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

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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

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

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

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

slab:

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

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° = 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).

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* 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

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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