Determination of Diffusion Coefficients Using the Stefan Cell

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The present study shows how interface-time data collected in a Stefan cell can be used to determine diffusivities for phase changes with a moving interface. The analysis used considers systems with varying or constant transport area and constant or concentration dependent diffusivities. Extension of standard methods is made to account more completely for the flux of components across the phase boundary.

THEORY

Consider a finite Stefan cell containing two separate phases separated by a sharp interface. Each phase contains two components A and B, and one of the phases (2) will be presumed to be insoluble in the other (1). Because either saturated *A* or pure *A* alone is presumed to exist below the interface, the concentration of *A* present just on the other side of the interface in phase 2 will remain constant at its equilibrium value C^*_{A2}. Phase 1 is a saturated solution of *B* in *A*. Examples (*A*/*B*) might include a liquid saturated with a gas (oxygen/water), a liquid saturated with another liquid (water/methyl-ethyl-ketone), a salt slurry (potassium chloride/water), or a solid cake of salt (potassium chloride).

As the transfer of *A* from the *A* rich (1) to the *B* rich (2) phase proceeds, the interface will slowly retreat. Interface level-time data (z_i, t) can be collected optically or electronically.

The *A* flux equation can be written for any position within the transfer phase (2) as (Ghai et al., 1973)

$$N_A = -D_{AB}\nabla C_A \Bigg/ \left[1 - C_A\left(\tilde{V}_A + \tilde{V}_B\frac{N_B}{N_A}\right)\right] \tag{1}$$

For binary gas systems, it is more convenient to use the equivalent form

$$N_A = -D_{AB}\nabla X_A \Bigg/ \left[1 - X_A\left(1 + \frac{N_B}{N_A}\right)\right] \tag{2}$$

For nonideal solutions, D_{AB} is a function of concentration.

With the exception of the analysis of Schwertz and Brow (1951), previous development have been based on the quasi steady state assumption that no accumulation of components occurs in the transfer phase. In such cases, the molar flow rates of *A* and *B* are constants, or

$$SN_j = S_i N_{ji} \tag{3}$$

The present analysis is based on a refinement of this equation which allows for component accumulation without the necessity of using partial differential equations to account for it.

For one-dimensional transfer with equilibria presumed at the interface, Equation (1) can be integrated to give

$$-SN_A = \frac{\displaystyle\int_{C_{Ao}}^{C^*_{A2}} \frac{D_{AB}dC_A}{1 - C_A\left[\tilde{V}_A + \tilde{V}_B\left(\frac{N_B}{N_A}\right)\right]}}{\displaystyle\int_0^{z_i}\frac{dz}{S(z)}} \tag{4}$$

On the assumption of quasi steady state, the flux ratio N_B/N_A is determined from its interfacial value according to Equation (3). Using the fact that at the interface the fluxes are of the form

$$-N_{ji} = C^*_{j1}\frac{dz_i}{dt} \tag{5}$$

we get

$$\frac{N_B}{N_A} = \frac{C^*_{B2} - C^*_{B1}}{C^*_{A2} - C^*_{A1}} \equiv \beta^* \tag{6}$$

It is seen that the flux ratio (defined as β^*) is a form of equilibrium distribution coefficient between phases, which is a constant for fixed temperature and total pressure. For the subcase, when *B* is insoluble in phase 1, β^* becomes equal to $-(C^*_2 - C^*_{A2}/(\rho_A - C^*_{A2})$. In previous studies (Pommersheim, 1971; Pommersheim and Ranck, 1973), no account was taken of the factor β^*. Integrating Equation (4), we get

$$t = (C^*_{A1} - C^*_{A2})\int_{z_1}^{z_i}\frac{S(\lambda)}{\alpha(\lambda)}\int_0^{\lambda}\frac{d\xi}{S(\xi)}\,d\lambda \tag{7}$$

where

$$\alpha(z) \equiv D_{\text{int}}(C^*_{A2} - C_{Ao}) = \int_{C_{Ao}(z)}^{C^*_{A2}}\frac{D_{AB}dC_A}{1 - [\tilde{V}_A + \beta^*\tilde{V}_B]C_A} \tag{8}$$

D_{int}, as defined by Equation (8), represents a corrected integral diffusivity. The term in the denominator of the integrand in Equation (8) corrects for solution nonideality. For ideal liquid solutions, D_{int} becomes equal to the regular value of the integral diffusivity (Stokes, 1951).

Nonconstant transport area cases of practical interest include both cylindrical and spherical geometries. For the most common subcase of constant cell transport area, Equation (7) becomes

$$t = (C^*_{A1} - C^*_{A2})\int_{z_1}^{z_i}\frac{\lambda d\lambda}{\alpha(\lambda)} \tag{9}$$

APPLICATION TO IDEAL FLUID SYSTEMS

For the condition where *B* is an ideal gas which is insoluble in liquid *A*, Equations (7) and (8) yield

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$$t = \frac{1}{D^{id}_{AB} P} \int_{z_1}^{z_t} \frac{(\rho RT - P)\, S(\lambda)}{\ln \left[\dfrac{P - \left(\dfrac{\rho RT - P}{\rho RT - P^*_A} \right) P_{Ao}}{P - \left(\dfrac{\rho RT - P}{\rho RT - P^*_A} \right) P^*_A} \right]} \int_0^{\lambda} \frac{d\xi}{S(\xi)}\, d\lambda \quad (10)$$

This reduces to the result derived by Pommersheim (1971) for $\rho RT/P >> 1$, a condition which obtains for most ideal gas situations.

When both phases are ideal liquids, the reciprocals of the partial molal volumes will equal the molar densities of the pure components. For this situation, the coefficient $(\tilde{V}_A + \beta^* \tilde{V}_B)$ becomes identically zero, and Equation (8) simplifies to

$$\alpha(z) = \int_{C_{Ao}(z)}^{C^*_{A2}} D^{id}_{AB}\, dC_A = \overline{D}^{id}_{AB} [C^*_{A2} - C_{Ao}(z)] \quad (11)$$

The activity coefficients of A and B will be unity so that the diffusivity can be set equal to its mean ideal value. Equation (11) defines the integral diffusivity for an ideal liquid-liquid system.

DETERMINATION OF INTEGRAL DIFFUSIVITY D_{int}

D_{int}, the diffusivity defined by Equation (8), can be determined from suitable component data. As an illustration, consider the system potassium chloride (*s*)-water at 25°C. For this system, Vaslow (1966) presents the relation

$$\phi = 26.886 + \int_0^{C_A^{1/2}} \left[1.873 + \frac{0.518x^4}{x^4 + 0.9^4} \right] dx \quad (12)$$

as a statistically adequate representation of the apparent molal volume. Partial molal volumes are computed from the relations (Harned and Owen, 1958)

$$\tilde{V}_A = \phi + \left[\frac{1\,000 - C_A \phi}{2\,000 + C_A^{3/2} \dfrac{d\phi}{dC_A^{1/2}}} \right] C_A^{1/2} \frac{d\phi}{dC_A^{1/2}} \quad (13)$$

and

$$\frac{\tilde{V}_B}{\tilde{V}_B{}^o} = \left[1 + \frac{C_A^{3/2}}{2\,000} \frac{d\phi}{dC_A^{1/2}} \right]^{-1} \quad (14)$$

The derivative $d\phi/dC_A^{1/2}$ is evaluated from Equation (12).

The diffusivity-concentration relation was established by curve fitting the published data of differential diffusion coefficient given separately by Gosting (1950), Harned and Nuttal (1949), and Stokes (1951) to an empirical curve of minimum variance using a nonlinear least squares routine (Greene, 1970).

The equation chosen was of the form

$$D_{AB} \times 10^5 = a + bC_A + \frac{c}{d + C_A} + eC_A^{1/2} \quad (15)$$

The data fit is shown in Figure 1. All data were within 0.02×10^{-5} cm²/s of the curve.

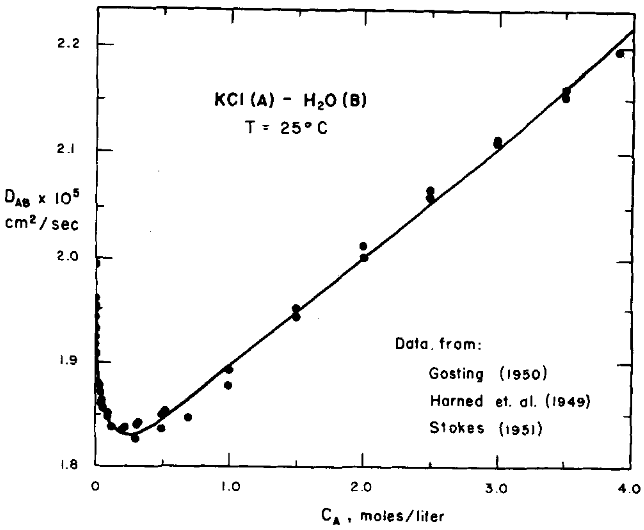

Fig. 1. Diffusivity as a function of concentration for potassium chloride-water at 25°C.

When we used the equations of this section along with Equation (8), D_{int} was calculated to be 1.964×10^{-5} cm²/s. The integration limits on Equation (8) were 0 to 4.171 moles/l (saturation). (The regular integral diffusivity is 2.013×10^{-5} cm²/s.) If the denominator of the integrand of Equation (8) is taken equal to its average value, the integral diffusivity which results is almost equal to the theoretical value. To test the value of D_{int}, experiments were conducted [Kenner (1973] in an open Stefan cell by the method of Greskovich et al. (1975). These authors obtained diffusivities for potassium chloride transferring at 25°C through porous nonsorbing media. In the present study, no hindering media were used. Diffusivities D_{int} of 1.87, 1.71, 2.22, and 1.99 $\times 10^{-5}$ cm²/s were found, with an average experimental value of 1.944×10^{-5} cm²/s. The theoretical value agrees well with this experimental average. It should be noted here that the hindrance factors reported by Greskovich et al. (1975) are based on this average.

CONCLUSIONS

The quasi steady state analysis developed here shows how interface-time data collected in a finite Stefan cell containing two insoluble phases can be used to predict diffusivities. Both variable and constant transport area are considered. From the methods of Greskovich et al. (1975), application was made to potassium chloride diffusing through water in an open system of constant transport area. For four runs, the average corrected integral diffusivity of potassium chloride at 25°C agreed with the value calculated from the literature.

It should be noted that the Stefan cell with a finite closed external volume is capable of yielding the variation of the diffusion coefficient with concentration, provided some component partial molal volume data are available. A simple extension of the theory presented here can be made to treat this case.

Although the finite Stefan cell with a moving phase boundary has certain inherent disadvantages, it does have a number of advantages over other cells now in use. Its use can be recommended as a viable alternative, especially when diffusion coefficients near saturation need to be measured, a situation which is of concern in contacting equipment. The absolute method presented here can serve as a standard for the measurement of hindered diffusivities through porous media.

ACKNOWLEDGMENT

The authors are grateful for helpful discussions with John C. Cooper of the Department of Chemistry, as well as to Frank W. Koko, David L. Koeberlein, and Jesse Van Kirk of the department for their computational assistance. The financial support of the National Science Foundation under Grant GK-32871 and the use of the facilities at the Bucknell University Computer Center are also gratefully acknowledged.

NOTATION

A, B = transferred components
C = total concentration, moles/cm^3
C_j = concentration of j (A or B) moles j/cm^3 (or 1)
C^*_j = equilibrium value of C_j
C_{jk} = concentration of component j in phase k
C^*_{jk} = equilibrium value of C_{jk}
$\overline{C}_{jk}$ = mean concentration of j in phase k
C_{jo} = concentration of j at cell top
D_{AB} = molecular diffusivity of A in B, cm^2/s
D^{id}_{AB} = value of D_{AB} for an ideal solution
$\overline{D}^{id}_{AB}$ = mean value of D^{id}_{AB}, defined by Equation (12)
D_{int} = corrected integral diffusivity, defined by Equation (8)
N_i = interfacial molar flux, moles/cm^2, s
N_j = molar flux of j (A or B)
N_{jk} = molar flux of j in phase k
P = total pressure, atm
P^*_A = vapor pressure of A
P_{Ao} = partial pressure of A at $z = 0$
R = universal gas constant
S_i = interfacial transport area, cm^2
t = time, s
T = temperature, °K
$\tilde{V}_{jk}$ = partial molal volume of component j in phase k, cm^3/mole
X_j = mole fraction of j
X^*_j = equilibrium value of X_j
z = diffusion depth (in phase 2), measured from cell top, cm
z_i = interface depth
z_1 = initial interface depth

Greek Letters

α = integral defined by Equation (8), moles/cm, s
β^* = equilibrium distribution coefficient, defined by Equation (6)
ρ_j = molar density of component j, moles j/cm^3 of j
λ, ξ = dummy variables of integration
∇ = gradient, cm^{-1}

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Manuscript received June 24 and accepted July 19, 1976.

Steady State Predictions for Nonequilibrium Parametric Pumps

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Recently, Foo and Rice (1975) presented an analysis of the ultimate separation obtainable in closed parapumps using linear adsorption equilibria along with the dissipative forces associated with axial dispersion, film resistance, and pore diffusion. The general theory was based on the experimental observation that the time-average flux (solute pumping rate) tends to zero for large times. In closed parapump systems, there is an additional constraint associated with the fact that total solute in the system is constant. In the present report, it is shown under what conditions the zero flux condition provide admissible solutions to the quasi steady (ultimate separation) transport equations.

Particular attention is focused on the value of initial feed composition which admits physically realizable separation factors using the previous (Foo and Rice, 1975) zero-flux theory. The previous work is extended to include a more general temperature dependence in the linear isotherm. Finally, the effects of reservoir dead volume are accounted for in the coupling of the zero-flux and constant mass equations.

ANALYSIS

The analysis proceeds exactly as given previously for the simple binary system except for the introduction of an