SEMI-ANNUAL PROGRESS REPORT

Contract NAG8-816

KINETICS OF DIFFUSIONAL DROPLET GROWTH
IN A LIQUID/LIQUID TWO-PHASE SYSTEM

BY

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Prepared for

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
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Submitted by

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September 15, 1992
This report consists of the attached manuscript titled, "Series Integration of the Diaphragm Cell Transport Equation When the Diffusion Coefficient Depends Upon Concentration", by Judith B. Cain and James K. Baird. The manuscript will appear as an article in the September 15, 1992 edition of The Journal of Chemical Physics. The work reported in this article was submitted by Judity B. Cain to the Graduate School of the University of Alabama in Huntsville as part of an M.S. thesis in chemistry. The University awarded Ms. Cain the M.S. degree at its June 1992 Commencement.

Integration of the the diaphragm cell transport equation in series was required in order to measure the diffusion coefficient in the system succinonitrile/water. A report on the measurements, themselves, is being prepared for publication.
Series Integration of the Diaphragm Cell Transport Equation
When the Diffusion Coefficient is a Function of Concentration

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Abstract

In the case of the diaphragm cell transport equation where the interdiffusion coefficient is a function of concentration, we have derived an integral of the form,

\[ t = B_0 + B_L \ln(\Delta c) + B_1(\Delta c) + B_2(\Delta c)^2 + \ldots \]

where \( t \) is the time and \( \Delta c \) is the concentration difference across the frit. The coefficient, \( B_0 \), is a constant of integration, while the coefficients, \( B_L, B_1, B_2, \ldots \), depend in general upon the cell constant, the compartment volumes, and the interdiffusion coefficient and various of its concentration derivatives evaluated at the mean concentration for the cell. Explicit formulae for \( B_L, B_1, B_2, \ldots \) are given.

*Submitted in partial fulfillment of the requirements of the M.S. degree from the University of Alabama in Huntsville.
1. Introduction

The diaphragm cell is the most convenient device for measuring diffusion coefficients in liquids.1-4 The cell consists of two well-stirred compartments containing solutions of different composition on opposite sides of a membrane, which is usually a sintered glass disk. The stirring guarantees that the contents of each compartment are uniform, so that mixing is limited to transport through the frit. In operation, the cell is oriented so that the normal to the plane of the frit is parallel to the gravity vector. The heavier solution is placed in the lower compartment, while the lighter solution is placed in the upper compartment; this arrangement obviates gravitational convection within the frit. Because molecular diameters are small as compared with the size of the interstitial spaces between the sintered glass beads, the diffusive transport within the frit is the same as in bulk solution.

In the absence of volume change on mixing, the center of volume within the frit is fixed with respect to the laboratory. Diffusion through the frit can then be referred to volume-fixed coordinates, in which reference frame a two component solution has but one diffusion coefficient.5

The diaphragm cell is a relative device, since it involves a cell constant which must be calibrated by analyzing data for a solution whose diffusion coefficient is already known.1-4 Once calibrated, however, the cell may be used to determine an unknown diffusion coefficient by following the time relaxation of the concentration difference across the frit.

For the important case where the diffusion coefficient is a function of concentration, we have recently shown that the relation between the relaxation time, $t$, and the concentration difference, $\Delta c$, is of the general form

$$t = B_0 + B_L \ln (\Delta c) + B_1(\Delta c) + B_2(\Delta c)^2 + \ldots \quad (1)$$

The $B_0$-coefficient is a constant of integration, while the remaining $B$-coefficients depend in general upon the cell constant, the compartment volumes and the interdiffusion coefficient and various of its concentration derivatives evaluated at the mean concentration for the cell.6,7 In our previous work, however, we have obtained explicit
expressions only for $B_L$, $B_1$, and $B_2$. Below, we extend our proof to derive a formula for the general $B$-coefficient.

2. Solution of the Transport Equation

For a planar system, Fick's first law states

$$J = -D(c) \frac{dc}{dx} \quad (2)$$

where $J$ is the flux, $c$ is the concentration, $D(c)$ is the functional form of the interdiffusion coefficient, and $x$ is the coordinate normal to the plane. Regardless of the initial solute distribution within the frit, diffusion through the frit rapidly achieves a steady state. In that case, $J$ is independent of coordinate, and Eq.(2) may be integrated across the frit to obtain

$$J = -\frac{1}{\ell} \int_{c_1}^{c_2} D(c) \, dc \quad (3)$$

In Eq.(3), $\ell$ is the effective thickness of the frit, and $c_1$ and $c_2$ are the concentrations below and above the frit, respectively.

We let $V_1$ and $V_2$ be the respective compartment volumes. If diffusion proceeds from $V_1$ into $V_2$, conservation of mass specifies that

$$V_1 \frac{dc_1}{dt} = -JA \quad (4)$$

and

$$V_2 \frac{dc_2}{dt} = JA \quad (5)$$

where $A$ is the cross-sectional area of the frit. Substitution of Eq.(3) into Eqs.(4) and (5) leads to the coupled equations describing the diaphragm cell:

$$V_1 \frac{dc_1}{dt} = -A \frac{1}{\ell} \int_{c_2}^{c_1} D(c) \, dc \quad (6)$$

$$V_2 \frac{dc_2}{dt} = A \frac{1}{\ell} \int_{c_2}^{c_1} D(c) \, dc \quad (7)$$
Combined with the initial conditions, $c_1(0)$ and $c_2(0)$, Eqs.(6) and (7) specify an initial value problem satisfied by the two concentrations, $c_1(t)$ and $c_2(t)$. As a pair of coupled, first order ordinary differential equations, Eqs.(6) and (7) are solved by two integrals.

2.1 First Integral

If Eqs. (6) and (7) are added, we obtain

$$V_1 \frac{d c_1}{d t} + V_2 \frac{d c_2}{d t} = 0 \quad (8)$$

The solution to Eq.(8) is

$$\bar{c} = \frac{V_1 c_1(t) + V_2 c_2(t)}{V_1 + V_2} = \frac{V_1 c_1(0) + V_2 c_2(0)}{V_1 + V_2} \quad (9)$$

where $\bar{c}$, the volume-averaged concentration, is a constant of the motion.

2.2 Second Integral

We divide Eq.(6) by $V_1$ and Eq.(7) by $V_2$ and subtract to obtain

$$\frac{d(c_1 - c_2)}{dt} = -\beta \int_{c_2}^{c_1} D(c) dc \quad (10)$$

where

$$\beta = \frac{\Delta}{\ell} \left( \frac{1}{V_1} + \frac{1}{V_2} \right) \quad (11)$$

is the cell constant. Eq.(10) is ordinarily considered as the transport equation for the diaphragm cell. 1-4

To solve Eq.(10) for the difference, $\Delta c(t) = c_1(t) - c_2(t)$, we introduce into the right hand side, $c = \bar{c} + y$, $dc = dy$, and

$$w = \frac{V_1 V_2 \Delta c}{V_1 + V_2} \quad (12)$$

Eq.(10) then becomes

$$\frac{d \Delta c}{dt} = -\beta \int_{-\frac{w}{V_1}}^{\frac{w}{V_2}} D(\bar{c} + y) \, dy \quad (13)$$
For electrolytes away from low concentration (in which regime the Debye-Huckel-Onsager theory requires terms involving \( c^{1/2} \)) and for nonelectrolytes at any concentration, we can expand \( D(\bar{c} + y) \) in a Taylor series about \( \bar{c} \):

\[
D(\bar{c} + y) = D(\bar{c}) + \sum_{k=1}^{\infty} \frac{D^{(k)}(\bar{c})}{k!} y^k
\]

where \( D^{(k)}(\bar{c}) = \left( \frac{d^k D(c)}{dc^k} \right)_{c = \bar{c}} \). Substitution of Eq.(14) into the right hand side of Eq.(13) followed by term-by-term integration gives the result,

\[
\frac{d\Delta c}{dt} = - \beta D(\bar{c}) \Delta c \left[ 1 + \sum_{k=1}^{\infty} b_k (\Delta c)^k \right]
\]

where

\[
b_k = \frac{D^{(k)}(\bar{c})}{(k+1)! D(\bar{c})} \frac{(V_2)^{k+1} - (-V_1)^{k+1}}{(V_1 + V_2)^{k+1}}
\]

Note in the case \( V_1 = V_2 \) that \( b_k = 0 \) for \( k \) odd.

The object is now to separate the variables, \( t \) and \( \Delta c \), in Eq.(15) and integrate. If we introduce the dimensionless time

\[
\tau = \beta D(\bar{c}) t
\]

the reciprocal of Eq.(15) can be written

\[
- \frac{d\tau}{d\ln(\Delta c)} = \left[ 1 + \sum_{k=1}^{\infty} b_k (\Delta c)^k \right]^{-1}
\]

When

\[
\left| \sum_{k=1}^{\infty} b_k (\Delta c)^k \right| < 1
\]

the right hand side of Eq.(18) can be expanded in a geometric series. The result is

\[
- \frac{d\tau}{d\ln(\Delta c)} = 1 + \sum_{m=1}^{\infty} (-1)^m \left( \sum_{k=1}^{\infty} b_k (\Delta c)^k \right)^m
\]
The multinominal theorem is stated by Abramowitz and Stegun\textsuperscript{10} in the form,

\[
\left( \sum_{k=1}^{\infty} \frac{x_k}{k} (\Delta c)^k \right)^m = m! \sum_{n=m}^{\infty} \frac{(\Delta c)^n}{n!} \sum (n;a_1,a_2,...,a_n)^* (x_1)^{a_1}(x_2)^{a_2}...(x_n)^{a_n} \tag{21}
\]

In Eq.(21),

\[(n;a_1,a_2,...,a_n)^* = n!/a_1!a_2!...a_n! \tag{22}\]

is a multinominal coefficient. The inner sum in Eq.(21) is carried out over all integral values of the a\(_j\)'s such that

\[a_1 + a_2 +...+a_n = m \tag{23}\]
\[a_1 + 2a_2 +...+ na_n = n \tag{24}\]

The values of the a\(_j\)'s may be established by considering the various partitions of n; a\(_j\) is the number of times that the integer, j, occurs in that partition, while m is the total number of integers in the partition.

If we identify b\(_k\) with x\(_k\)/k, we may substitute Eq.(21) into Eq.(20). After interchange of summations with respect to n and m, the result is

\[
d\tau = d\Delta c \left[ 1 + \sum_{n=1}^{\infty} \frac{(\Delta c)^n}{n!} \sum_{m=1}^{n} (-1)^m m! \sum (n;a_1,a_2,...,a_n)^* (b_1)^{a_1}(2b_2)^{a_2}...(nb_n)^{a_n} \right] \tag{25}
\]

In eq.(25), the variables \(\tau\) and \(\Delta c\) are separated, and the right hand side can be integrated term-by-term. After reintroducing the variable, \(t\), through Eq.(17), we obtain for the integrated form of Eq.(25) the result

\[t = B_0 + B_L \ln(\Delta c) + \sum_{n=1}^{\infty} B_n (\Delta c)^n \tag{26}\]

where \(B_0\) is the constant of integration, while

\[B_L = -\left( \beta D (\bar{c}) \right)^{-1} \tag{27}\]

and
\[ B_n = \left( \frac{B_L}{n!} \right) \sum_{m=1}^{n} (-1)^m \frac{m!}{m!} \sum_{n_1, a_2, \ldots, a_n} (b_1)^{a_1} (2b_2)^{a_2} \cdots (nb_n)^{a_n} \]  

(28)

Eqs.(26)-(28) solve Eq.(10) and complete the derivation of Eq.(1). Eq.(27) defines \( B_L \) while Eq.(28) is a formula for generating the polynomial \( B \)-coefficient of arbitrary order.

Abramowitz and Stegun list in their Table 24.2 all the partitions of \( n \) for \( n = 1 \) to 10 and give values for the corresponding binomial coefficients, \( (n; a_1, a_2, \ldots, a_n)^* \). On the basis of that table, it can be seen that the complexity of the double sum in Eq.(28) grows slowly with \( n \); specifically, as \( n \) advances from 1 to 10, the number of terms appearing in Eq.(28) is 1, 2, 3, 5, 7, 11, 15, 22, 30, and 42, respectively. This integer sequence represents the number of partitions of \( n \) and has been tabulated by Abramowitz at Stegun and by Sloane.

3. Discussion

Of physical interest is the determination of the values of \( D(\bar{c}) \) and the instantaneous derivatives, \( D^{(k)}(\bar{c}) \). This can be accomplished by fitting \( t \) vs. \( \Delta c \) experimental data to Eq.(1) and treating the \( B \)-coefficients as least squares parameters. Once the \( B \)-coefficients have been evaluated, \( D(\bar{c}) \) follows from Eq.(27) while the \( D^{(k)}(\bar{c}) \) follow from Eqs.(16) and (28). Since any \( t \) vs. \( \Delta c \) data set is necessarily finite in extent, Eq.(1) must first be truncated so that the number of \( B \)-coefficients to be determined does not exceed the number of experimental data points available. Accurate truncation is always possible, however, since for small enough \( \Delta c \), the sum of all terms dropped can be made less than the last term retained. Having derived previously expressions for \( B_L \), \( B_1 \), and \( B_2 \), we have successfully carried out this procedure to determine \( D(\bar{c}) \), \( D^{(1)}(\bar{c}) \) and \( D^{(2)}(\bar{c}) \) for aqueous hydrochloric acid at \( \bar{c} = 1 \text{ M} \).

To the extent that the accuracy of the experimental data will allow, the higher derivatives can be evaluated using Eqs.(16) and (28). Specifically, by virtue of Eq.(16), each \( b_k \) is proportional to \( D^{(k)}(\bar{c}) \); the \( b_k \) are in turn related to the \( B_n \) by a triangularized system of linear, algebraic equations. Employing Eqs.(27) and (28), we have tabulated in Table 1 explicit expressions for the first four \( B \)-coefficients. This triangularized system can be readily solved for the \( b_k \) in terms of the \( B_n \). The first four solutions have been listed in Table 2.
When integrating Eq.(10), we could have expanded $D(c)$ in a Taylor series about any fixed concentration consistent with the solution properties of electrolytes and non-electrolytes. We chose $\bar{c}$, however, because as is evident from Eq.(16) and Table 1, this origin makes $B_n = 0$ whenever $V_1 = V_2$ and $n$ is odd. This property may be exploited experimentally in situations where only the value of $D(\bar{c})$ is desired; since in this case the number of polynomial coefficients is reduced by half, a finite $t$ vs. $\Delta c$ data set may be fitted more accurately, because Eq.(1) can be extended to higher order in $\Delta c$ than would be possible otherwise.$^{13,14}$

Acknowledgments

This research was sponsored by the National Aeronautics and Space Administration in part through contract NAGW-812 with the Consortium for Materials Development in Space at the University of Alabama in Huntsville and in part through contract NAG8-816 from the Marshall Space Flight Center.
References


8. C. Barnes, Physics 5, 4 (1934).


Table 1. Triangularized system of linear algebraic equations for the $B_n$-coefficients in Eq.(1) expressed in terms of the $b_k$-coefficients defined by (16). The parameter $\lambda = \beta D(\bar{c})$.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$B_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$b_1/\lambda$</td>
</tr>
<tr>
<td>2</td>
<td>$(b_2 - b_1^2)/2\lambda$</td>
</tr>
<tr>
<td>3</td>
<td>$(b_3 - 2b_1b_2 + b_1^3)/3\lambda$</td>
</tr>
<tr>
<td>4</td>
<td>$(b_4 - 2b_1b_3 - b_2^2 + 3b_1^2b_2 - b_1^4)/4\lambda$</td>
</tr>
</tbody>
</table>
Table 2. Equations in Table 1 solved for the $b_k$-coefficients in terms of the $B_n$-coefficients. The parameter $\lambda = \beta D(\xi)$.

<table>
<thead>
<tr>
<th>$k$</th>
<th>$b_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\lambda B_1$</td>
</tr>
<tr>
<td>2</td>
<td>$2\lambda B_2 - \lambda^2 B_1^2$</td>
</tr>
<tr>
<td>3</td>
<td>$3\lambda B_3 + 4\lambda^2 B_1 B_2 - 3\lambda^3 B_1$</td>
</tr>
<tr>
<td>4</td>
<td>$4\lambda B_4 + 2\lambda^2 (3B_1 B_3 + 2B_2^2) - 2\lambda^2 B_1^2 B_2 - \lambda^4 B_1^4$</td>
</tr>
</tbody>
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