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ANALYSIS OF TERNARY DIFFUSION: SOLUTIONS OF DIFFUSION EQUATIONS AND CALCULATED CONCENTRATION DISTRIBUTION

Berkeley, California

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March 31, 1965

ANALYSIS OF TERNARY DIFFUSION: SOLUTIONS OF DIFFUSION EQUATIONS AND CALCULATED CONCENTRATION DISTRIBUTION*

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ABSTRACT

Solutions have been given in closed form to the simultaneous differential equations for ternary diffusion where the coefficient terms are described in terms of three intrinsic diffusion coefficients. Concentration distributions for various combinations of the three intrinsic diffusion coefficients are calculated here with the solutions for semi-infinite diffusion coupling, and behavior of the respective species is discussed together with the resultant concentration distributions. Numerical solution by the finite-difference approximations has been carried out separately for the same diffusion equations, and the resultant concentration distributions are compared with those obtained by the closed-form solutions. A parameter has been derived for description of the characteristics of the ternary diffusion profile.

I. INTRODUCTION

The flux densities for one-dimensional substitutional ternary diffusion have been described as Eqs. (1) in terms of intrinsic diffusion coefficients by the author, provided that the total molar concentration of the system is constant with varied composition:[1]

$$J_1 = - D_1 \frac{\delta C_1}{\delta x} - N_1 \left\{ (D_1 - D_2) \frac{\delta C_2}{\delta x} + (D_1 - D_3) \frac{\delta C_3}{\delta x} \right\} \tag{1a}$$

$$J_2 = - D_2 \frac{\delta C_2}{\delta x} - N_2 \left\{ (D_2 - D_3) \frac{\delta C_3}{\delta x} + (D_2 - D_1) \frac{\delta C_1}{\delta x} \right\} \tag{1b}$$

$$J_3 = - D_3 \frac{\delta C_3}{\delta x} - N_3 \left\{ (D_3 - D_1) \frac{\delta C_1}{\delta x} + (D_3 - D_2) \frac{\delta C_2}{\delta x} \right\}. \tag{1c}$$

Here we have

$$C_1 + C_2 + C_3 = C_0 = \text{constant}, \tag{2}$$

J_i is the diffusion flux density, subscript numbers refer to the species, D_i is the intrinsic diffusion coefficient, x is the distance, C_i and C_0 are molar concentrations of the individual species and of the entire system, respectively, and N_i is the molar fraction, i.e.,

$$N_i = C_i/C_0 . \tag{3}$$

Characteristics of ternary diffusion have been discussed by the author to a limited extent based on Eqs. (1) before the closed-form solutions are known. In order to describe the detailed behavior of the respective species in substitutional ternary diffusion, the diffusion equations have been given solutions in two ways: one is in closed form for the simultaneous differential Eqs. (7) derived from Eqs. (1), and the other is by a numerical solution for Eqs. (1).

The solutions in closed form have been obtained with an approximation of the ternary diffusion equations as linear differential equations. The closed-form solutions are convenient for calculating explicitly the concentrations of three species for a given diffusing time and distance. Where the diffusion equations cannot be approximated as linear, a procedure of finite-difference approximations has been carried out.

By using the solutions, characteristics of ternary diffusion such as the curved diffusion path on the composition diagram, diffusion with no initial gradient, and uphill diffusion have been demonstrated quantitatively.

II. SOLUTION OF TERNARY DIFFUSION EQUATIONS

In the present solution, the intrinsic diffusion coefficients, D_i, are regarded as independent of the concentrations and constant. By substitution of

$$\frac{\delta C_1}{\delta x} + \frac{\delta C_2}{\delta x} + \frac{\delta C_3}{\delta x} = 0 , \tag{4}$$

which is derived from Eq. (2), Eqs. (1) are simplified with respect to subsequent mathematical derivation by eliminating one of the concentrations, resulting in two simultaneous equations (5):

$$J_1 = - \left\{ D_1 + N_1 \left(D_3 - D_1 \right) \right\} \frac{\delta C_1}{\delta x} - N_1 \left(D_3 - D_2 \right) \frac{\delta C_2}{\delta x} \tag{5a}$$

$$J_2 = - \left\{ D_2 + N_2 \left(D_3 - D_2 \right) \right\} \frac{\delta C_2}{\delta x} - N_2 \left(D_3 - D_1 \right) \frac{\delta C_1}{\delta x} . \tag{5b}$$

Substituting Eqs. (5) into

$$\frac{\delta C_i}{\delta t} = - \frac{\delta J_i}{\delta x} , \tag{6}$$

which describes the mass conservation for each species, gives the differential equations for one-dimensional ternary diffusion,

$$\frac{\delta C_1}{\delta t} = \frac{\delta}{\delta x}\left[\left\{D_1 + N_1\ (D_3 - D_1)\right\}\ \frac{\delta C_1}{\delta x} + N_1\ (D_3 - D_2)\ \frac{\delta C_2}{\delta x}\right] \tag{7a}$$

and

$$\frac{\delta C_2}{\delta t} = \frac{\delta}{\delta x}\left[\left\{D_2 + N_2\ (D_3 - D_2)\right\}\ \frac{\delta C_2}{\delta x} + N_2\ (D_3 - D_1)\ \frac{\delta C_1}{\delta x}\right], \tag{7b}$$

where t is the diffusing time. From the solutions of Eqs. (7) C_1 and C_2 can be calculated for a given t and x. The corresponding concentration of the third species, C_3, can be calculated by substituting the obtained C_1 and C_2 into Eq. (2). Since the prederivative terms on the right side of Eqs. (7) are concentration-dependent, as can be seen when Eq. (3) is substituted into them, Eqs. (7) are nonlinear differential equations. Their solutions may not be easily obtainable in closed form. If this is the case, the numerical solutions will be useful to analyze cases of diffusion where the range of concentration variation is relatively large. Where the concentration variation is relatively small and the N_i can be regarded as constant, Eqs. (7) are approximated as linear differential equations. The more nearly equal are D_1, D_2, and D_3, the closer the approximation. Fujita and Gosting solved the simultaneous differential equations described by

$$\frac{\delta C_1}{\delta t} = A\ \frac{\delta^2 C_1}{\delta x^2} + B\ \frac{\delta^2 C_2}{\delta x^2} \tag{8a}$$

$$\frac{\delta C_2}{\delta t} = E\ \frac{\delta^2 C_2}{\delta x^2} + F\ \frac{\delta^2 C_1}{\delta x^2}, \tag{8b}$$

where A, B, E, and F are constants.[2] Their solutions were derived by employing the Boltzmann's transformation.[3] Therefore, the application of their solutions is limited to the diffusion in infinite and semi-infinite media with uniform initial distributions.[4] In 1939 Henry solved his simultaneous diffusion equations which described the coupling diffusion of heat and moisture through absorbing media.[5] In the mathematical sense, the derivation used in his solution is applicable to solution of Eqs. (7). Henry's derivation employing normal coordinates does not require the Boltzmann's transformation. Hence, the solutions obtained in his derivation can be applied to diffusion in the finite media and do not necessarily require uniformity in the initial distribution. In the present work Henry's derivation is employed for solution of Eqs. (7).

A. Solutions for Linear Differential Equations

Equations (7) can be rewritten as Eqs. (8) by substituting Eqs. (9) through (12) when N_1 and N_2 are regarded as constant:

$$A = D_1 + N_1 (D_3 - D_1) \tag{9}$$

$$B = N_1 (D_3 - D_2) \tag{10}$$

$$E = D_2 + N_2 (D_3 - D_2) \tag{11}$$

$$F = N_2 (D_3 - D_1) . \tag{12}$$

Equations (13a) and (13b) are reduced from Eqs. (8a) and (8b) by using [Eq. (8b) x A - Eq. (8a) x F] and [Eq. (8a) x E - Eq. (8b) x B], respectively:

$$A \frac{\delta C_2}{\delta t} - F \frac{\delta C_1}{\delta t} = (AE - BF) \frac{\delta^2 C_2}{\delta x^2} \tag{13a}$$

$$E \frac{\delta C_1}{\delta t} - B \frac{\delta C_2}{\delta t} = (AE - BF) \frac{\delta^2 C_1}{\delta x^2} . \tag{13b}$$

Equations (13a) and (13b) are reduced to

$$\mathcal{D}_1 \frac{\delta^2 C_1}{\delta x^2} - \frac{\delta}{\delta t} (C_1 - \alpha_1 C_2) = 0 \tag{14a}$$

$$\mathcal{D}_2 \frac{\delta^2 C_2}{\delta x^2} - \frac{\delta}{\delta t} (C_2 - \alpha_2 C_1) = 0 \tag{14b}$$

by substituting

$$\mathcal{D}_1 = \frac{AE - BF}{E} = D_1 + \frac{N_1 D_2 (D_3 - D_1)}{D_2 + N_2 (D_3 - D_2)} \tag{15}$$

$$\mathcal{D}_2 = \frac{AE - BF}{A} = D_2 + \frac{N_2 D_1 (D_3 - D_2)}{D_1 + N_1 (D_3 - D_1)} \tag{16}$$

$$\alpha_1 = \frac{B}{E} = \frac{N_1 (D_3 - D_2)}{D_2 + N_2 (D_3 - D_2)} \tag{17}$$

and

$$\alpha_2 = \frac{F}{A} = \frac{N_2 (D_3 - D_1)}{D_1 + N_1 (D_3 - D_1)} . \tag{18}$$

Equations (14) correspond mathematically to the simultaneous equations Henry derived and can be reduced to a single differential equation by introducing the normal coordinates in the same manner as his derivation. In his case, C_1 and C_2 represent the water-vapor concentration and temperature.

Addition of Eq. (14a) multiplied by $s/\mathcal{D}_1$ and Eq. (14b) multiplied by $r/\mathcal{D}_2$ results in

$$\frac{\delta^2}{\delta x^2} (rC_2 + sC_1) - \frac{\delta}{\delta t} \left\{ \left(\frac{r}{\mathcal{D}_2} - \frac{s\alpha_1}{\mathcal{D}_1} \right) C_2 + \left(\frac{s}{\mathcal{D}_1} - \frac{r\alpha_2}{\mathcal{D}_2} \right) C_1 \right\} = 0 . \tag{19}$$

With proper ratios of r and s to satisfy

$$\frac{1}{r}\left(\frac{r}{\mathcal{D}_2} - \frac{s\alpha_1}{\mathcal{D}_1}\right) = \frac{1}{s}\left(\frac{s}{\mathcal{D}_1} - \frac{r\alpha_2}{\mathcal{D}_2}\right) = \mu^2 , \tag{20}$$

Eq. (19) reduces

$$\frac{\delta^2 C}{\delta x^2} - \frac{\delta}{\delta t}(\mu^2 C) = 0, \tag{21}$$

where

$$C = rC_2 + sC_1 . \tag{22}$$

Equation (21) is mathematically in the same form as Fick's law, with a diffusion coefficient μ^{-2} for the new variable C. Differentiation proves that Eq. (23) is a solution of Eq. (21):

$$\begin{aligned} C &= rC_2 + sC_1 \\ &= \frac{A}{t^{1/2}} \exp\left(-x^2\mu^2/4t\right) , \end{aligned} \tag{23}$$

where A is an arbitrary constant.

In a similar way to diffusion of a single species,[6] the combined distribution of C_1 and C_2 for diffusion of a total amount M for time t from a plane source is described by

$$rC_2 + sC_1 = \frac{M\mu}{2(\pi t)^{1/2}} \exp\left(-x^2\mu^2/4t\right). \tag{24}$$

Constants μ^2 and r/s are given by Eq. (20). Since Eq. (20) is quadratic for r/s, two values for r/s and correspondingly for μ^2 are given as

$$\mu^2 = \frac{\mathcal{D}_1 + \mathcal{D}_2 \pm \sqrt{(\mathcal{D}_1 - \mathcal{D}_2)^2 + 4\,\alpha_1\alpha_2\mathcal{D}_1\mathcal{D}_2}}{2\,\mathcal{D}_1\mathcal{D}_2} \tag{25}$$

$$\frac{r}{s} = \frac{\mathcal{D}_2 - \mathcal{D}_1 \mp \sqrt{(\mathcal{D}_1 - \mathcal{D}_2)^2 + 4\,\alpha_1\alpha_2\mathcal{D}_1\mathcal{D}_2}}{2\,\alpha_2\mathcal{D}_1} \tag{26}$$

Substitution of two pairs of μ^2 and the corresponding r/s reduces the solution, Eq. (23) [or Eq. (24)], to two simultaneous equations. Therefore, by solving the resultant simultaneous equations, C_1 and C_2 can be calculated separately. An example of the calculation is given in the next section.

B. Solutions for Extended Initial Distributions

In order to apply the solution for diffusion from a plane source, Eq. (24), to that for diffusion from an extended source, the equation must be superposed for the boundary conditions. The superposition of the elementary solution (24) should be mathematically sound, since the combination of C_1 and C_2 is linear, and μ is constant in the solution. Advantages of the present solution are that it is applicable to diffusion in finite media, and initial distributions in the media need not absolutely be homogeneous.

1. Semi-infinite Media

The initial and boundary conditions for diffusion between a couple of semi-infinite media with differing compositions are

$$t = 0,\ x < 0,\ C_1 = C_{1a},\ C_2 = C_{2a},\ C_3 = C_{3a}$$

$$x > 0,\ C_1 = C_{1b},\ C_2 = C_{2b},\ C_3 = C_{3b}, \tag{27}$$

where initially the three species are uniformly distributed. Superposition of the elementary solution (24) for conditions (27) results in

$$\left(\frac{r}{s} C_2 + C_1\right)_{t,x} = \left(\frac{r}{s} C_{2b} + C_{1b}\right) + \frac{1}{2}\left\{\frac{r}{s}(C_{2a} - C_{2b}) + (C_{1a} - C_{1b})\right\} \operatorname{erfc} \frac{x\mu}{2t^{1/2}} \tag{28}$$

in the same way as for diffusion of single species.[7] Since two sets of μ^2 and r/s are given by Eqs. (25) and (26), two simultaneous equations are reduced from Eq. (28). From these simultaneous equations we obtain C_1 and C_2 separately as

$$C_1 = C_{1b} + \frac{1}{2(S_1 - S_2)} \left\{ (S_1\Delta C_1 + \Delta C_2) \operatorname{erfc} \frac{x\mu_1}{2t^{1/2}} - (S_2\Delta C_1 + \Delta C_2) \operatorname{erfc} \frac{x\mu_2}{2t^{1/2}} \right\} \tag{29a}$$

$$C_2 = C_{2b} + \frac{1}{2(R_1 - R_2)} \left\{ (\Delta C_1 + R_1\Delta C_2) \operatorname{erfc} \frac{x\mu_1}{2t^{1/2}} - (\Delta C_1 + R_2\Delta C_2) \operatorname{erfc} \frac{x\mu_2}{2t^{1/2}} \right\} \tag{29b}$$

where

$$\Delta C_1 = C_{1a} - C_{1b} \tag{30}$$

$$\Delta C_2 = C_{2a} - C_{2b} \tag{31}$$

$$\mu_1 = \left\{ \frac{D_1 + D_2 + N_1\, {}_3\underline{D}_1 + N_2\, {}_3\underline{D}_2 + \left\{ {}_2\underline{D}_1^2 + 2\, {}_2\underline{D}_1 (N_2\, {}_3\underline{D}_2 - N_1\, {}_3\underline{D}_1) + (N_1\, {}_3\underline{D}_1 + N_2\, {}_3\underline{D}_2)^2 \right\}^{\frac{1}{2}}}{2\, (D_1D_2 + N_1D_2\, {}_3\underline{D}_1 + N_2D_1\, {}_3\underline{D}_2} \right\}^{\frac{1}{2}} \tag{32a}$$

$$\mu_2 = \left\{ \frac{D_1 + D_2 + N_1\, {}_3\underline{D}_1 + N_2\, {}_3\underline{D}_2 - \left\{ {}_2\underline{D}_1^2 + 2\, {}_2\underline{D}_1 (N_2\, {}_3\underline{D}_2 - N_1\, {}_3\underline{D}_1) + (N_1\, {}_3\underline{D}_1 + N_2\, {}_3\underline{D}_2)^2 \right\}^{\frac{1}{2}}}{2\, (D_1D_2 + N_1D_2\, {}_3\underline{D}_1 + N_2D_1\, {}_3\underline{D}_2} \right\}^{\frac{1}{2}} \tag{32b}$$

$$R_1 = \frac{1}{S_1} = (r/s)_1 =$$

$$\frac{{}_2\underline{D}_1 - N_1\, {}_3\underline{D}_1 + N_2\, {}_3\underline{D}_2 - \left\{ {}_2\underline{D}_1^2 + 2\, {}_2\underline{D}_1 (N_2\, {}_3\underline{D}_2 - N_1\, {}_3\underline{D}_1) + (N_1\, {}_3\underline{D}_1 + N_2\, {}_3\underline{D}_2)^2 \right\}^{\frac{1}{2}}}{2\, N_2\, {}_3\underline{D}_1} \tag{33a}$$

and

$$R_2 = \frac{1}{S_2} = (r/s)_2 =$$

$$\frac{{}_2\underline{D}_1 - N_1\,{}_3\underline{D}_1 + N_2\,{}_3\underline{D}_2 + \left\{{}_2\underline{D}_1^2 + 2\,{}_2\underline{D}_1(N_2\,{}_3\underline{D}_2 - N_1\,{}_3\underline{D}_1) + (N_1\,{}_3\underline{D}_1 + N_2\,{}_3\underline{D}_2)^2\right\}^{\frac{1}{2}}}{2\,N_2\,{}_3\underline{D}_1} \tag{33b}$$

where ${}_i\underline{D}_k = D_i - D_k$. Equations (32) are reduced from Eq. (25) and Eqs. (33) from Eq. (26) by substituting Eqs. (15) through (18).

Equations (29) are essentially the same as and can be reduced to the solutions Fujita and Gosting derived for the same boundary conditions.

2. Finite and Semi-infinite Media

For the diffusion between two homogeneous media with different compositions where initially one medium is confined in the region $-h < x < h$ and the other extended from $\pm h$ to $\pm\infty$, the initial and boundary conditions are given by

$$t = 0,\ -h < x < h,\ C_1 = C_{1a},\ C_2 = C_{2a},\ C_3 = C_{3a}$$

$$-h > x > h,\ C_1 = C_{1b},\ C_2 = C_{2b},\ C_3 = C_{3b}\ . \tag{34}$$

In the same way as in the previous section, the linear combinations of C_1 and C_2 are described for a given t and x by

$$R_1C_2 + C_1 = (R_1C_{2b} + C_{1b}) + \frac{1}{2}\left\{R_1(C_{2a} - C_{2b}) + (C_{1a} - C_{1b})\right\} \times \left\{\operatorname{erf}\frac{(h-x)\mu_1}{2t^{1/2}} + \operatorname{erf}\frac{(h+x)\mu_1}{2t^{1/2}}\right\} \tag{35a}$$

$$R_2C_2 + C_1 = (R_2C_{2b} + C_{1b}) + \frac{1}{2}\left\{R_2(C_{2a} - C_{2b}) + (C_{1a} - C_{1b})\right\} \times \left\{\operatorname{erf}\frac{(h-x)\mu_2}{2t^{1/2}} + \operatorname{erf}\frac{(h+x)\mu_2}{2t^{1/2}}\right\}. \tag{35b}$$

Solving simultaneous equations (35a) and (35b) for a given t and x, we have

$$C_2 = C_{2b} + \frac{1}{2(R_1 - R_2)} \left[(R_1\Delta C_2 + \Delta C_1) \left\{ \mathrm{erf}\, \frac{(h-x)\mu_1}{2t^{1/2}} + \mathrm{erf}\, \frac{(h+x)\mu_1}{2t^{1/2}} \right\} - (R_2\Delta C_2 + \Delta C_1) \left\{ \mathrm{erf}\, \frac{(h-x)\mu_2}{2t^{1/2}} + \mathrm{erf}\, \frac{(h+x)\mu_2}{2t^{1/2}} \right\} \right] \quad (36a)$$

and

$$C_1 = C_{1b} + \frac{1}{2(S_1 - S_2)} \left[(\Delta C_2 + S_1\Delta C_1) \left\{ \mathrm{erf}\, \frac{(h-x)\mu_1}{2t^{1/2}} + \mathrm{erf}\, \frac{(h+x)\mu_1}{2t^{1/2}} \right\} - (\Delta C_2 + S_2\Delta C_1) \left\{ \mathrm{erf}\, \frac{(h-x)\mu_2}{2t^{1/2}} + \mathrm{erf}\, \frac{(h+x)\mu_2}{2t^{1/2}} \right\} \right]. \quad (36b)$$

Equations (36) also give the distribution in a semi-infinite system which results from cutting the system in half with a plane at $x = 0$.

3. Finite Media

For diffusion proceeding between two homogeneous media, one of which is confined in the region $0 < x < h$ and the other of which extends from h to a finite length ℓ, Eqs. (37) describe the boundary condtions for no flows of either species 1 and 2 through the end surface.

$$\delta C_1/\delta x = 0, \quad \delta C_2/\delta x = 0, \quad x = \ell . \quad (37)$$

Equations (37) reduce independently of r/s to

$$\delta(rC_2 + sC_1)/\delta x = 0, \quad x = \ell . \quad (38)$$

The concentration distributions that satisfy condition (38) are obtained by reflecting the linear combination $(rC_2 + sC_1)$ at the boundary and superposing the reflected curve on the original one. Reflection is repeated at $x = \ell$, then at $x = 0$ and again at $x = \ell$, and so on. The mathematical consequence of this successive reflection and superposition is the same as that for the diffusion of a single species in the same boundary

conditions.[8] Superposition of each reflection on the original curve given by Eqs. (35a) and (35b) results in

$$R_1C_2 + C_1 = (R_1C_{2b} + C_{1b})$$

$$+ \frac{1}{2}(R_1\Delta C_2 + \Delta C_1)\sum_{n=-\infty}^{\infty}\left\{\mathrm{erf}\,\frac{(h + 2n\ell - x)\mu_1}{2t^{1/2}} + \mathrm{erf}\,\frac{(h - 2n\ell + x)\mu_1}{2t^{1/2}}\right\} \quad (39a)$$

and

$$R_2C_2 + C_1 = (R_2C_{2b} + C_{1b})$$

$$+ \frac{1}{2}(R_2\Delta C_2 + \Delta C_1)\sum_{n=-\infty}^{\infty}\left\{\mathrm{erf}\,\frac{(h + 2n\ell - x)\mu_2}{2t^{1/2}} + \mathrm{erf}\,\frac{(h - 2n\ell + x)\mu_2}{2t^{1/2}}\right\}, \quad (39b)$$

where $n = 1, 2, 3 \cdots$.

Solving these simultaneous equations, we have

$$C_1 = C_{1b} + \frac{1}{2(S_1 - S_2)}\left[(\Delta C_2 + S_1\Delta C_1)\sum_{n=-\infty}^{\infty}\left\{\mathrm{erf}\,\frac{(h + 2n\ell - x)\mu_1}{2t^{1/2}} + \mathrm{erf}\,\frac{(h - 2n\ell + x)\mu_1}{2t^{1/2}}\right\}\right.$$

$$\left. - (\Delta C_2 + S_2\Delta C_1)\sum_{n=-\infty}^{\infty}\left\{\mathrm{erf}\,\frac{(h + 2n\ell - x)\mu_2}{2t^{1/2}} + \mathrm{erf}\,\frac{(h - 2n\ell + x)\mu_2}{2t^{1/2}}\right\}\right] \quad (40a)$$

$$C_2 = C_{2b} + \frac{1}{2(R_1 - R_2)}\left[(R_1\Delta C_2 + \Delta C_1)\sum_{n=-\infty}^{\infty}\left\{\mathrm{erf}\,\frac{(h + 2n\ell - x)\mu_1}{2t^{1/2}} + \mathrm{erf}\,\frac{(h - 2n\ell + x)\mu_1}{2t^{1/2}}\right\}\right.$$

$$\left. - (R_2\Delta C_2 + \Delta C_1)\sum_{n=-\infty}^{\infty}\left\{\mathrm{erf}\,\frac{(h + 2n\ell - x)\mu_2}{2t^{1/2}} + \mathrm{erf}\,\frac{(h - 2n\ell + x)\mu_2}{2t^{1/2}}\right\}\right]. \quad (40b)$$

The number of the error-function terms inside the brackets in Eqs. (40) may be chosen depending upon the accuracy desired for C_1 and C_2.

C. Numerical Solution of Nonlinear Equations for Ternary Diffusion

With respect to application of the solutions in the closed forms described in the previous section to analysis of actual diffusion, whether

or not Eqs. (1), i.e., Eqs. (7), can be regarded as linear depends first upon the magnitudes of concentration variations of the respective species, and second upon the relative magnitudes of D_1, D_2, and D_3 in the actual cases. The problem is reduced to the magnitudes of variations of μ given by Eqs. (32) and R given by Eqs. (33) for the given boundary conditions.

Where two pairs of μ and the corresponding R cannot be regarded as constant, numerical solutions of the original diffusion equations are useful. In the present work, a finite-difference method is demonstrated for the boundary conditions given by Eqs. (27) which describe the diffusion between semi-infinite media. The consequence of the finite-difference approximation is to replace the derivatives in the diffusion equations with corresponding gradients over a finite interval of time or distance instead of solving the differential equations into closed forms. If the flux density for a species is calculable, the concentration of the species can be calculated by using

$$\frac{\delta C_i}{\delta t} = \frac{-\delta J_i}{\delta x} \quad . \tag{41}$$

For convenient calculation by a computer, using Eqs. (1) with symmetrical expression may have an advantage, rather than starting with Eqs. (5). The calculation is shown only for species 1. The same procedure applies to the cases for species 2 and 3.

For the purpose of the finite-difference method, the derivatives in Eq. (1a) are replaced with the corresponding gradients, resulting in

$$J_1 = - D_1 \frac{\Delta C_1}{\Delta x} - C_1 \left\{ (D_1 - D_2) \frac{\Delta C_2}{\Delta x} + (D_1 - D_3) \frac{\Delta C_3}{\Delta x} \right\}. \tag{42}$$

In Eq. (42) the concentrations are given in fractions for simplicity, i.e., $C_0 = 1$ in Eq. (3), resulting in $N_i = C_i$. The subsequent procedure for Eq. (42) also applies to cases where the concentrations are given in other units, by multiplying the flux density and concentrations in Eq. (42) by a constant factor. The flux density of species 1 at time t and distance x_n is calculated by using

$$J_1(x_n) = -D_1\left\{\frac{C_1(x_n + 1/2) - C_1(x_n - 1/2)}{\Delta x}\right\}$$
$$- C_1(x_n)\left[(D_1 - D_2)\left\{\frac{C_2(x_n + 1/2) - C_2(x_n - 1/2)}{\Delta x}\right\}\right.$$
$$\left. + (D_1 - D_3)\left\{\frac{C_3(x_n + 1/2) - C_3(x_n - 1/2)}{\Delta x}\right\}\right], \qquad (43)$$

which is derived from Eq. (42) by substituting ΔC_i with the corresponding differences of the concentrations between two points distant from x_n by a half of Δx.[9]

This calculation is repeated at points $\pm x_n$ ($n = 0, 1, 2, 3, \cdots$) and at the centers of two adjacent points, where x_0 is the interface, $x_n = x_0 + n\Delta x$, and $x_n \pm 1/2$ are the centers of x_n and $x_n \pm 1$. The $C_1(x_n)$ corresponding to $J_1(x_n)$ is calculated from

$$\frac{C_1(x_n + 1/2, t_{k+1}) - C_1(x_n + 1/2, t_k)}{\Delta t}$$
$$= \frac{J_1(x_n, t_k) - J_1(x_{n+1}, t_k)}{\Delta x}, \qquad (44)$$

which is derived from Eq. (41) by substituting the derivatives with the corresponding gradients. First $C_1(x_n + 1/2, t_k)$ is calculated, then Eq. (44) gives C_1 for the next time interval, $C_1(x_n + 1/2, t_k)$. An average

of $C_1(x_n + 1/2)$ and $C_1(x_n - 1/2)$ is

$$C_1(x_n) = \frac{1}{2}\left\{C_1(x_n + 1/2) + C_1(x_n - 1/2)\right\}. \tag{45}$$

The calculation is repeated from time zero and distance zero to the given t and x. The finite-difference method requires proper magnitudes of Δt and Δx to minimize the error entering the approximation. This is particularly so in an early stage of diffusion where a discontinuity of concentrations exists initially in the neighborhood of the interface.

Whether or not the magnitudes of intervals Δx and Δt are proper to calculate the concentrations within the desired precision can be checked with the values calculated by using the solutions in closed form, if such solutions are available. Another means of checking if Δx and Δt are small enough and proper is to repeat the finite-difference approximations by employing successively smaller magnitudes of Δx and Δt and compare the results. If the smaller intervals yield results satisfactorily close to the previous results, the magnitudes of Δx and Δt may be regarded as proper. When, as an example, the initial boundary conditions are given by Eqs. (27) and we have $C_{1a} = 0.3139$, $C_{1b} = 0.2302$, $C_{2a} = 0.4559$, $C_{2b} = 0.5527$ (in fractions), and $D_1 = 2.16 \times 10^{-6}$, $D_2 = 2.40 \times 10^{-7}$, $D_3 = 6.65 \times 10^{-7}$, and $t = 500$, the values of C_1, C_2, and C_3 calculated with combinations of Δx and Δt (0.005 and 1.0), (0.005 and 0.5), (0.002 and 0.5), and (0.002 and 0.1) according to Eqs. (43), (44), and (45), are identical to four significant figures over the entire distance.

Table I compares the concentration distributions calculated by using Eqs. (29) and by the finite-difference method with $\Delta x = 0.005$ and $\Delta t = 1.0$, with satisfactorily good agreement. The relatively large discrepancies

in the neighborhood of the interface are due to the approximation made for the closed-form solutions.

In order to prevent the error caused by the initial discontinuity, it is also a practical method to calculate the concentrations at a short time by using the closed-form solutions instead of initiating the first step of the finite-difference approximations, and then start the finite-difference approximations with the resultant C_1, C_2, and C_3.[10]

III. CHARACTERISTICS OF TERNARY DIFFUSION

One means to clearly demonstrate the characteristics of concentration distribution for ternary diffusion is to plot the path of composition variation on the ternary diagram. The diffusion path on the diagram does not indicate the diffusion time and distance, but only shows as a continuous path all the compositions that appear in the concentration distribution.

With respect to the boundary conditions, characteristics of ternary diffusion are generally described by a diffusion couple of semi-infinite length with different compositions whose initial distributions are homogeneous. The boundary conditions are given by Eqs. (27).

A diffusion path for ternary diffusion is generally curved on the composition diagram. The author has proved that the condition $D_1 = D_2 = D_3$ is required to result in a linear diffusion path, and that there are two special cases resulting in a linear diffusion path where only two of the three intrinsic diffusion coefficients are required to be equal.[1] The proof was given schematically by using the diffusion equations, Eqs. (1) or those transformed from Eqs. (1). An explicit proof can be given for the same problem by the closed-form solutions of the diffusion equations for the above-described boundary conditions, i.e., Eqs. (29).

In Eqs. (29), S_1, S_2, R_1, R_2, μ_1, and μ_2 are constants determined by N_i and D_i, as described by Eqs. (32) and (33). Hence, Eqs. (29) describe the concentration variations of species 1 and 2, and accordingly

species 3, with variation of x and t as linear combinations of two error functions. For given D_i and N_i, therefore, the same $x/2t^{1/2}$ with varied combinations of x and t results in the same C_1 and C_2, and accordingly C_3, i.e., the same composition. This means that for given N_i and D_i, the concentration distributions against distance for various diffusion times results in a single diffusion path when plotted on the composition diagram. In other words, the curved diffusion path on the diagram is explicitly determined by given N_i and D_i. Kirkaldy and Brown have made essentially the same statement for the diffusion paths in single-phase ternary diffusion.[11]

A parameter has been derived to describe the deviation of the diffusion path on the diagram from the straight line. It is noted that application of the present solutions in closed form to a symmetrical boundary condition results in symmetrical concentration distributions, as indicated, for instance, by Eqs. (29). According to Eqs. (29), the concentration of a species i at x = 0 is always given by

$$C_i = C_{ib} + \frac{1}{2} \Delta C_i \, , \tag{46}$$

because erfc (0) = 1. The interface composition is always calculated as an average of the two initial compositions, because of the approximation in derivation of the solutions. In a mathematically strict sense, however, the interface composition should be shifted from the average composition with increasing diffusion time in the case where the D_i differ from each other. This shift of interface composition will be shown by the finite-difference method.

A. Condition for a Linear Diffusion Path on a Composition Diagram

Assume that diffusion takes place between two arbitrary compositions A and B on the ternary diagram for species 1, 2, and 3, as shown in Fig. 1. If both sides are semi-infinite, the boundary conditions are given by Eqs. (27) where A represents the negative x side and B the positive x side.

The condition that the composition at x is on the straight line AB is given by

$$\frac{C_1 - C_{1b}}{C_2 - C_{2b}} = \frac{C_{1a} - C_{1b}}{C_{2a} - C_{2b}} = \frac{\Delta C_1}{\Delta C_2} , \tag{47}$$

where C_1 and C_2 are the concentrations of species 1 and 2 at x. The C_1 and C_2 for a given x and t are given by Eqs. (29). Substitution of Eqs. (29) in Eq. (47) results in

$$\left(\frac{\Delta C_1}{\Delta C_2} + R_1 + R_2 + R_1R_2 \frac{\Delta C_2}{\Delta C_1}\right)\left(\operatorname{erfc} \frac{x\mu_1}{2t^{1/2}} - \operatorname{erfc} \frac{x\mu_2}{2t^{1/2}}\right) = 0 \tag{48}$$

For the diffusion path at time t to be a straight line on the diagram, Eq. (48) must hold for the entire range of x. That is, we must have

$$\operatorname{erfc} \frac{x\mu_1}{2t^{1/2}} = \operatorname{erfc} \frac{x\mu_2}{2t^{1/2}}$$

or

$$\mu_1 = \mu_2 , \tag{49}$$

or

$$\frac{\Delta C_1}{\Delta C_2} + R_1 + R_2 + R_1R_2 \frac{\Delta C_2}{\Delta C_1} = 0 . \tag{50}$$

In general, Eq. (50) does not hold except in two special cases which will be explained later; otherwise Eq. (49) must hold. By substituting Eqs. (32), Eq. (49) reduces to

$$D_2 - D_1 = N_1 (D_3 - D_1) - N_2 (D_3 - D_2) \pm \left\{4 N_1 N_2 (D_3 - D_2)(D_3 - D_1)\right\}^{\frac{1}{2}}. \qquad (51)$$

Equation (51) is satisfied if $D_1 = D_2 = D_3$, but is not satisfied if one differs from the other two.

In two special cases which are represented by A'B' and A"B" in Fig. 1 and described by Eq. (52) and (53) respectively, Eq. (50) is satisfied by $D_1 = D_2$, even if D_3 differs from the other two:

$$\Delta C_1 / \Delta C_2 = N_1 / N_2 \qquad (52)$$

$$\Delta C_1 = \Delta C_2 . \qquad (53)$$

In summary, the condition $D_1 = D_2 = D_3$ is required for general ternary diffusion to result in a linear diffusion path on the composition diagram. In two special cases where the concentrations of two species in the two compositions have the same ratio or the two species have the same gradients, the intrinsic diffusion coefficient of the third species need not necessarily be the same as the other two in order to produce a linear diffusion path.

B. Parameter for a Curved Diffusion Path

When the diffusion path between compositions A and B is curved, as in Fig. 2, the C_1 and C_2 which correspond to the maximum deviation from

the straight line AB satisfy

$$\frac{\delta C_1}{\delta C_2} = \frac{\Delta C_1}{\Delta C_2} , \tag{54}$$

i.e., the tangents of the curve are parallel to AB. Equation (54) reduces to

$$\Delta C_2 \frac{\delta C_1}{\delta x} = \Delta C_1 \frac{\delta C_2}{\delta x} . \tag{55}$$

For the general cases substitution of Eqs. (29) reduces Eq. (55) to

$$\pm \left\{ \frac{\ln(\mu_1/\mu_2)}{\mu_1^2 - \mu_2^2} \right\}^{\frac{1}{2}} = \frac{x}{2t^{1/2}} \tag{56}$$

where $t \neq 0$ and $(S_1 - S_2)(R_1 - R_2) \neq 0$. Equation (56) gives a parameter, in terms of N_i and D_i as described by Eqs. (32) and (33), which determines the diffusion time and distances to give the composition with the greatest deviation from the straight line. One distance is negative and the other positive. The corresponding C_1 and C_2 are calculated from Eqs. (29) with substitution of Eq. (56) for $x/2t^{1/2}$.

C. Diffusion with No Initial Gradient

If D_2 and D_3 are not equal, species 1 must diffuse, even with no initial gradient.[1] In this case, the first term in Eq. (1a) is initially zero, but $\delta C_2/\delta x$ and $\delta C_3/\delta x$, which are the same in magnitude initially, serve as the driving force for diffusion of species 1.

For the boundary conditions described by Eq. (27), where $C_{1a} = C_{1b}$, this case reduces Eq. (29a) to

$$C_1 = C_{1b} + \frac{\Delta C_2}{2(S_1 - S_2)} \left(\operatorname{erfc} \frac{x\mu_1}{2t^{1/2}} - \operatorname{erfc} \frac{x\mu_2}{2t^{1/2}} \right). \tag{57}$$

The maximum and minimum, C_{1m}, in the distribution of C_1 are given by

$$C_{1m} = C_{1b} + \frac{\Delta C_2}{2(S_1 - S_2)} \left(\mathrm{erf}\left[\pm \left\{ \frac{\ln(\mu_1/\mu_2)}{(\mu_1/\mu_2)^2 - 1} \right\}^{\frac{1}{2}} \right] - \mathrm{erf}\left[\pm \left\{ \frac{\ln(\mu_1/\mu_2)}{1 - (\mu_2/\mu_1)^2} \right\}^{\frac{1}{2}} \right] \right) \tag{58}$$

which is reduced from Eq. (57) by substituting Eq. (56). Figure 3 shows an example of concentration distributions of a species with no initial gradient and of the other two species for successive diffusion times. It should be noted that the maximum and minimum of C_1 remain constant, though their locations are shifted with increasing time. As already explained, these distributions result in a single diffusion path when they are plotted on the diagram. Figure 4 shows the diffusion path shifted by variation of D_1 with constant D_2 and D_3, where the less D_1 is, the more the path deviates from a straight line. Figure 5 shows the manner of shifting the diffusion paths by variation of D_3 from 10^{-2} to 10^{-7} with constant D_1 and D_2. The larger is D_3, the more the path deviates from the straight line. When $D_3 = D_2$, the path is a straight line as explained already. When D_3 becomes smaller than D_2, the path deviates in the opposite direction. The distributions of C_1 corresponding to the paths in Fig. 5 are shown in Fig. 6.

As is indicated by Eq. (1a), variation of the concentration level of species 1, i.e. N_1, varies the diffusion path even if D_1, D_2, and D_3 are constant. This is shown in Fig. 7, where only the deviation of C_1 from the initial constant value is plotted against $x/2t^{1/2}$. In all cases, the ratio of C_2 and C_3 for the average composition of the diffusion couple is unity, the negative x side is higher in C_2 and the positive

x side higher in C_3. The higher the concentration level of C_1, the greater the deviation from the straight line for the same D_i, ΔC_2, and ΔC_3. The value of $x/2t^{1/2}$ for maximum deviation is also shifted with varied C_1 levels.

D. Uphill Diffusion

If the difference of D_2 over D_3 is relatively large and D_1 is relatively small, species 1 can diffuse against its own gradient.[1] In this case, the maximum and minimum in the distribution of C_1, in a mathematical strictness, differ from the C_1 which deviates most from the straight line AB. The condition for the maximum and minimum of C_1 is given by

$$\pm \left[\ln \left\{ \frac{\mu_1 (S_1 \Delta C_1 + \Delta C_2)}{\mu_2 (S_2 \Delta C_1 + \Delta C_2)} \right\} / (\mu_1^2 - \mu_2^2) \right]^{\frac{1}{2}} = \frac{x}{2t^{1/2}} , \tag{59}$$

which is derived by equating to zero the derivative of Eq. (29a) with respect to x:

$$\frac{\delta C_1}{\delta x} = 0 .$$

Figure 8 shows an example of uphill diffusion with respect to C_3 for successive diffusing times. The maximum and minimum of C_1 remain constant with increasing time as well as in the no initial gradient case.

E. Shift of the Interface Composition

When the concentration variation is relatively large in ternary diffusion, the shift of the interface composition becomes noticeable with increasing diffusion time, even if the boundary condition is symmetrical. This shift of the interface composition results in asymmetrical

concentration distributions. Details of the shifted interface composition can be calculated by using finite-difference approximations, which have been explained already. Table II shows the calculated interface composition shifting with increasing diffusion time for a semi-infinite couple. The composition at time zero corresponds to the average of the two initial compositions. In such a case, calculation using the closed-form solutions is accompanied by an error, because μ_1, μ_2, R_1, and R_2 are not constant.

IV. SUMMARY

Solutions of ternary diffusion equations have been given in closed form and by a finite-difference approximation. The solutions in closed form are useful when the concentration variation in diffusion is relatively small. The solutions describe the linear combination of two concentrations obeying the diffusion law and are applicable to finite media diffusion where the initial distributions are not necessarily required to be homogeneous. If the concentration variation is relatively large, the finite-difference method is useful. Uncertainty in the application of the finite-difference approximations to the early stage of diffusion where the concentration distribution is initially discontinuous can be decreased by combination with the closed-form solutions; instead of the first step of the finite-difference approximations, the concentrations for a short time are calculated by using the closed-form solutions, and then the finite-difference approximations are started with the resultant concentrations.

The closed-form solutions have been superposed for the boundary conditions for the cases of the semi-infinite media, the semi-infinite—finite media, and the finite media.

The theoretical concentration distributions for the semi-infinite media diffusion have been calculated for the cases of no initial gradient and uphill diffusion. A parameter has been derived which describes the maximum deviation of the diffusion path from linearity on the ternary diagram. This parameter is determined by the composition and the three diffusion coefficients and determines $x/2t^{1/2}$ which gives the maximum deviation.

The shift of the interface composition was calculated by the finite-difference method.

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FOOTNOTES AND REFERENCES

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+Author on leave from the Faculty of Engineering, Kyushu University, Fukuoka, Japan, where he is professor of materials science.

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Table I. Concentration distributions calculated as linear differential equations by using closed-form solutions and as nonlinear by the finite-difference method. $C_{1a} = 0.2302$, $C_{1b} = 0.3139$, $C_{2a} = 0.5527$, $C_{2b} = 0.4559$, $C_{3a} = 0.2171$, $C_{3b} = 0.2302$; $D_1 = 2.16 \times 10^{-6}$, $D_2 = 2.40 \times 10^{-7}$, $D_3 = 6.65 \times 10^{-7}$; $t = 300$.

x	C_1			C_2			C_3		
	Linear	Nonlinear	Difference	Linear	Nonlinear	Difference	Linear	Nonlinear	Difference
-0.120	0.2302	0.2302	-0.0000	0.5527	0.5527	0.0000	0.2171	0.2171	0.0000
-0.080	0.2307	0.2307	0.0000	0.5524	0.5523	+0.0001	0.2169	0.2170	-0.0001
-0.060	0.2325	0.2326	-0.0001	0.5513	0.5511	+0.0002	0.2162	0.2163	-0.0001
-0.040	0.2385	0.2386	-0.0001	0.5471	0.5467	+0.0004	0.2144	0.2147	-0.0003
-0.025	0.2476	0.2476	0.0000	0.5384	0.5383	+0.0001	0.2140	0.2141	-0.0001
-0.010	0.2613	0.2610	+0.0003	0.5206	0.5211	-0.0005	0.2181	0.2179	+0.0002
0.000	0.2720	0.2716	+0.0004	0.5043	0.5052	-0.0009	0.2237	0.2232	+0.0005
+0.010	0.2828	0.2826	+0.0002	0.4880	0.4885	-0.0005	0.2292	0.2290	+0.0002
+0.025	0.2964	0.2964	0.0000	0.4702	0.4702	0.0000	0.2333	0.2335	-0.0002
+0.040	0.3056	0.3057	-0.0001	0.4615	0.4613	+0.0002	0.2329	0.2330	-0.0001
+0.060	0.3115	0.3116	-0.0001	0.4574	0.4572	+0.0002	0.2311	0.2312	-0.0001
+0.080	0.3134	0.3134	0.0000	0.4562	0.4561	+0.0001	0.2304	0.2304	0.0000
+0.120	0.3139	0.3138	+0.0001	0.4559	0.4559	0.0000	0.2302	0.2303	-0.0001

Table II. Interface compositions shifted with diffusion time.
$C_{1a} = 0.31387$, $C_{1b} = 0.23019$, $C_{2a} = 0.45589$, $C_{2b} = 0.55270$,
$C_{3a} = 0.23024$, $C_{3b} = 0.21711$;
$D_1 = 2.16 \times 10^{-6}$, $D_2 = 2.40 \times 10^{-7}$, $D_3 = 6.65 \times 10^{-7}$

t	Interface Composition		
	C_1	C_2	C_3
0	0.27203	0.50430	0.22367
0.1	0.27203	0.50430	0.22367
1.0	0.27191	0.50446	0.22363
10.0	0.27165	0.50505	0.22330
100.0	0.27162	0.50514	0.22324

FIGURE LEGENDS

Fig. 1. Linear diffusion paths on a ternary diagram.

Fig. 2. Schematic diffusion path curved on a ternary diagram.

Fig. 3. Concentration distributions for semi-infinite media diffusion with no initial gradient for C_1. The numbers on the curves are times. $C_1 = 0.3333 - 0.3333$, $C_2 = 0.3833 - 0.2833$, $C_3 = 0.2833 - 0.3833$; $D_1 = 10^{-10}$, $D_2 = 10^{-6}$, $D_3 = 10^{-7}$.

Fig. 4. Diffusion paths for various D_1 with constant $D_2 = 10^{-6}$ and $D_3 = 10^{-8}$. Numbers on the curves are D_1. $C_1 = 0.2000 - 0.2000$, $C_2 = 0.3500 - 0.4500$, $C_3 = 0.4500 - 0.3500$.

Fig. 5. Diffusion paths for various D_3 with constant $D_1 = 10^{-6}$, $D_2 = 10^{-6}$. Numbers on the curves are D_3. $C_1 = 0.2000 - 0.2000$, $C_2 = 0.3500 - 0.4500$, $C_3 = 0.4500 - 0.3500$.

Fig. 6. Distributions of C_1 for various D_3 with constant $D_1 = 10^{-6}$, $D_2 = 10^{-6}$. Numbers on the curves are D_3. $C_1 = 0.2000 - 0.2000$, $C_2 = 0.3500 - 0.4500$, $C_3 = 0.4500 - 0.3500$.

Fig. 7. Distributions of C_1 for various C_1 levels with no initial gradient. Numbers on the curves are the initial C_1. $D_1 = 10^{-9}$, $D_2 = 10^{-3}$, $D_3 = 10^{-6}$.

Fig. 8. Concentration distributions for various diffusion times for uphill diffusion with respect to C_1. Numbers on the curves are times. $C_1 = 0.3433 - 0.3233$, $C_2 = 0.3733 - 0.2933$, $C_3 = 0.2833 - 0.3833$; $D_1 = 10^{-10}$, $D_2 = 10^{-6}$, $D_3 = 10^{-7}$.

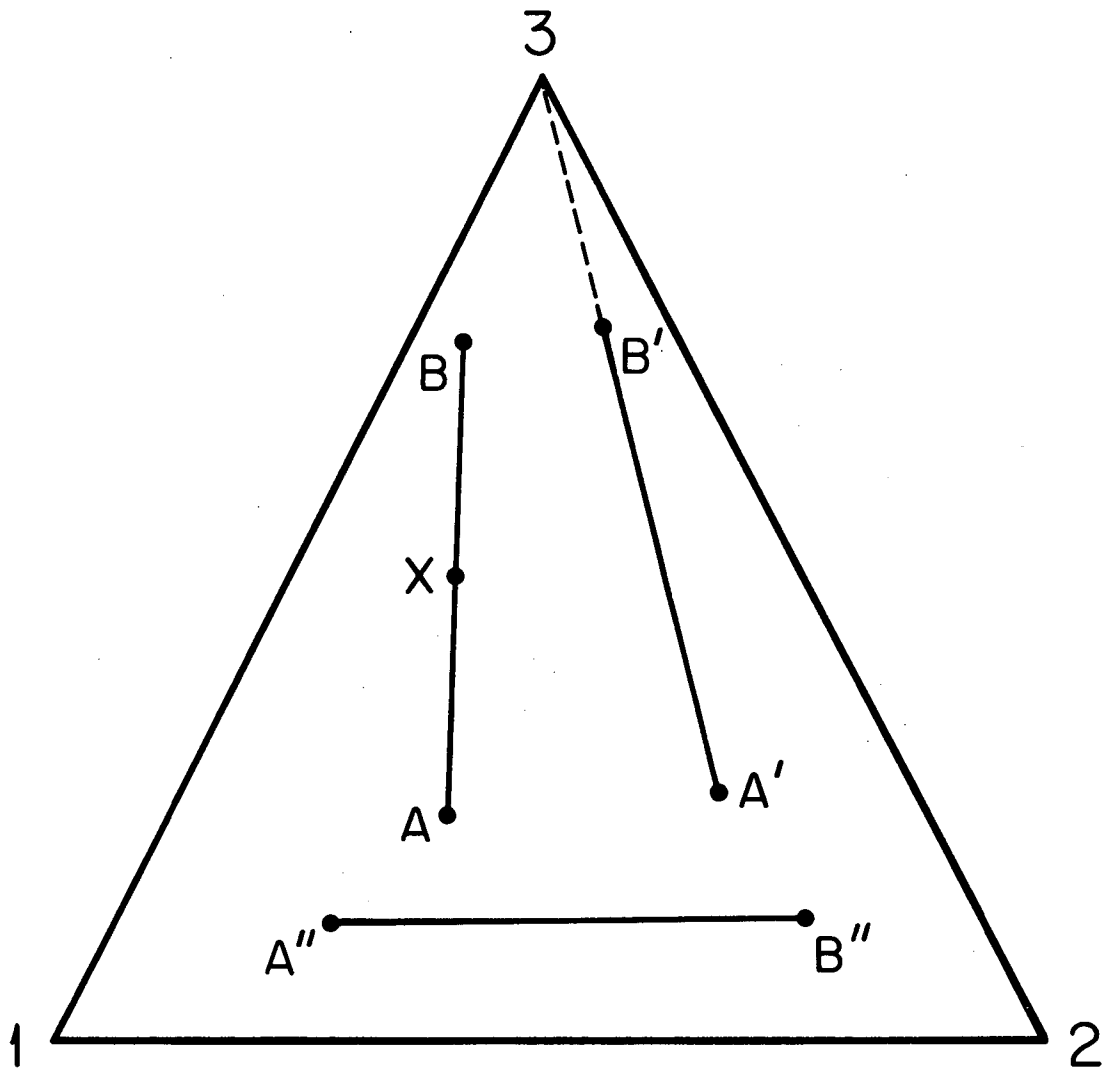

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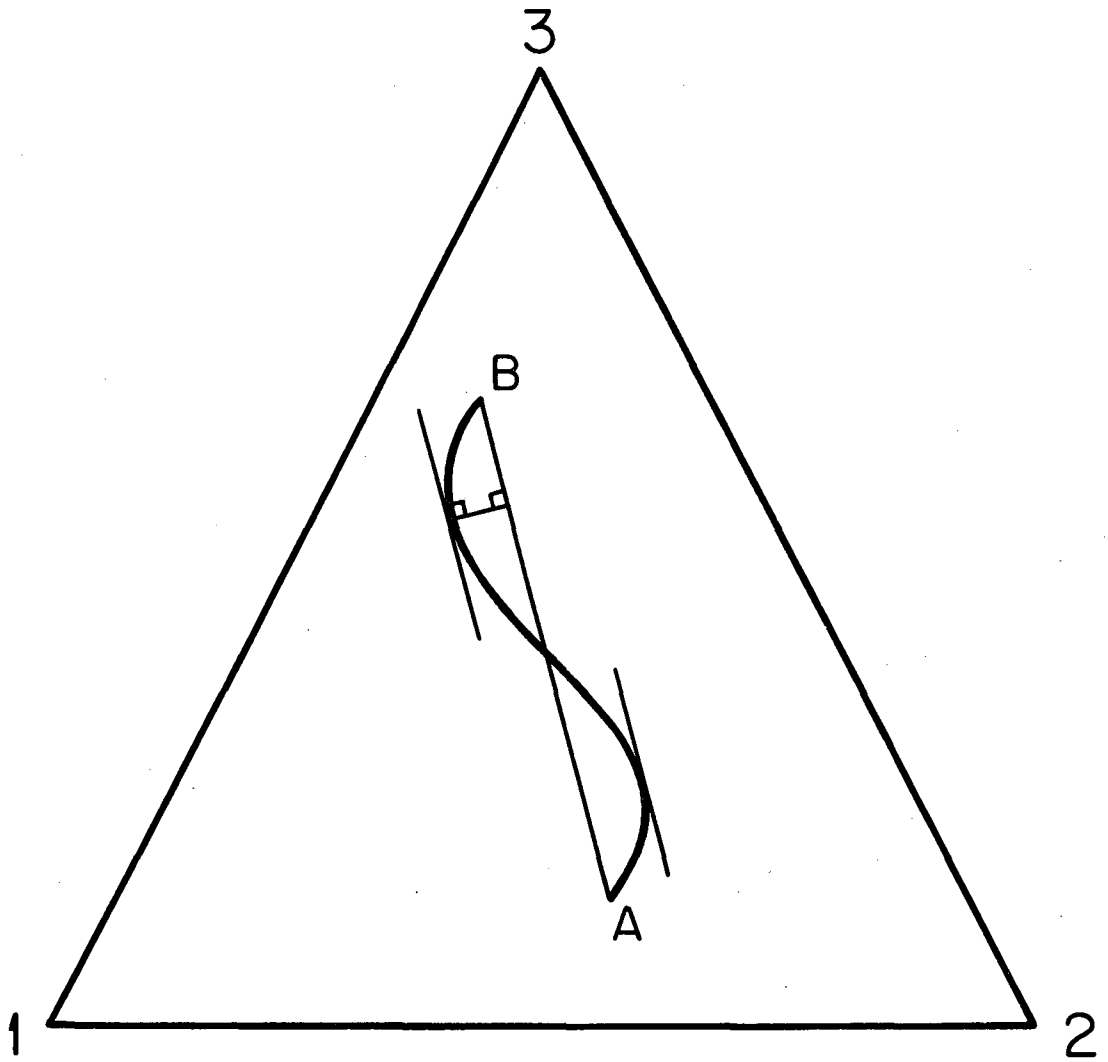
Fig. 1



MUB-5677

Fig. 2

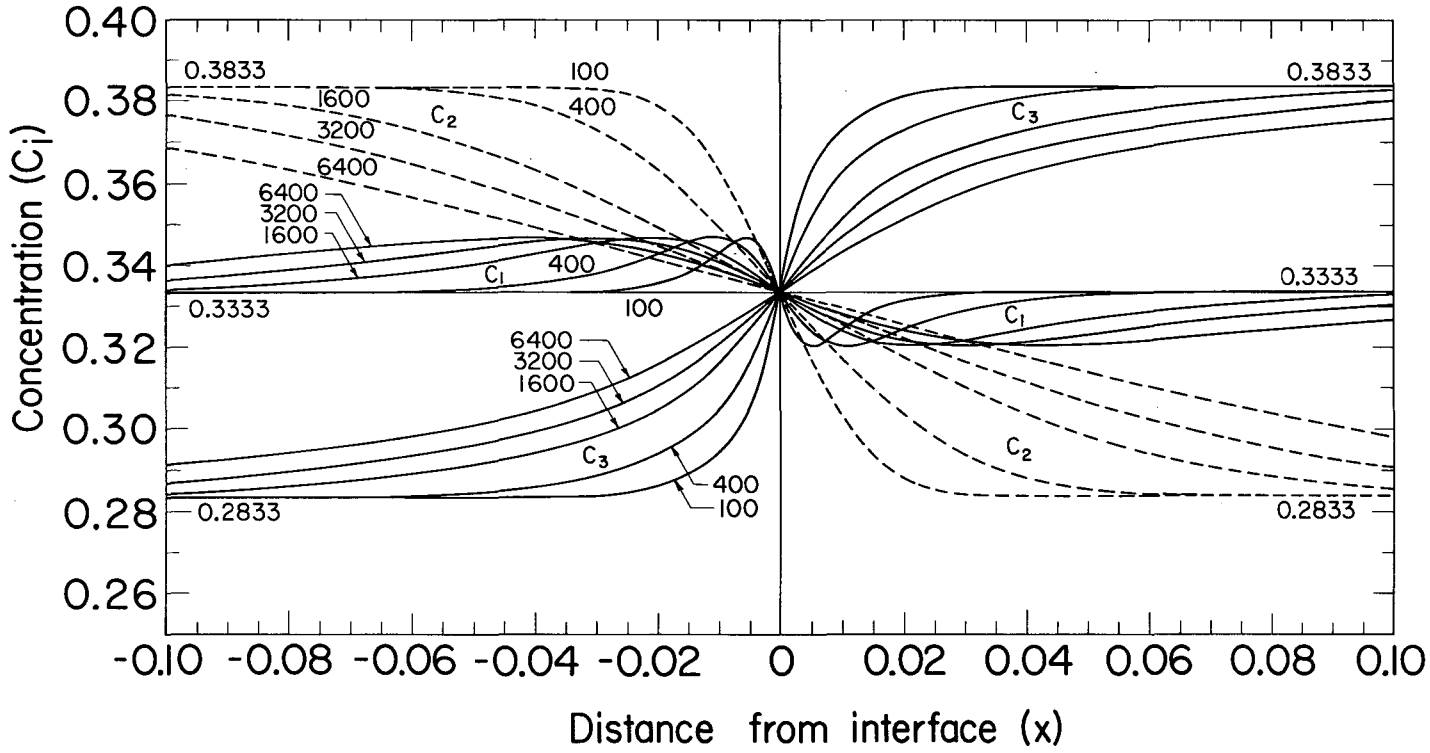


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Fig. 3

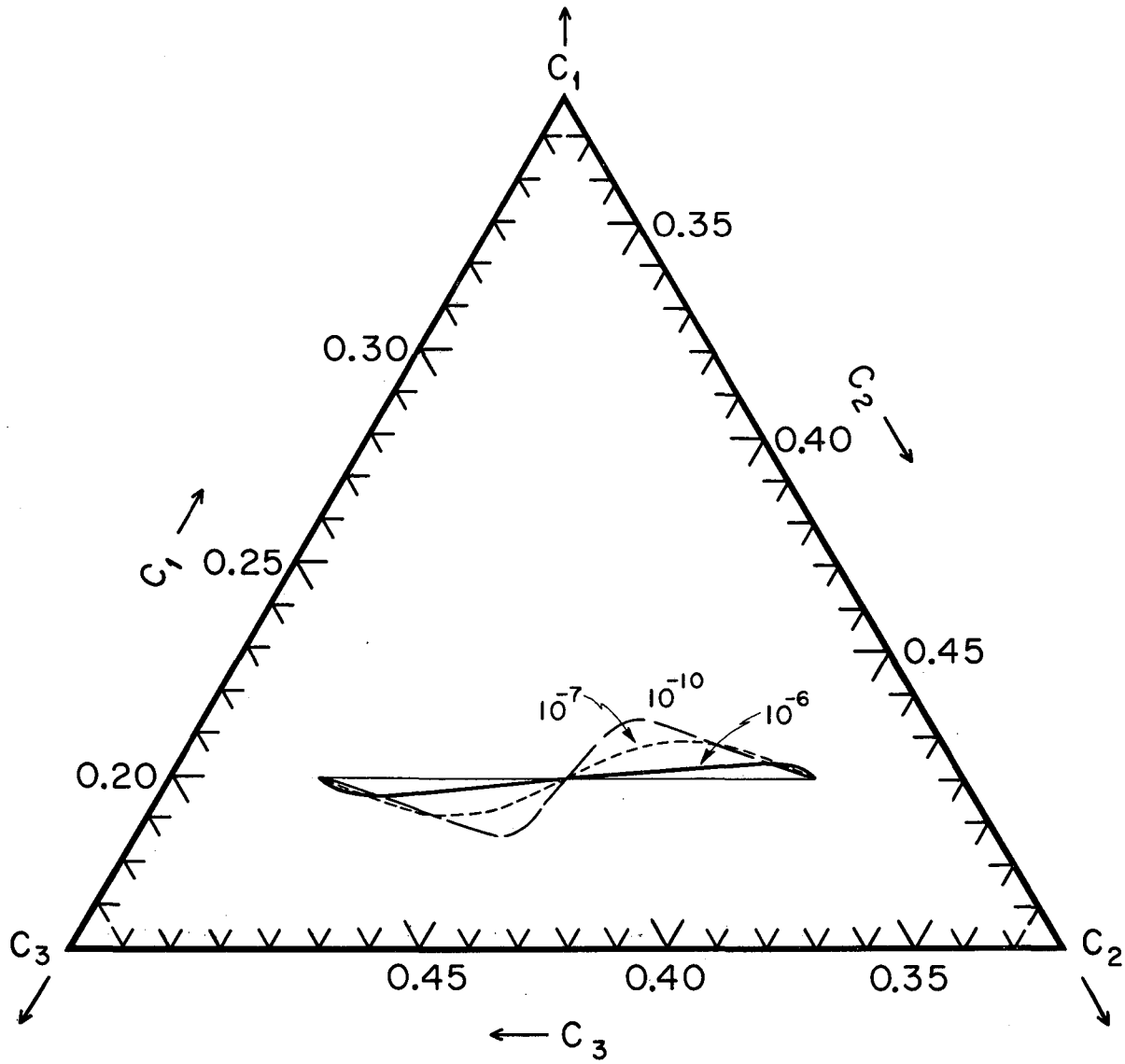

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Fig. 4

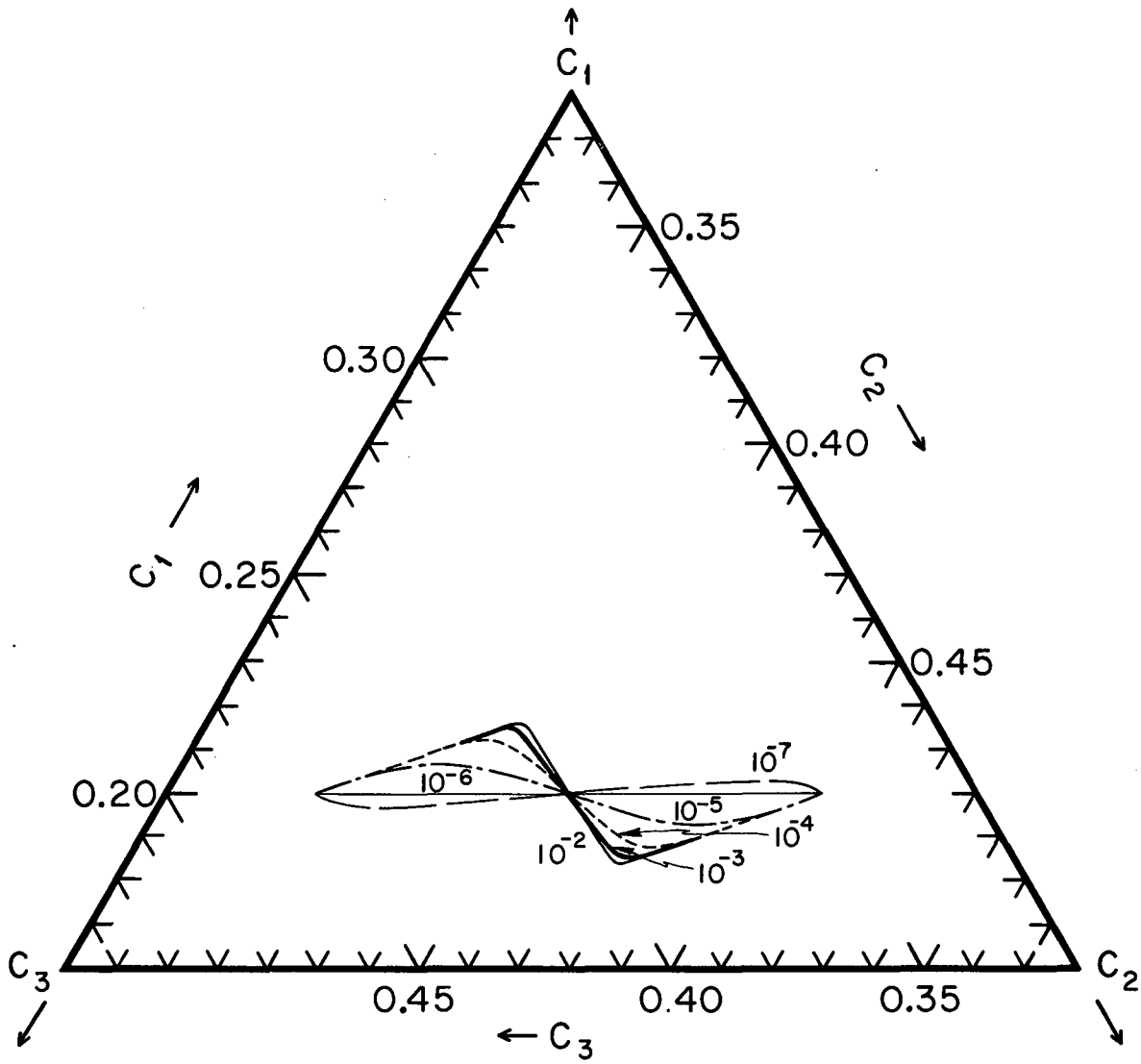

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Fig. 5

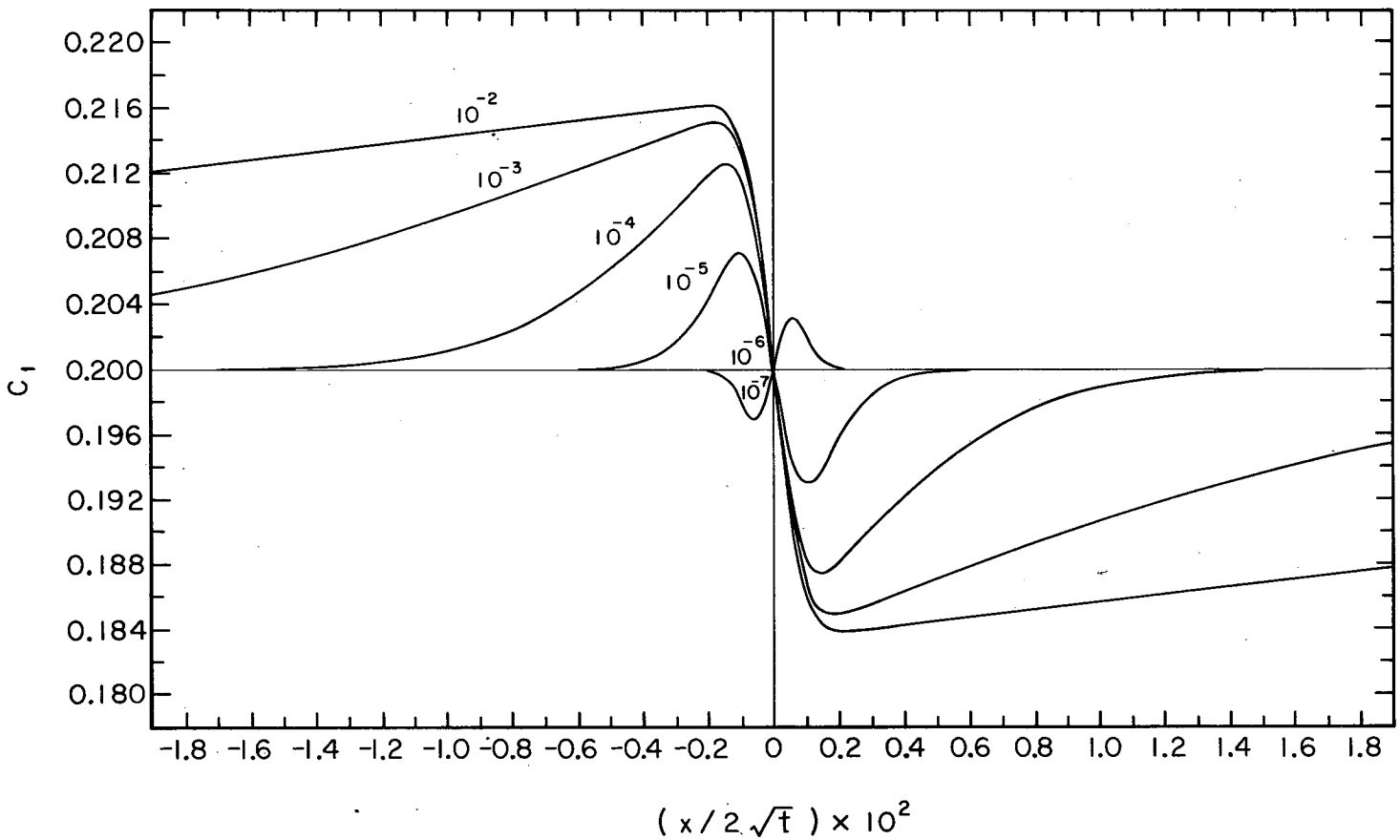

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Fig. 6

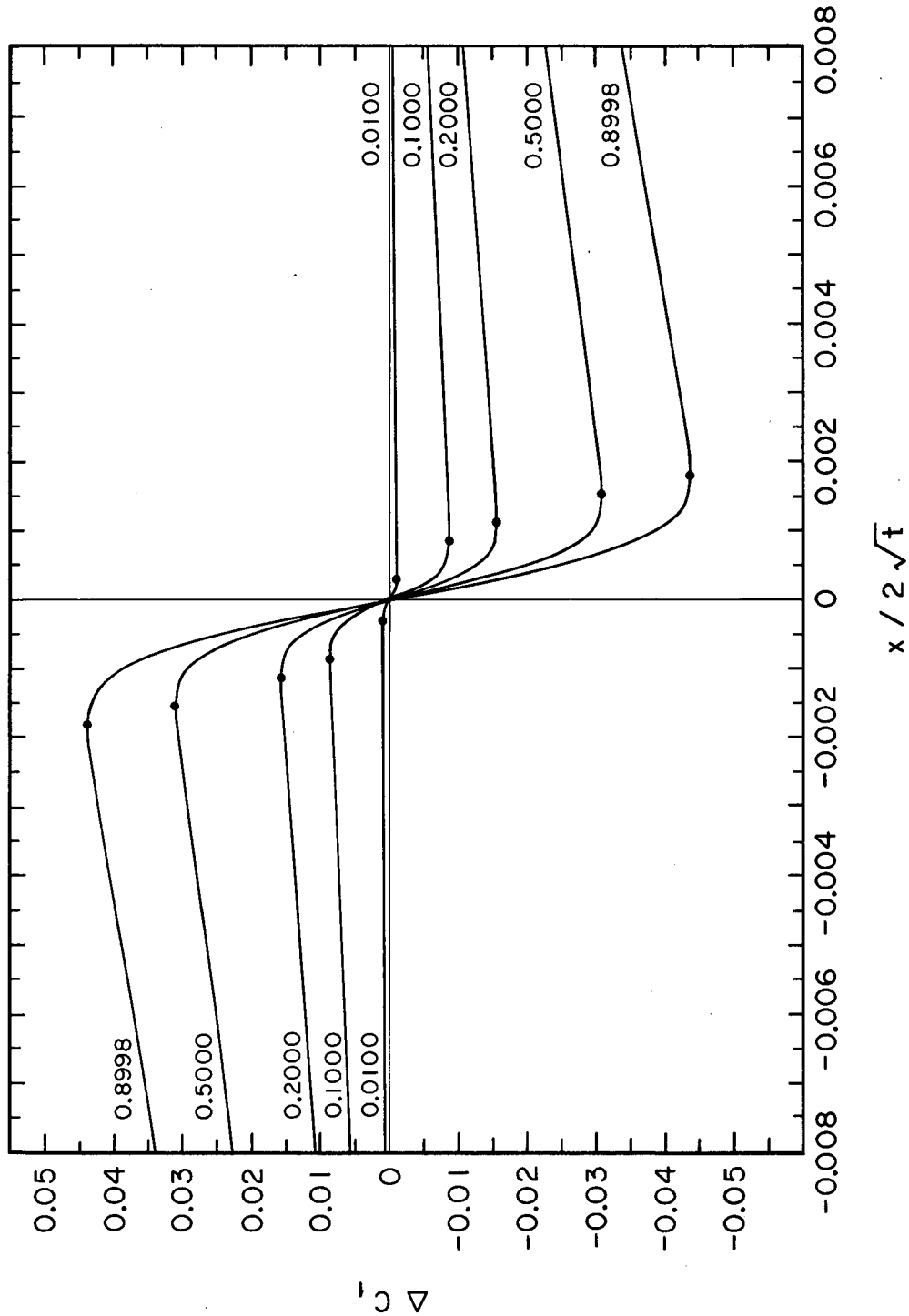

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Fig. 7

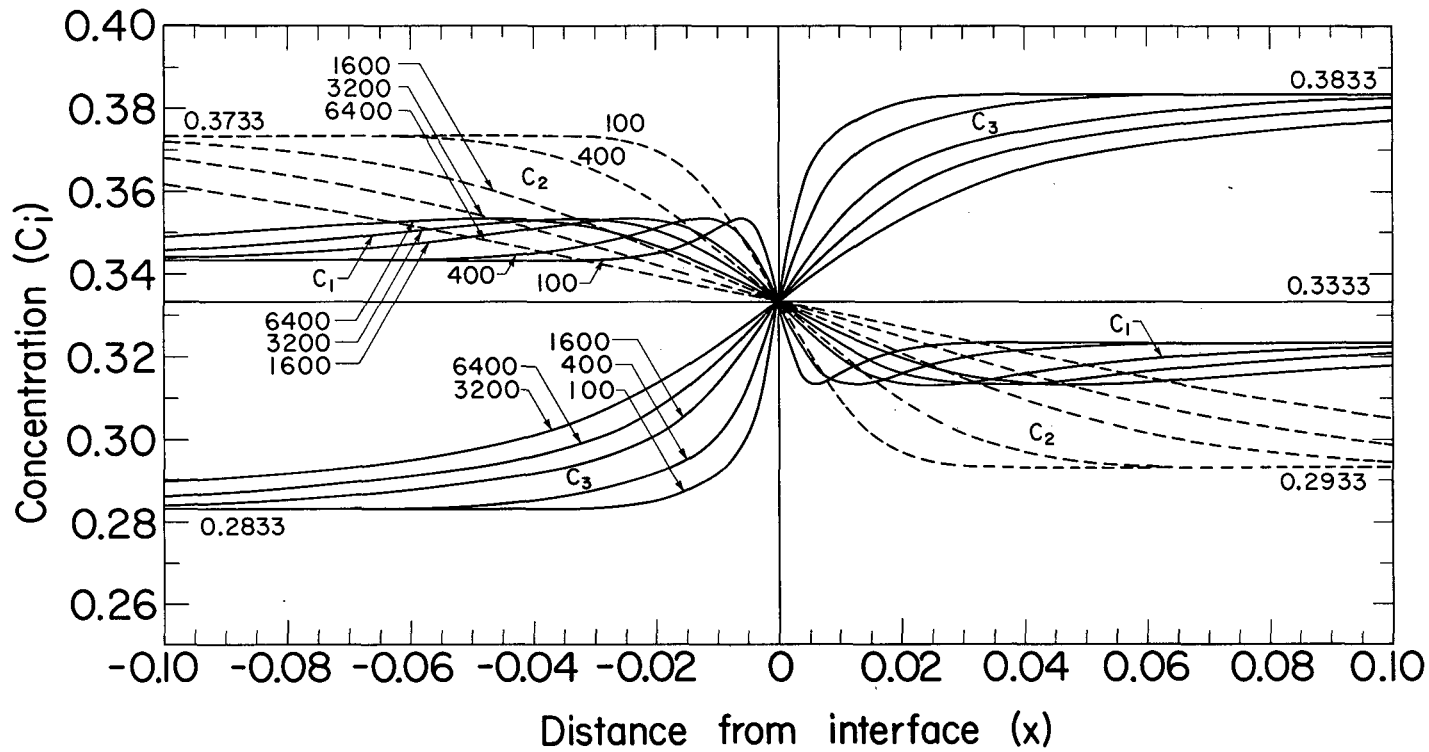

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Fig. 8

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