[ \frac{S_{239}C_{239} + S_{240}C_{240}}{S_{238}} \right]^2 \left[ \frac{\gamma_{1ij}(\gamma_{1ij} + \gamma_{2ij})}{(\gamma_{2ij})^3} \right]$$  [8]

and the appropriate weight, $W_{ij}$, for $C_{ij}$ is

$$W_{ij} = \frac{1}{\left( \frac{\hat{\sigma}}{\hat{\sigma}}_{C_{ij}} \right)^2}$$  [9]

Estimates of the parameters $\mu_j$, $D_o$, and $Q$ in equation [5] are found by minimizing the function

$$G = \sum_{i=1}^{n_1} W_{1i} (C_{1i} - f_{1i})^2 + \sum_{i=1}^{n_2} W_{12} (C_{12} - f_{12})^2 + \ldots + \sum_{i=1}^{n_k} W_{ik} (C_{ik} - f_{ik})^2$$  [10]

where

$$f_{1i} = \frac{C_{ij} - C_{1i}}{2} \left[ 1 + \frac{2}{\sqrt{\pi}} \int_0^{(\gamma_{ij} - \mu_j)\left[4D_ot_j e^{-Q/RT_j} \right]^{1/2}} e^{-x^2} dx \right] + C_{ij}$$  [11]
with respect to the parameters \( \mu_1, \mu_2, \ldots, \mu_k, D_0, \) and \( Q. \) It is important to note that \( Q \) and \( D_0 \) remain constant for all terms of \( G \) but \( \mu_j \) changes. The technique of minimizing a sum of squares of differences between observed data and the hypothesized functional form is well known. Minimizing the sum of the squares could be accomplished by taking partial derivatives of \( G \) with respect to the parameters and solving the resulting equations to obtain estimates of the parameters. Unfortunately the resulting equations in this case are non-linear; hence they are extremely difficult to solve.

The technique employed to overcome this difficulty is known as the Gauss Iteration Method. The method and its adaptability to high speed computing machines is discussed in great detail by Moore and Zeigler. The method will be discussed briefly for the specific case of determining self diffusion plutonium coefficients so that the reader may readily follow the procedure.

The first step is to find provisional estimates of the parameters. Techniques for finding original guesses will be given below. The next step is to approximate the original function (see equation (11)) in the form of a truncated Taylor's series about the estimates of the parameters. Thus, after dropping second and higher order terms, equation (11) may be approximated as

\[
C_{ij} = f_{ij}^0 + \sum_{j=1}^{k} \left( \frac{\partial f_{ij}^0}{\partial \mu_j} \right) \Delta \mu_j + \left( \frac{\partial f_{ij}^0}{\partial D_0} \right) \Delta D_0 + \left( \frac{\partial f_{ij}^0}{\partial Q} \right) \Delta Q \tag{12}
\]

If original estimates of the parameters are denoted as \( D_0^0, Q^0, \) and \( \mu_j^0 \) (the superscript 0 denotes original estimates), then \( f_{ij}^0 \) is the function
evaluated at the i, jth point using the initial guesses, and the unknown increments are defined as
\[ \Delta \mu_j = \mu_j^1 - \mu_j^0, \quad \Delta D_o = D_o^1 - D_o^0, \quad \text{and} \quad \Delta Q = Q^1 - Q^0, \]
where the superscript 1 denotes the new values after the first iteration.

Note that in \[ [12] \] the equation is linear in the unknown quantities \( \Delta \mu_j, \Delta D_o, \) and \( \Delta Q \). These values are found by minimizing

\[
\sum_i \sum_j \left[ C_{ij} - f_{ij}^0 - \sum_j \left( \frac{\partial f_{ij}^0}{\partial \mu_j} \right) \Delta \mu_j - \left( \frac{\partial f_{ij}^0}{\partial D_o} \right) \Delta D_o - \left( \frac{\partial f_{ij}^0}{\partial Q} \right) \Delta Q \right]^2 \tag{15}
\]

with respect to the increments \( \Delta \mu_j, \Delta D_o, \) and \( \Delta Q \). The resulting equations (the normal equations of the least squares method) are linear and the increments \( \Delta \mu_j, \Delta D_o \) and \( \Delta Q \) are found by solving the set of normal equations.

These results are added to the original estimates to give \( \mu_j^1, D_o^1, \) and \( Q^1 \) and the computations are repeated to find \( \mu_j^2, D_o^2, \) and \( Q^2 \). The iterations are continued until some desirable convergence criterion is achieved.

In the plutonium experiments the criterion was that the smallest change in the increment was \( 10^{-6} \) times the value of the parameter.

For the special case where refined estimates of \( D_j \) are desired, a computer code has been written which fits the hypothesized function to the jth set of data in an analogous manner. The function fitted is

\[
g_{ij} = C_{ij} - c_{ij} \left[ \frac{y_{ij} - \mu_j}{\left[ \frac{1}{4} D_j t_j \right]^{1/2}} \right]^{1/2} e^{-\lambda^2} d\lambda + c_{ij} \tag{14}
\]

The initial guesses of the parameters \( \mu_j, D_j, D_o, \) and \( Q \) may be obtained by graphical techniques. For each diffusion couple the
concentration-penetration data are plotted on probability paper - the
normalized concentration, \((C_i - c_l)/(C_o - c_l)\), on the probability axis and
the measured distance on the linear axis. A straight line is then drawn
through the data points.\(^*\) The estimate of \(\mu_j\) is found by approximating the
abcissa corresponding to the point on the line at the 50th percentile point.
The value of \(D_j\) is found by approximating the abcissa corresponding to the
point on the line at the 84th percentile point and subtracting from this the
estimate of \(\mu_j\). If this difference is noted \(\sigma_j\), then

\[
D_j = \sigma_j^2 / 2t_j
\]

Values of \(D_o\) and \(Q\) may be estimated from a plot of \(D_j\) and \(T_j\) - values
of \(D_j\) are plotted on a logarithmic scale and \(1/T_j\) on a linear scale. As
is well known, a straight line through the data points represents equation
[4], and estimates of \(Q\) and \(D_o\) are, respectively, the slope and intercept
of this line.

The least squares fit of equation [5] is obtained by programming a
subroutine for the General Least Squares Code of Moore and Zeigler.\(^{10}\) This
code is written in FORTRAN language for the IBM 7090 computer. The sub-
routine is verified by fitting synthetic data calculated independently by
using equations [3] and [4]. From the experimental data the least squares
estimates of the parameters \(\hat{D}_o\), \(\hat{Q}\), and \(\hat{\mu}_j\) (\(j = 1,2,...k\)) are obtained.

\(^*\) Non-linear plots indicate that \(D\) varies with concentration and that use
of the Boltzman-Matano method is appropriate.
The results also include the standard deviations of the parameters 
\( \hat{\sigma}_p, \hat{\sigma}_q, \) and \( \hat{\sigma}_w \), and the weighted variance of the fit of the function to the data.

ACKNOWLEDGMENTS

The authors are obliged to R. K. Zeigler for suggesting the methods of solution and to R. H. Moore for valuable discussions.

REFERENCES