NATIONAL BUREAU OF STANDARDS REPORT

9654

Progress Report

on

CALCULATIONS OF DIFFUSION COEFFICIENTS IN TERNARY SYSTEMS FROM DIAPHRAGM CELL EXPERIMENTS

NBS

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CALCULATIONS OF DIFFUSION COEFFICIENTS IN TERNARY SYSTEMS FROM DIAPHRAGM CELL EXPERIMENTS

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Abstract

The general solution of the flux equations in ternary systems, with the diaphragm cell conditions, cannot be used to calculate the four diffusion coefficients without mathematical approximations and specific restrictions in the initial conditions. Furthermore, two experimental arrangements are required. A new method is presented which requires neither approximations nor restrictions and permits the calculation of the diffusion coefficients from one experimental arrangement. It is based upon a generalized least square procedure in which the diffusion coefficients and their errors are calculated simultaneously with the adjustment of the weighted observables--concentrations of the two solute components and time--subject to the condition functions given by the general solution for diffusion fluxes. The method was tested with diffusion data for the system NaCl(1)-Manitol(2)-H_2O (F. J. Kelly, Ph. D. Thesis, University of New England, Armidale, Australia, 1961). The values obtained

for the diffusion coefficients were $10^5 D_{11} = 0.557 \pm 0.002$, $10^5 D_{12} = 0.03 \pm 0.03$, $10^5 D_{21} = 0.232 \pm 0.011$ and $10^5 D_{22} = 1.56 \pm 0.16$, $\mathrm{cm}^2/\mathrm{sec}$, which compare with the two diffusion coefficients reported by Kelly, $10^5 D_{11} = 0.559 \pm 0.004$, and $10^5 D_{21} = 0.232 \pm 0.001$. The new method was thoroughly investigated using artificial data to assess the effects of experimental errors, duration of experiments and errors in cell constant on the values and errors of the diffusion coefficients. Methods are given to obtain good initial estimates for the diffusion coefficients, required by this procedure, to insure convergence.

CALCULATIONS OF DIFFUSION COEFFICIENTS IN TERNARY SYSTEMS FROM DIAPHRAGM CELL EXPERIMENTS

1. INTRODUCTION

The methods reported for the calculation of diffusion coefficients in ternary systems from diaphragm cell data require either restrictions in the experimental conditions[1,2] or approximations in the flux equations[3]. A new method is reported here that obviates the limitations of previous procedures when concentrations of the diffusing solutes are directly measured in the cell compartments. Although the present method was derived independently of a procedure recently reported by Cussler and Dunlop[4], the two approaches to the problem are similar. The present derivations, however, allow a more complete and direct treatment of the subject, particularly for the calculation of errors.

2. THEORY

The general equations that define diffusion flows, $(J_i)_V$, in ternary systems relative to a volume-fixed frame of reference are[5,6]

$$(J_i)_V = - \sum_{j=1}^{2} (D_{ij})_V \frac{\partial C_j}{\partial x} \qquad (i = 1, 2) \qquad [1]$$

in which $(D_{ij})_V$ are practical diffusion coefficients and C_i is the concentration of component i (molar scale is used throughout these derivations). Integration of equation [1], considering the conditions for the diaphragm cell, assuming linear concentration gradients and no changes in volume during the diffusion process, gives the general solution[7]

$$\Delta C_i = A_i e^{-\beta m_1 t} + B_i e^{-\beta m_2 t} \qquad (i = 1, 2) \qquad [2]$$

in which ΔC_i is the concentration difference of component i between the two compartments at any time t, β is the cell constant and the other quantities are defined by

$$\left.\begin{aligned} A_i &= \frac{\Delta C_i^0 (D_{ii} - m_2) + D_{ij} \Delta C_j^0}{m_1 - m_2} \qquad [3] \\[2ex] B_i &= \frac{\Delta C_i^0 (D_{ii} - m_1) + D_{ij} \Delta C_j^0}{m_2 - m_1} \qquad [4] \end{aligned}\right\} \quad \begin{aligned} i &= 1, 2 \\ j &= 1, 2 \\ i &\neq j \end{aligned}$$

$$m_1, m_2 = \tfrac{1}{2}\left[D_{11} + D_{22} \pm \sqrt{(D_{11} + D_{22})^2 - 4(D_{11} D_{22} - D_{12} D_{21})}\right] \qquad [5]$$

In equations [3] and [4], ΔC°, denotes concentration differences at $t = o$, and D_{ij} are the integral cell diffusion coefficients.

The calculation of D_{ij} is accomplished by a generalized least squares procedure[8] using equation [2] as the mathematical model. Thus, the condition equations are of the form

$$F = (X_1 - X_2) - A_1 e^{-\beta m_1 T} - B_1 e^{-\beta m_2 T} \qquad [6]$$

$$L = (Y_1 - Y_2) - A_2 e^{-\beta m_1 T} - B_2 e^{-\beta m_2 T} \qquad [7]$$

in which X and Y represent the concentrations of components 1 and 2, respectively, in the compartments indicated by their subscripts at the observation time T.

If observations (determinations of X and Y) are made at the end of each of the N time intervals, there will be 2N condition equations. The number of condition equations may not be a multiple of 2, however, if either X or Y is not determined at the end of some of the intervals.

When observations are made in only one of the compartments, for example compartment 2, the condition equations take the form

$$F' = (\Delta X^\circ - 2X_2) - A_1 e^{-\beta m_1 T} - B_1 e^{-\beta m_2 T} \qquad [8]$$

$$L' = (\Delta Y^\circ - 2Y_2) - A_2 e^{-\beta m_1 T} - B_2 e^{-\beta m_2 T} \qquad [9]$$

in which ΔX° and ΔY° are concentration differences for the two components at time $T = o$.

The aim of the procedure is to compute the adjustments of the observables and the corrections for the initial estimates of the diffusion coefficients in such a way that

$$F^{(n)}(x_1^{(n)}, x_2^{(n)}, t^{(n)}, D_{11}, D_{12}, D_{21}, D_{22}) \approx 0 \qquad [10]$$

and $(n = 1, 2 \cdots N)$

$$L^{(n)}(y_1^{(n)}, y_2^{(n)}, t^{(n)}, D_{11}, D_{12}, D_{21}, D_{22}) \approx 0 \qquad [11]$$

in which x, y, and t are adjusted observables, and D_{ij} are the final estimates of coefficients. This adjustment is done subject to the least squares criterion that the weighted sum of squares of the residuals (observed value - adjusted value) of the observables X, Y, and T be a minimum. In these derivations, the cell constant, β, is considered as an "external parameter", that is, a quantity obtained from independent experiments and, therefore, not susceptible of adjustment. However, the error in β is taken into account in the estimation of the error bounds for D_{ij}, as explained below.

Linearization of the condition equations [8] and [9] is done about the observed points (X_1, X_2, T, D^0_{11}, D^0_{12}, D^0_{21}, D^0_{22}) and (Y_1, Y_2, T, D^0_{11}, D^0_{12}, D^0_{21}, D^0_{22}) using the best available initial estimates, D^0_{ij}, for the diffusion coefficients. A procedure to obtain good initial estimates for D_{ij} is described later.

The 2N reduced condition equations, resulting from the linearization mentioned above, may be written, in matrix notation,

$$BV + P\alpha = M \qquad [12]$$

in which B is the matrix (2N x 5N) of the derivatives of the condition functions [8] and [9] with respect to the five observables, V is the column vector (5N x 1) of the residuals, P is the matrix (2N x 4) of the derivatives of the condition functions with respect to D_{ij}, α is the column vector (4 x 1) of the corrections for the D^0_{ij} (i.e., $\alpha_{ij} = D^0_{ij} - D_{ij}$) and M is the column vector (2N x 1) of the values of the condition functions. The condition functions and their derivatives are evaluated using the experimental values of the observables and the initial estimates for the diffusion coefficients.

The sum of squares of the residuals, S^2, is given by

$$S^2 = \tilde{V}WV \qquad [13]$$

in which W is the diagonal matrix of the weights, $W_{obs.}$, for the 5N observables and the tilde represents transposition. These weights are calculated from

$$W_{obs.} = \frac{\sigma_0^2}{\sigma_{obs.}^2} \qquad [14]$$

in which $\sigma_{obs.}$ is the standard deviation for the observable in question and σ_0 is an arbitrary constant conveniently selected for calculation purposes.

Minimization of S^2 (equation [13]) subject to the conditions [12], effected by the use of a Lagrange multiplyer, Λ, and the subsequent elimination of V, results in 2N + 4 normal equations with 2N unknown λ's (the elements of column vector Λ), and four unknown α's. These equations may be written as

$$\left[\begin{array}{c|c} R & P \\ \hline \tilde{P} & O \end{array}\right] \times \left[\begin{array}{c} \Lambda \\ \hline \alpha \end{array}\right] = \left[\begin{array}{c} M \\ \hline O \end{array}\right]$$

or $\qquad [15]$

$$G \times \left[\begin{array}{c} \Lambda \\ \hline \alpha \end{array}\right] = \left[\begin{array}{c} M \\ \hline O \end{array}\right]$$

in which $R = BW^{-1}\tilde{B}$, of dimension 2N x 2N.

The solution of the above system of equations yields

$$\begin{bmatrix} \Lambda \\ \hdashline \alpha \end{bmatrix} = G^{-1} \begin{bmatrix} M \\ \hdashline 0 \end{bmatrix} \qquad [16]$$

Since G^{-1} is symmetric, like G, it can be partitioned similarly as follows:

$$G^{-1} = \left[\begin{array}{c:c} Q & H \\ \hdashline \tilde{H} & E \end{array}\right] \qquad [17]$$

Then, the solutions for Λ and α can be written as,

$$\Lambda = QM$$

$$\alpha = \tilde{H}M$$

The values thus obtained for α_{ij} can be now used to calculate new estimates of D_{ij}, since

$$D_{ij} = D^{o}_{ij} - \alpha_{ij} \qquad [18]$$

These new estimates of D_{ij} are used iteratively as initial estimates (substituting for D^{o}_{ij}) until convergence in S^2, calculated by equation [13], is obtained. At this point the final residuals are calculated from $V = W^{-1}\tilde{B}\Lambda$. The error vector Δ, (ΔD_{11}, ΔD_{12}, ΔD_{21}, ΔD_{22}), can be found[9] from the 4 x 4 error submatrix E, of G^{-1}:

$$\Delta = - \sigma_{\text{ext.}} \sqrt{E_{jj}} \qquad [19]$$

in which the standard error, $\sigma_{ext.}$, is given by $\sqrt{\{S^2/(2N-4)\}}$, 2N-4 being the degrees of freedom.

The value of the ratio $\sigma^2_{ext.}/\sigma^2_0$ is indicative of systematic errors in an experimental set of data; in the absence of systematic errors, this ratio should be about unity[10].

The errors as obtained from equation [19] do not reflect the influence of the error, σ_β, in the independently determined cell constant β. Therefore, bounds to these errors are estimated by repeating the calculations _ab initio_ using successively the values $\beta + \sigma_\beta$ and $\beta - \sigma_\beta$ for the cell constant and assigning the maximum resulting errors in the diffusion coefficients to the set of coefficients obtained without considering any error in β.

A requirement for the convergence of the iterative procedure in the calculation of D_{ij} is that the initial estimates of these parameters be close to the final estimates. Various procedures have been suggested[11,12,13] to insure convergence in problems of this nature. In this investigation it was found that, for ternary systems, good initial estimates for only two of the four coefficients are required to insure convergence, their identity being determined by the initial experimental conditions. Three cases of initial conditions are possible in a ternary system: (1) Both diffusing components have non-zero concentration gradients; (2) Component 1 has a non-zero gradient and component 2 has a zero gradient; (3) Component 2 has a non-zero gradient and component 1 has a zero gradient. The two diffusion coefficients for which good initial estimates are required in each one of the three cases are: for case (1) D_{11} and D_{22}; for case (2) D_{11} and D_{21}; and for case (3) D_{22} and D_{12}. The initial estimates for the remaining 2 coefficients in each case can be taken as zero. In the flux equations [1] the main contribution to the flux of one component is given by those terms involving the component for which there is an initial concentration gradient. Then, ignoring, as a first approximation, those terms that contribute the least to the diffusion fluxes, performing the corresponding integrations, the resulting expressions may be written in the logarithmic form,

$$\ln \frac{\Delta C_i}{\Delta C_j^\circ} = - D_{ij} \beta t \qquad \begin{matrix} i = 1, 2 \\ j = 1, 2 \end{matrix} \qquad [20]$$

which covers the three cases given above. The required initial estimates of the diffusion coefficients are then obtained by a simple linear regression using the appropriate experimental data. In this way, convergence was obtained after 4 to 6 cycles in all the cases tested.

3. TEST OF THE METHOD

The procedure was thoroughly tested by constructing artificial "experimental" data. It was considered that in these hypothetical experiments, concentrations for the two components were determined in one compartment only. Exact solutions of equations [2] were obtained for different arbitrary sets of D_{ij}, β, and initial concentration differences. The "true" points thus obtained were transformed into "experimental" observations by the use of a table of normal deviates[8], and the foregoing method was applied to these data. Thus the following factors affecting the estimated values for D_{ij} and their errors were investigated: a) fraction of the components that have diffused at end of experiment, b) errors in the observables, and c) number of time intervals at which observations are made.

An example of the effect that the fraction of component diffused has on the estimated D_{ij} and their errors is shown in Table 1. The time given at the top of each column corresponds to the longest interval in a time arrangement consisting of eight intervals, the time increment for each successive interval being one-eighth of the longest interval. Values for the per cent decrease of the initial concentration differences of components 1 and 2, R_1 and R_2, at the end of the longest interval for the particular time sequence are given in the second and third rows. For most purposes and for the selected experimental conditions, the estimated values for D_{ij} and their errors obtained from the time arrangement having a maximum interval of 96 hours are reasonably close to the "true" values. The errors in D_{ij}, however, decrease significantly by extending the maximum interval to 200 or 400 hours (although the number of observations is the same in all cases). The minimum amount of components diffused required to obtain good values for D_{ij} depends on the initial conditions, values of D_{ij} and the value of the cell constant. From the results in Table 1, and other investigated systems not reported here, we conclude that acceptable values for D_{ij} are obtained when the per cent decrease in the initial concentration difference for each component lie between 40 and 60 per cent. As might have been anticipated, the values for the ratio $\sigma^2_{\mathrm{ext.}}/\sigma^2_0$ in Table 1 are about unity since the procedure to obtain the "experimental" data involved a randomization process.

The effect of the number of intervals on the estimated values of D_{ij} is shown in Table 2. Calculations for this table were made using the same initial conditions and set of parameters used in Table 1. The longest time interval used was 200 hours. It is apparent that the values for D_{ij} become closer to the true values and their errors become significantly smaller as the number of intervals is augmented. However, a comparison of Tables 1 and 2 shows that the fraction of components diffused is a much more critical factor in the accuracy of the estimated D_{ij}.

The effect of errors in the concentration measurements on the estimated values for D_{ij} is shown in Table 3. It is apparent that with large errors in the observables, the values for D_{ij} obtained by the adjustment procedure may be very inaccurate; this situation is particularly true for the cross-term diffusion coefficients.

The adjustment procedure described in this paper was applied to the diffusion data reported by Kelly[1] for the ternary system mannitol (1) - NaCl (2) - H_2O, using the condition equations [6] and [7]. Kelly had obtained the values for D_{ij} from the results of two experimental arrangements with initial conditions given at the head of Table 6. His results and the results obtained by the present procedure are shown, side by side, in the same table.

Satisfactory agreement was obtained between the results obtained by the present procedure and those obtained by Kelly in those systems where he could calculate diffusion coefficients, with the exception of the value for D_{11} in the system 2-A. The values for D_{ij} estimated from Kelly's experimental data for system 1-A should have agreed, in theory, with those obtained from the experimental data for the system 1-B. The cause of these discrepancies is that, usually, when one of the components has zero initial concentration gradient, the amount diffused is so small that a reliable estimation of the D_{ij} is impossible (see Table 1).

The discrepancies in systems 2-A and 2-B are explained on the same basis; however, the large value for the ratio $\sigma^2_{ext}/\sigma^2_0$ for system 2-A suggests the presence of considerable systematic errors in the experimental data which cast serious doubts about the values for D_{ij} obtained from them.

Cussler and Dunlop[4] also estimated D_{ij} from Kelly's data. It is not clear in their publication whether they combined the data for systems 1-A and 1-B or estimated D_{ij} from each arrangement separately. The values they obtained are in good agreement with those obtained by the present method and reported in Table 4 with the exception of the value for D_{21} which is about 5 per cent lower than the figure reported here. Significant differences, however, do exist between the errors reported by Cussler and Dunlop and those obtained in the present investigation.

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TABLE 1

EFFECT OF THE AMOUNT OF COMPONENTS DIFFUSED ON THE ESTIMATED VALUES AND ERRORS OF THE DIFFUSION COEFFICIENTS

Longest interval, hr.	12	24	48	96	200	400	TRUE DIFF. COEFFS.
$100\,\Delta X/\Delta X°$	91.3	83.3	69.2	47.7	20.8	3.6	
$100\,\Delta Y/\Delta Y°$	95.0	90.5	82.0	67.5	44.7	21.0	
$D_{11}\mathrm{x}10^5$	2.628 ±0.562	2.184 ±0.166	1.965 ±0.068	2.035 ±0.040	2.015 ±0.015	1.999 ±0.010	2.000
$D_{12}\mathrm{x}10^5$	−0.828 ±0.923	−0.104 ±0.269	0.261 ±0.108	0.144 ±0.060	0.182 ±0.021	0.202 ±0.013	0.200
$D_{21}\mathrm{x}10^5$	0.266 ±0.187	0.176 ±0.056	0.122 ±0.023	0.115 ±0.014	0.108 ±0.005	0.101 ±0.004	0.100
$D_{22}\mathrm{x}10^5$	0.729 ±0.307	0.877 ±0.090	0.965 ±0.037	0.979 ±0.021	0.990 ±0.008	0.999 ±0.005	1.00
$\frac{\sigma^2_{ext}}{\sigma^2_{int}}$	1.21	0.81	0.74	1.02	0.49	0.43	——

Total Number of intervals: 8

Adopted errors: $E_{X,Y} = \pm\ 0.2\%$; $E_T = \pm$ 60 Sec.; $E_{\Delta X°,\,\Delta Y°} = \pm\ 0.1\%$; $E_\beta = \pm\ 0.1\%$

TABLE 2

EFFECT OF NUMBER OF INTERVALS ON THE ESTIMATED VALUES AND ERRORS OF THE DIFFUSION COEFFICIENTS

Number of intervals	3	4	5	6	7	8	TRUE DIFF. COEFFS.
$D_{11} \times 10^5$	1.970 ±0.035	1.970 ±0.037	1.997 ±0.032	2.016 ±0.021	1.988 ±0.018	2.015 ±0.015	2.000
$D_{12} \times 10^5$	0.229 ±0.047	0.249 ±0.051	0.203 ±0.045	0.178 ±0.029	0.214 ±0.025	0.182 ±0.021	0.200
$D_{21} \times 10^5$	0.102 ±0.012	0.094 ±0.013	0.104 ±0.011	0.116 ±0.007	0.104 ±0.006	0.108 ±0.005	0.100
$D_{22} \times 10^5$	0.998 ±0.017	1.009 ±0.018	0.993 ±0.016	0.978 ±0.010	0.994 ±0.006	0.990 ±0.008	1.00
$\frac{\sigma^2_{ext}}{\sigma^2_{int}}$	0.79	1.36	1.33	0.65	0.59	0.49	———

Longest interval: 200 hr.

Adopted errors: $E_{X,Y} = \pm 0.2\%$; $E_T = \pm 60$ Sec.; $E_{\Delta X°, \Delta Y°} = \pm 0.1\%$; $E_{\beta} = \pm 0.1\%$

TABLE 3

EFFECT OF ERRORS IN OBSERVABLES ON THE ESTIMATED VALUES AND ERRORS OF THE DIFFUSION COEFFICIENTS

$E_{X,Y}$	2.0%	0.2%	0.02%	TRUE DIFF. COEFFS.
$D_{11} \times 10^5$	2.487 ±0.291	2.015 ±0.015	1.999 ±0.004	2.000
$D_{12} \times 10^5$	-0.532 ±0.411	0.182 ±0.021	0.202 ±0.006	0.200
$D_{21} \times 10^5$	0.047 ±0.097	0.108 ±0.005	0.099 ±0.002	0.100
$D_{22} \times 10^5$	1.081 ±0.138	0.990 ±0.008	1.001 ±0.002	1.000
$\frac{\sigma^2_{ext}}{\sigma^2_{int}}$	1.47	0.49	2.02	———

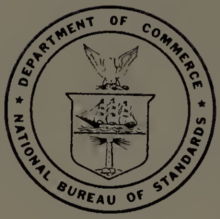
Total Number of intervals: 8; Longest interval: 200 hr.
Fixed Errors: $E_{\Delta X^\circ, \Delta Y^\circ} = \pm 0.1\%$; $E_\beta = \pm 0.1\%$; $E_T = \pm 60$ Sec.

TABLE 4

COMPARISON OF KELLY'S ESTIMATED VALUES OF THE DIFFUSION COEFFICIENTS WITH THOSE ESTIMATED BY THE PRESENT PROCEDURE USING KELLY'S EXPERIMENTAL DATA FOR THE SYSTEM MANNITOL (X) - NaCl (Y)-H

Average conc.	$\overline{X} = 0.2M$; $\overline{Y} = 1.5M$				$\overline{X} = 0.2M$; $\overline{Y} = 3.0M$			
Initial conditions	$\Delta X° = 0.4$ $\Delta Y° = 0.0$		$\Delta X° = 0.0$ $\Delta Y° = 0.5$		$\Delta X° = 0.4$ $\Delta Y° = 0.0$		$\Delta X° = 0.0$ $\Delta Y° = 1.0$	
System	1 - A 5 intervals		1 - B 4 intervals		2 - A 6 intervals		2 - B 3 intervals	
	This paper	Kelly's thesis	This paper	Kelly's thesis	This paper	Kelly's thesis	This paper	Kelly's thesis
$D_{11} x10^5$	0.557 ±0.002	0.559 ±0.004	1.129 ±0.235	———	1.010 ±0.014	0.448 ±0.006	0.410 ±0.597	———
$D_{12} x10^5$	0.027 ±0.036	———	0.018 ±0.001	0.016 ±0.010	0.524 ±0.064	———	0.013 ±0.002	0.013 ±0.008
$D_{21} x10^5$	0.232 ±0.015	0.232 ±0.001	0.139 ±1.848	———	0.499 ±0.072	0.456 ±0.003	0.008 ±9.734	———
$D_{22} x10^5$	1.557 ±0.219	———	1.388 ±0.011	1.390 ±0.002	1.147 ±0.293	———	1.469 ±0.042	1.469 ±0.003
$\frac{\sigma^2_{ext}}{\sigma^2_{int}}$	5.21	———	4.39	———	171.75	———	39.39	———

$E_{\Delta X°, \Delta Y°} = \pm 0.02\%$; $E_{X,Y} = \pm 0.02\%$; $E_T = \pm 60$ Sec.; $E_{\beta} = \pm 0.1\%$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