Diffusion or Ion Exchange with Variable Diffusion Coefficient. Calculation of Rates and Concentration Profiles

FRIEDRICH HELFFERICH
Shell Development Company, Emeryville, California

Numerical solutions of the diffusion equation

$$\frac{\partial C}{\partial t} = \text{div}\,(D \text{ grad } C) \qquad (1)$$

with concentration-dependent diffusion coefficient of the form

$$D(C) = \frac{D_o}{1 + a\,C/C^o} \qquad (2)$$

with values of a as listed in Table 1 have been calculated for spheres and finite slabs with the initial and boundary conditions

sphere:

$$\begin{array}{lll} t = 0, & 0 \leqq r < r_o, & C = C^o \\ t \geqq 0, & r = r_o, & C = 0 \qquad (3) \end{array}$$

slab:

$$\begin{array}{lll} t = 0, & 0 < x \leqq d, & C = C^o \\ t \geqq 0, & x = 0, & C = 0 \qquad (4) \end{array}$$

Tables of the concentration profiles $C(r, t)$ [or $C(x, t)$], the amounts $Q(t)$ in the sphere or slab, and the effusion rates $dQ(t)/dt$ are available.[*]

Within the limits of validity of the Nernst-Planck model for binary ion exchange (*1*) the tables also describe exchange of two counterions A and B of equal valence and with mobility ratios D_A/D_B as listed in Table 1. Furthermore, by simple transformations of variables (*1, 2*) the tables can be used for initial and boundary conditions other than (3) and (4), provided that the boundary condition is constant and the initial distribution within the sphere or slab is uniform.

The tables were calculated on an IBM 7090 computer with a Fortran II program now available through the IBM SHARE organization (*3*). This program is restricted to one concentration variable and one space coordinate and thus is applicable only to one-component diffusion or coupled binary interdiffusion as in ion exchange and to unidimensional diffusion (slabs, membranes, etc.) or systems with cylindrical or spherical symmetry. Otherwise, the program is general in that any initial and boundary conditions and any dependence of the diffusion coefficient on concentration, time, location, and concentration gradient can be specified and that the differential equation (1) can be modified, for example, by addition of terms for sources, sinks, and convection.

TABLE 1. PARAMETER VALUES

Diffusion	$a =$	(49), (19), 9, 4, 1, −0.5, −0.8, −0.9, (−0.95), (−0.98)
Ion exchange	$D_A/D_B =$	(50), (20), 10, 5, 2, 1/2, 1/5, 1/10, (1/20), (1/50)

(Calculations with values in brackets were carried out for spheres only.)

NOTATION

a = constant parameter, dimensionless
C = concentration of diffusing species, mmoles/ml.
C^o = initial concentration of diffusing species in medium, m-moles/ml.
d = thickness of finite slab, cm.
D = diffusion coefficient, sq. cm./sec.
D_o = diffusion coefficient at vanishing concentration, sq. cm./sec.
Q = amount of diffusing species in medium, m-moles
r = distance from center of sphere, cm.
r_o = radius of sphere, cm.
t = time, sec.
x = distance from boundary of slab, cm.

LITERATURE CITED

1. Helfferich, Friedrich, and M. S. Plesset, *J. Chem. Phys.*, **28**, 418 (1958).
2. Helfferich, Friedrich, *J. Polymer Sci.*, **B1**, 87 (1963).
3. Helfferich, Friedrich, "Diffusion With Variable Diffusion Coefficient," Program No. 3187, IBM SHARE Distribution Agency, White Plains, N. Y. (1964).

---

[*] Tabular material has been deposited as document 8210 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $68.75 for photoprints or $21.50 for 35-mm. microfilm.

A Derivation of the Riccati Difference Equation for Ternary Extraction Systems

R. R. DAVISON and W. D. HARRIS
Texas A&M University, College Station, Texas

Finite difference solutions were recently (*1*) obtained for stage-by-stage mass transfer processes in which the equilibrium relation and the quantity of each phase were allowed to vary with concentrations. The same problem was solved several years ago with almost identical results (*2*), but the formulation was somewhat different, and a comparison should be interesting. Solvent extraction will be used in this discussion, but the methods are applicable to other operations, such as distillation with variable overflow.

In each analysis the assumption was made that segments of the mutual solubility curves could be represented by straight lines. Martin (*1*) assumed that the equilibrium concentrations could be expressed by

$$y = \frac{\alpha x + \gamma}{1 - \beta x} \qquad (1)$$

in which α, γ, and β are constants. The assumption made in this development was that equilibrium could be expressed by

$$y = \frac{x}{K_1 + K_2 x} \qquad (2)$$

In handling the linear solubility curves, Martin assumed that

$$Z_B = m_B x + b_B \qquad (3)$$

$$Z_A = m_A y + b_A \qquad (4)$$

in which m_B, b_B, m_A, and b_A are constants.

These two equations and Equation (1) were combined with material balances on both components C and B in Martin's derivation to obtain the Riccati difference equation.

An alternative procedure consists in transforming the system into a simpler one requiring only one material balance For countercurrent extraction, a material balance yields

$$E_{n+1}x_{n+1} - R_n y_n = E_1 x_1 - F y_F = S x_S - R_N y_N \qquad (5)$$

Neither E_{n+1} nor R_n is constant, and they must be expressed as functions of concentration. For both the A-rich and B-rich phase (Figure 1) it is assumed that Z, the concentration of component B, varies linearly with the concentration of component C, the solute. If the quantity of component B were constant in the B-rich phase, that is insoluble in the A phase, the quantity of extract would be given by $E_{n+1} = \dfrac{SZ_S}{Z_{Bn+1}}$, and then from a material balance

$$R_n = F - E_1 + E_{n+1} = F - E_1 + \frac{SZ_S}{Z_{Bn+1}} \qquad (6)$$

Of course, the quantity of B in the B-rich phase is not equal to SZ_S except in the entering solvent stream, but any system can be transformed into one for which a calculated quantity SZ'_S remains constant. This is accomplished by the manipulation shown in Figure 1. The axis is translated a distance Z_{AI} and rotated through an angle θ by

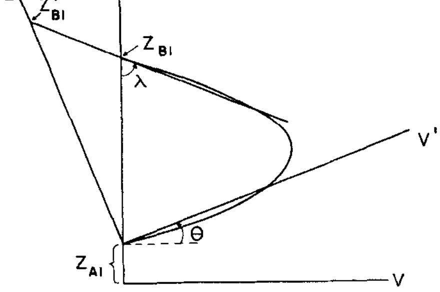

Fig. 1. Transformation of coordinates.

$$Z' = (Z - Z_{AI})\cos\theta - V\sin\theta \qquad (7)$$

$$V' = V\cos\theta + (Z - Z_{AI})\sin\theta \qquad (8)$$

in which V is either x or y. The material balance for this system becomes

$$E_{n+1}x'_{n+1} - R_n y'_n = E_1 x'_1 - F y'_F = S x'_S - R_N y'_N \equiv \Delta \qquad (9)$$

For the transformed system

$$E_{n+1} = SZ'_S / Z'_{Bn+1} \qquad (10)$$

If L is defined as $\cot(\lambda - \theta)$ and Z'_{BI} is the intercept of the B-phase line with the Z' axis, then

$$Z'_{Bn+1} = Z'_{BI} - L x'_{n+1} \qquad (11)$$

Substituting (11) into (10) one gets

$$E_{n+1} = SZ'_S / (Z'_{BI} - L x'_{n+1}) \qquad (12)$$

and from a material balance

$$R_n = F - E_1 + \frac{SZ'_S}{Z'_{BI} - L x'_{n+1}} \qquad (13)$$

If Equations (7) and (8) are applied to Equation (2), one obtains

$$y' = \frac{ax' - b}{cx' + d} \qquad (14)$$

in which

$$a = \cos\theta + L\sin\theta \qquad (14a)$$

$$b = Z'_{BI}\sin\theta \qquad (14b)$$

$$c = aK_2\cos\theta \qquad (14c)$$

$$d = \cos\theta\,(K_1 - K_2 Z'_{BI}\sin\theta) \qquad (14d)$$

Substituting Equations (12, (13), and (14) into (9) one obtains

$$A_1 x'_{n+1} + A_2 x'_n x'_{n+1} + A_3 x'_n + A_4 = 0 \qquad (15)$$

in which

$$A_1 = [SZ'_S d - (F - E_1)\,Lb + \Delta Ld]$$

$$A_2 = [SZ'_S c + (F - E_1)\,La + \Delta Lc] \qquad (15a)$$

$$A_3 = -[SZ'_S a + (F - E_1)Z'_{BI}a + \Delta Z'_{BI}c]$$

$$A_4 = [SZ'_S b + (F - E_1)\,Z'_{BI}b - \Delta Z'_{BI}d]$$

If the material balance is made on y, the concentration in the A phase, an equation identical to (15) is obtained with y's in place of x's and in which

$$A_1 = [SZ'_S d + \Delta(Z'_{BI}c + Ld)]$$

$$A_2 = [SZ'_S c + (F - E_1)(Z'_{BI}c + Ld)]$$

$$A_3 = -[SZ'_S a + (F - E_1)(Z'_{BI}a - Lb)]$$

$$A_4 = [SZ'_S b - \Delta(Z'_{BI}a - Lb)] \qquad (15b)$$

Equation (15) is the Riccati difference equation.

These results are identical to those obtained by Martin except that two constants instead of three are used in the equilibrium relation and the solubility lines are defined by two angles and two intercepts instead of two slopes and two intercepts. Martin discussed methods for solving the equation and the applications of the solutions obtained.

NOTATION

A = component A
A_1, A_2, A_3, A_4 = coefficients of the Riccati difference equation
a = a constant in the transformed equilibrium relation
B = component B, the major constituent of the solvent
b = constant in the transformed equilibrium relation
C = component C, the solute
c = constant in the transformed equilibrium relation
d = constant in the transformed equilibrium relation
E = extract, refers to B-rich phase
F = feed, refers to A-rich phase
K_1, K_2 = constants in the equilibrium equation
L = slope of the B-rich solubility line after rotation of the axis
R = raffinate, refers to A-rich phase
S = solvent
V = the concentration of component C in either phase, that is the abscissa on a two coordinate phase diagram
x = the concentration of component C in the B-rich phase
y = the concentration of component C in the A-rich phase
Z = the concentration of component B in either phase, that is the ordinate on a two coordinate phase diagram
Δ = constant defined by Equation (9)
θ = angle formed by the A-rich phase line and the ordinate
λ = angle formed by the B-rich phase line and the ordinate

Subscripts

A = A-rich phase
B = B-rich phase
F = feed
I = intercept
n = the nth stage
N = the Nth or last stage
R = raffinate
S = solvent
1 = the first stage

Superscripts

$'$ = values in the transformed system

LITERATURE CITED

1. Martin, J. J., *A.I.Ch.E. Journal*, 9, 646 (1963).
2. Davison, R. R., M.S. thesis, Texas A&M University, College Station, Texas (1958).