An Engineering Approach to an Unsolved Problem in Multicomponent Diffusion

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Both practical and conceptual problems arise in standard theories of multicomponent diffusion. They include the sometimes arbitrary and even artificial selection of one component as the solvent, the lack of explicit dependence on the properties of the solvent, and the difficulty in formulating compositionally dependent diffusion coefficients that satisfy material-balance constraints. Two alternative approaches based on tracer diffusion coefficients for various components are physically reasonable and overcome these difficulties. Both approaches predict cross-diffusion, that is, diffusion of component A as a result of a gradient in component B. Either approach can be used in systems where component diffusivities differ greatly in magnitude and where the number of chemical species is large, as in polymerizations.

Introduction

At a fine scale of scrutiny, the last step in any mixing process is molecular diffusion, and this step may be rate limiting, particularly in laminar flow processes. The standard formulations for multicomponent diffusion (Stefan-Maxwell, Fickian, Onsager) treat a system of N components by using $N-1$ diffusion equations and one material balance. The $N-1$-by-$N-1$ matrix of diffusion coefficients is generally asymmetric and the coefficients generally depend on composition. Except for ideal gas mixtures, there is no accepted way of estimating these coefficients other than by exhaustive experimentation. The approach typically used for multicomponent liquid systems is to set the principal (diagonal) coefficients equal to self-diffusion coefficients as measured say by spin-echo NMR and to set the cross-diffusion coefficients to zero. This approach is adequate when the various components have similar diffusivities or when there is one dominant component, the ‘‘solvent.’’ However, it becomes problematic when the diagonal coefficients differ substantially in magnitude, say, by a factor or 4 or more. The assumption of constant coefficients and, indeed, anything but an exquisitely formulated compositional dependence can lead to nonphysical results where, for example, the Nth, balancing component has a negative concentration. The problem is particularly severe in polymer systems where there may be no dominant component and where diffusivities can vary by many orders of magnitude.

We give two methods for resolving this problem by using N diffusion equations that are constructed to automatically satisfy the material-balance constraint. The necessary input data are a set of N diffusion coefficients, nominally the tracer diffusion coefficients of each component in the total mixture. Unlike the standard treatments, where the various diffusion coefficients must necessarily depend on concentration, the diffusion coefficients used in these methods can be, but need not be, independent of concentration and still satisfy the material-balance constraint. Thus, a realistic diffusion problem can be specified using a minimum of data that can be determined either experimentally or theoretically, say by reptation theory (Daoud and De Gennes, 1979) in the case of polymers. Our formulations reduce to the normal result for binary diffusion and for various limiting cases of multicomponent diffusion. Both formulations predict cross-diffusion, but differ in the extent of cross-diffusion. This may ultimately provide a basis for choosing between them.

Conventional Treatment

The standard generalization of Fick's first law is

$$J_i = -\sum_{j=1}^{N-1} D_{ij} \nabla C_j, \tag{1}$$

where J is the flux, the C_j are the component concentrations, and the D_{ij} are elements of an $N-1$ by $N-1$ matrix of diffusivities. The species continuity equations are

$$\frac{\partial C_i}{\partial t} = -\nabla J_i = \nabla \sum_{j=1}^{N-1} D_{ij} \nabla C_j. \tag{2}$$

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One component is arbitrarily designated the balancing component or solvent, and so is designated as component N. Its concentration is calculated from

$$C_N = \rho - \sum_{i=1}^{N-1} C_i, \tag{3}$$

where ρ is the total molar density. If constant, this density can be used to normalize the component concentrations so that they become mole fractions. In some applications the appropriate assumption will be constant mass density or constant volume, and the normalized concentrations will be mass fractions or volume fractions rather than mole fractions.

The fact that Eq. 3 can predict negative concentrations has been largely ignored in the literature, although necessary conditions on the compositional dependence of the diffusion coefficients have been stated (Shuck and Toor, 1963). It appears that these conditions are not sufficient to avoid negative concentrations. Typical literature examples of multicomponent diffusion use a dominant component as the Nth balancing component. This approach facilitates the use of constant diffusivities in the solutions of Eqs. 2 and 3 while giving physically reasonable results (Tyrrel and Harris, 1984). Alternatively, if the diffusivities are sufficiently close in magnitude, the situation of negative C_N does not arise. However, real systems and particularly polymer systems can exhibit diagonal coefficients that differ by many orders of magnitude and that can lead to negative predictions for C_N. In gaseous mixtures, large differences in diffusivity (such as helium vs. nitrogen) can lead to local pressure differences and variations in the molar density; but we are primarily concerned with less severe changes and with liquid systems where an assumption of constant mass density may be reasonable.

Negative predictions for C_N are a common occurrence when constant diffusivities are assumed. Choosing another component as the balancing component does not solve the problem if the original values for $D_{ij,}$ $i < N$, $j < N$ are unchanged. Negative values for C_N are caused by cross-diffusion. Cross-diffusion of the balancing component is an inevitable mathematical consequence of the standard formulation of multicomponent systems whenever the diagonal diffusivities, D_{ii}, differ in magnitude. Because of this cross-diffusion, some physically possible choices of initial conditions will give negative values for C_N.

Cross-Diffusion and Negative Concentrations

The choice of the balancing component can have a major effect on the matrix of coefficients, even causing the main-line coefficients to be negative in certain cases (Miller, 1986). The purpose of this section is to illustrate the near inevitability of cross-diffusion and its effects on calculated concentrations. Consider ternary diffusion, with independent components A and B and dependent or balancing component C having mass or volume fractions of a, b, and c. The flux equations based on concentration gradients are

$$-\begin{pmatrix} J_A \\ J_B \end{pmatrix} = \begin{pmatrix} D_{AA} & D_{AB} \\ D_{BA} & D_{BB} \end{pmatrix} \begin{pmatrix} \nabla a \\ \nabla b \end{pmatrix} = M_{AB} \begin{pmatrix} \nabla a \\ \nabla b \end{pmatrix}, \tag{4}$$

where the notation M_{AB} indicates the choice of independent component concentrations. This choice is arbitrary, however, and component C could equally well have been chosen as one of the independent component. Using Eq. 3 to replace B with C gives

$$-\begin{pmatrix} J_A \\ J_C \end{pmatrix} = \begin{pmatrix} D_{AA} - D_{AB} & -D_{AB} \\ -D_{AA} - D_{BA} + D_{AB} + D_{BB} & D_{AB} + D_{BB} \end{pmatrix} \begin{pmatrix} \nabla a \\ \nabla c \end{pmatrix} = M_{AC} \begin{pmatrix} \nabla a \\ \nabla c \end{pmatrix}. \tag{5}$$

A similar result for M_{BC} is obtained by interchanging subscripts. It is clear that the off-diagonal elements, which correspond to cross-diffusion of C, will usually be different from zero, even when the original M_{AB} is diagonal. At least one component of a ternary mixture will exhibit cross-diffusion except for the trivial case where $D_{AA} = D_{BB}$ and $D_{AB} = D_{BA} = 0$. Furthermore, the magnitude of the cross-diffusion coefficients can be quite large. If $D_{AA} \gg D_{BB}$ and $D_{AB} \sim D_{BA}$, one of the cross-diffusion coefficients will be similar in magnitude to D_{AA}.

Consider ternary diffusion with constant diffusivities of $D_{AA} = 1$, $D_{BB} = 0.25$, $D_{AB} = D_{BA} = 0$. Suppose initial conditions of $a = 0.7$, $b = 0.1$, $c = 0.2$ for $x < L/2$; $a = 0.1$, $b = 0.7$, $c = 0.2$ for $x > L/2$. Then the concentration of component C shows a substantial deviation from its initial value of 0.2, and for this example, achieves a maximum value of 0.38 before returning to its steady-state value, which is again 0.2. Figure 1 illustrates the solution at the time that $c(x)$ achieves its maximum. Note that the maximum occurs at $x = 0$. Some cross-diffusion is intuitively reasonable and has been experimentally verified (Dunlop and Gosting, 1955). However, the standard case with constant diagonal coefficients overestimates the extent of cross-diffusion. It is the overestimation that can violate the material-balance constraint. This particular simulation does not give negative values for c, but negative values are observed if the initial conditions are changed to $a = 0.8$, $b = 0.1$, $c = 0.1$ for $x < L/2$; $a = 0.1$; $b = 0.8$, $c = 0.1$ for $x > L/2$.

A second example using constant diffusivities is an analytical solution for ternary diffusion due to Cussler (1997). It represents a semi-infinite domain being brought into contact

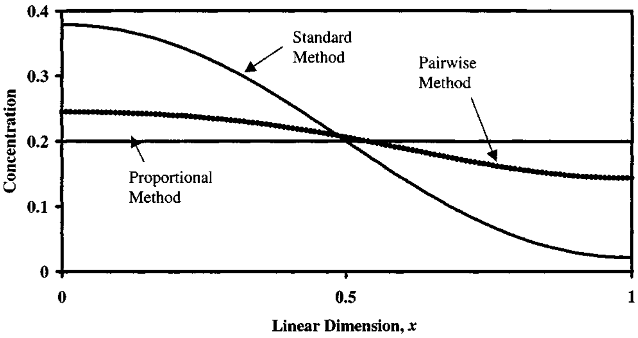

Figure 1. Concentration of the balancing component at the time for maximum deviation from $c = 0.2$ as calculated by the standard method.

with a source plane of fixed composition. Suppose $D_{AA} = 1$, $D_{BB} = 0.25$, $D_{AB} = D_{BA} = 0$. Suppose further that the source plane has the fixed values $a = 0.8$, $b = 0.1$, $c = 0.1$, and that the semi-infinite domain has initial concentrations, $a = 0.1$, $b = 0.8$, $c = 0.1$. Then $c = 1 - a - b$ becomes negative near the source plane at small values of time.

It is properly argued that such nonphysical results are due to the assumption of constant diffusivities when in fact the diffusivities must be functions of composition. These functions have been reported for ternary, ideal gas mixtures (Cussler, 1997; Toor, 1964). The compositionally dependent ternary coefficients depend on the binary coefficients that presumably can be constant. However, Cussler's results for the ternary coefficients are not immune to the problem of negative concentrations. For example, suppose the binary coefficients have constant values of $\mathfrak{D}_{AB} = 1$, $\mathfrak{D}_{AC} = 0.25$, $\mathfrak{D}_{BC} = 0.25$. Then $c < 0$ at early times when the initial conditions are $a = 0.8$, $b = 0.1$, $c = 0.1$ for $x < L/2$; $a = 0.1$, $b = 0.8$, $c = 0.1$, for $x > L/2$. The earlier formulation of Toor (1964) is more robust, but it too gives negative concentrations some initial conditions. In any event, Toor's formulation is difficult to generalize to systems containing more than three components. The approach of Zielinski and Hanley (1999) using averaged friction factors has also given useful results in specific cases, but is difficult to formulate when there are many components, as in polymer systems. Also, their methodology can violate the material balance constraint if the self-diffusivities used in their procedure are independent of concentration.

It can be argued that the generalized Fick's law should use chemical potential as the driving force for diffusion (Darken, 1948). However, numerical examples using Flory-Huggins thermodynamics show that the diffusivities must be functions of concentration even when the diffusive fluxes are properly based on gradients in chemical potential.

It can also be argued that the cross-diffusion coefficients must be constructed to satisfy the Onsager reciprocal relationships. Attempts to do this by assigning constant values for D_{AA}, D_{BB}, and D_{AB} and then calculating a compositionally dependent D_{BA} according to the formulation of deGroot and Mazur (1962) gave a set of coefficients that predicted negative concentrations for some initial conditions. Again, the diffusion coefficients must be functions of concentration to avoid negative concentrations for some initial conditions.

As seen earlier, it is difficult to properly formulate the compositionally dependent diffusion coefficients that are necessary to maintain a material balance in a constant or specified density system. Truly fundamental approaches such as molecular dynamics should be immune to the problem. Ising-type models and some cell occupancy models (such as Theodorou and Wei, 1983) should also be immune. As a practical matter, however, it is necessary to model multicomponent diffusion using continuum mechanics and a minimum of experimentally or theoretically determined parameters.

Alternative Approaches Using Continuum Mechanics

A simple approach to multicomponent diffusion writes N flux equations, one for each component, and then balances the positive and negative fluxes at each point to satisfy the material balance. The idea of using a dependent set of N components has been suggested previously, but was not developed on the grounds that additional diffusion coefficients would be required compared to the $N - 1$ case (Miller et al., 1986). If a full N-by-N matrix of compositionally dependent coefficients is allowed, it is clearly possible to duplicate the conventional approach to multicomponent diffusion. However, our goal is to develop an approximate method that uses only the N diagonal coefficients and that automatically satisfies Eq. 3, even when the coefficients are constant. We write

$$J_i = -D_i \nabla C_i, \qquad i = 1 \text{ to } N, \tag{6}$$

and then individually sum the positive and negative fluxes. The larger in magnitude of the positive and negative fluxes is scaled down to match the other flux, the scaling being done proportionately for each species. This method is called the proportional-flux method. A code fragment illustrating the method is shown in Table 1.

Table 1. Program Fragment for the Proportional-Flux Method

This program fragment applies Fick's law individually to each component. The sum of component concentrations is held constant by forcing positive and negative fluxes to balance when summed over all components. In an exchange between two adjacents cells, the fluxes in each direction are calculated, and the larger flux is scaled downward in magnitude to match the smaller flux, the scaling being applied proportionately to each component that contributes to thelarger flux.

```
FOR i = 2 TO Isize
    Fin = 0: fout = 0
       FOR n = 1 TO Ncomp
          f(n, i) = - Diff(n)*(conc(n, i) - conc(n, i - 1))
          IF f(n, i) > 0 THEN
                Fin = fin + f(n, i)
          ELSE
    Fout = fout - f(n, i)
          END IF
  NEXT
    IF fout > fin THEN
  Fact = fin/fout
  FOR n = 1 TO Ncomp
    IF f(n, i) < 0 THEN f(n, i) = f(n, i)* fact
  NEXT
  END IF
  IF fout < fin THEN
  Fact = fout/fin
  FOR n = 1 TO Ncomp
    IF f(n, i) > 0 THEN f(n, i) = f(n, i)* fact
  NEXT
END IF
NEXT

FOR i = 2 TO Isize
FOR n = 1 TO Ncomp
  Conc(n, i - 1) = conc(n, i - 1) - dt* f(n, i)
  Conc(n, i) = conc(n, i) + dt* f(n, i)
NEXT: NEXT
```

Our second approach to multicomponent diffusion also uses one tracer diffusion coefficient per component, but selects components pairwise and allows binary, counterdiffusion between the selected pair while all other components are held immobile. All possible pairs are considered. When a particular pair of components is selected, the amount of material transferred depends upon the smaller of the two tracer

Table 2. Program Fragment for the Pairwise-Diffusion Method

This program fragment allows binary counterdiffusion between each pair of components while treating the other components as momentarily nondiffusing.

```
FOR i = 1 TO Isize
FOR n = 1 TO Ncomp
  Amount(n, i) = 0
NEXT: NEXT

FOR i = 1 TO Isize
  FOR n = 1 TO Ncomp
  FOR m = n + 1 TO Ncomp
    dmin = Diff(n)
    IF Diff(m) < Diff(n) THEN dmin = Diff(m)
    s1 = conc(n, i) + conc(m, i)
    s2 = conc(n, i + 1) + conc(m, i + 1)
    Area = s1
    IF s2 < s1 THEN Area = s2
    IF AREA > 0 THEN
      r1 = conc(n, i)/s1
      r2 = conc(n, i + 1)/s2
      del = Area* dmin* (r2 − r1)* dt
      Amount(n, i) = Amount(n, i) + del
      Amount(m, i) = Amount(m, i) − del
      Amount(n, i + 1) = Amount(n, i + 1) − del
      Amount(m, i + 1) = Amount(m, i + 1) + del
    END IF
  NEXT m: NEXT n
Next i

FOR i = 1 TO Isize
  FOR n = 1 TO Ncomp
    conc(n, i) = conc(n, i) + Amount(n, i)
  NEXT n
NEXT i
```

diffusion coefficients. The flux also depends upon the difference in the amounts of each particular component relative to the other component in that pair. The amount of material of one component moving in one direction is always compensated for by the movement of the same amount of material of the paired component moving in the opposite direction. This conserves mass, moles, or volume, as appropriate to the system being studied. See Table 2 for a code fragment illustrating the pairwise diffusion method.

Numerical Example 1: Ternary System

Consider one-dimensional diffusion in a rectangular coordinate system with zero flux at the boundaries and with the initial condition $a = 0.7$, $b = 0.1$, $c = 0.2$ for $x < L/2$ and $a = 0.1$, $b = 0.7$, $c = 0.2$ for $x > L/2$. The equilibrium solution is of course $a = 0.4$, $b = 0.4$, $c = 0.2$, As shown in Figure 1, the conventional treatment of the transient problem with $D_{AA} = 1$, $D_{BB} = 0.25$, $D_{AB} = D_{BA} = 0$ substantially overestimates the extent of cross-diffusion and give unrealistically large displacement in the concentration of component C from its initial and long-term profiles. Corresponding to these large displacements, the faster diffusing component, A, quickly enters the region $x > L/2$.

When the proportional flux model is used with $D_A = 1$, $D_B = 0.25$, $D_C = 1$, no cross-diffusion is predicted and $c(x) = 0.2$ everywhere and at all times. Component A in this case is restricted to diffuse at the speed of component B. As indicated earlier, this is contrary to both intuition and experience. However, it does satisfy the material balance constraint of Eq. 3.

When the pairwise diffusion model is applied using the same coefficients, cross-diffusion does occur and the profile of component A approaches its equilibrium values relatively faster than component B. Again, Eq. 3 is satisfied. The extent of cross-diffusion is moderate, and the maximum value of $c(x)$ is approximately 0.24 compared to 0.38 in the standard treatment. It should be noted that the absolute times needed to achieve a given approach to equilibrium are different for the three models. To obtain commensurate time behavior, the various diffusivities would have to be adjusted between models while keeping the same ratio of diffusivities within a model.

The conventional approach predicts no cross-diffusion for the case of equal diffusivities, $D_{AA} = D_{BB}$, $D_{AB} = D_{BA} = 0$, and the proportional flux model becomes identical to the conventional model in this case if $D_A = D_B = D_C$. As an apparent anomaly, the pairwise diffusion model continues to predict a small amount of cross-diffusion that increases the concentration of component C in the region near $x = L/2$.

Numerical Example 2: Mixtures of Oligomers

Diffusion between two slabs of oligomers that differed by a factor of 3 in number-average molecular weight was simulated using all three methods: standard, proportional flux, and pairwise. In these simulations the concentration variables must be explicitly interpreted as volume fractions rather than mole fractions or molar concentrations. This is necessary to preserve mass in a constant density system when the molecular species differ significantly in size. The mass balance is

$$\sum_{i=1}^{N} i v C_i' = 1 = v \mu_1, \tag{7}$$

where i is the number of mers per chain, v is the volume per mer, and C_i' is the molecular true concentration, that is, chains of length i per unit volume, and μ_1 is the first moment of the chain-length distribution. The key assumption, not really true but a reasonable place to start, is that v is independent of i, as indicated earlier. Then Eq. 7 becomes equivalent to Eq. 3 when the C_i are volume fractions proportional to iC_i'.

Results are shown in Figures 2, 3 and 4 for a 100-component system. Chain lengths ranged from 1 to 100, and the individual diffusion coefficients were assumed to be inversely proportional to chain length, as might be reasonable for polymer chains shorter than the entanglement length. Equal amounts of each component were used, but chain lengths 1−50 were initially placed on the lefthand side of the one-dimensional domain and chain lengths 51−100 were placed on the righthand side.

Results for the standard method are shown in Figure 2. The concentration of each component is plotted so the intensely dark areas show the range of behavior. This behavior appears reasonable except for the component of chain length 100, which was chosen to be the balancing component. It quickly goes to negative concentrations where it was present initially and to unrealistically high concentration where it was

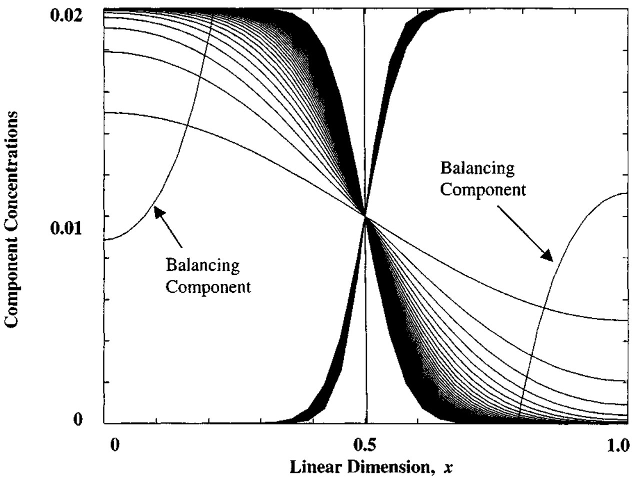

Figure 2. Slab diffusion of oligomers solved by the conventional method.

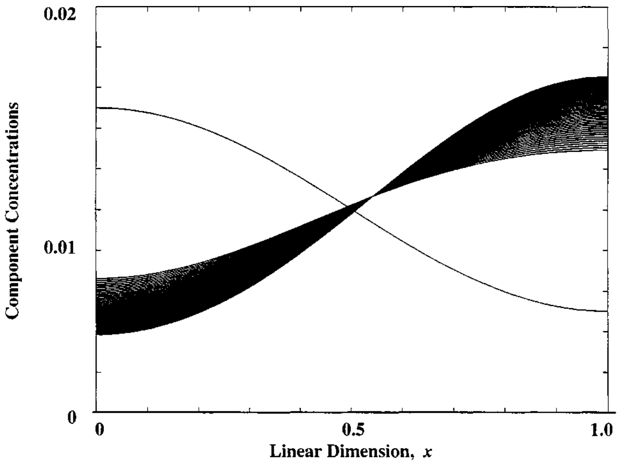

Figure 4. Slab diffusion of oligomers solved by the pairwise method.

absent initially. Changing the balancing component from the 100-mer to the monomer does not help. The curve for what was previously the fastest-moving component now becomes a vertical line at the center of the domain.

Figure 2 shows results for the proportional flux method. The results are qualitatively reasonable and the material balance is satisfied.

The pairwise diffusion method in Figure 3 predicts that the small molecules originally on the lefthand side of the domain all diffuse into the righthand side at the same rate. All of them are fast enough to diffuse to fill vacancies as fast as they appear, and with this particular initial condition, they share equally.

A third approach was attempted with this problem. It is conceptually similar to the proportional flux method, but the material balance was maintained by scaling the concentrations rather than the flux. No concentration became negative, but oligomers 10–50 simultaneously exceeded their initial concentrations of 0.02 at one point in the test problem. This amount of cross-diffusion seems nonphysical.

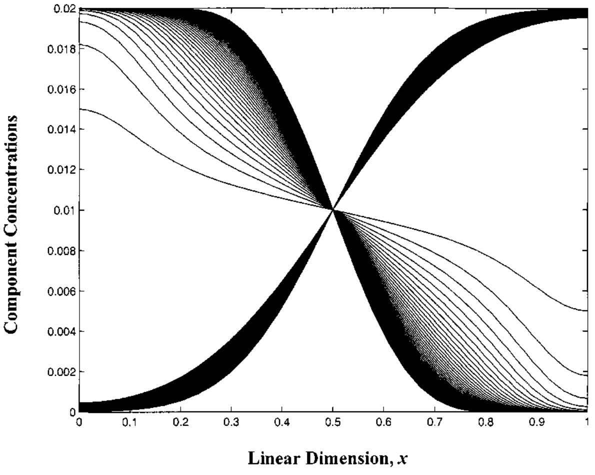

Figure 3. Slab diffusion of oligomers solved by the proportional-flux method.

Conclusions

Conventional diffusion theory provides little guidance for the important situation where the components of a mixture have significantly different diffusivities. Nonphysical results are predicted unless the diffusion coefficients are functions of composition, and there is no clear methodology short of exhaustive (and exhausting) experimentation for determining these functions. The present article develops two models that satisfy the material-balance constraint while requiring only one input diffusivity, nominally a tracer diffusivity (for example, as measured by spin-echo NMR), per chemical species. These models are clearly ad hoc. Yet, the need for a continuum mechanical approach is real, and there are no reasonable alternatives currently available. The pairwise diffusion model presented here seems particularly well suited for the case of widely varying coefficients, since it predicts physically reasonable levels of cross-diffusion. The proportional flux model may be better when the diffusivities are nearly equal and is computationally faster. We are currently exploring these models for solving a problem in anionic polymerization in a tubular reactor (Kim and Nauman, 1977).

Literature Cited

Cussler, E. L., *Diffusion Mass Transfer in Fluid Systems*, 2nd ed., Cambridge Univ. Press, Cambridge (1997).

Darken, L. S., "Diffusion, Mobility and Their Interrelation Through Free Energy in Binary Metallic Systems," *Trans. AIME*, **175**, 184 (1948).

Daoud, M., and P. G De Gennes, "Some Remarks on the Dynamics of Polymer Melts," *J. Poly. Sci., Poly. Phys. Ed.*, **17**, 1971 (1979).

Dunlop, P. J., and L. J. Gosting, "Interacting Flows in Liquid Diffusion: Expressions for the Solute Concentration Curves in Free Diffusion, and Their Use in Interpreting Gouy Diffusiometer Data for Aqueous Three-Component Systems," *J. Amer. Chem. Soc.*, **77**, 5238 (1955).

DeGroot, S. R., and P. Mazur, *Non-Equilibrium Thermodynamics*, Interscience, New York (1962).

Kim, D.-M., and E. B. Nauman, ‘‘Non-Terminating Polymerizations in Continuous Flow Systems,’’ *Ind. Eng. Chem. Res.*, **36**, 1088 (1997).

Miller, D. G., ‘‘Ternary Isothermal Diffusion and the Validity of the Onsager Reciprocity Relations,’’ *J. Phys. Chem.*, **63**, 570 (1959).

Miller, D. G., ‘‘Some Comments on Multicomponent Diffusion: Negative Main Term Diffusion Coefficients, Second Law Constraints, Solvent Choices, and Reference Frame Transformations,’’ *J. Phys. Chem.*, **90**, 1509 (1986).

Shuck, F. O., and H. L. Toor, ‘‘Diffusion in the Three Component Liquid System Methyl Alcohol-*n*-Propyl Alcohol-Isobutyl Alcohol,’’ *J. Phys. Chem.*, **67**, 540 (1963).

Theodorou, D. N., and J. Wei, ‘‘Diffusion and Reaction in Blocked and High Occupancy Zeolite Catalysts,’’ *J. Catal.*, **83**, 205 (1983).

Toor, H. L., ‘‘Solution of the Linearized Equations of Multicomponent Mass Transfer: I,’’ *AIChE J.*, **10**, 448 (1964).

Tyrell, H. J. V., and K. R. Harris, *Diffusion in Liquids*, Butterworths, London (1984).

Zielinski, J. M., and B. F. Hanley, ‘‘Practical Friction-Based Approach to Modeling Multicomponent Diffusion,’’ *AIChE J.*, **45**, (1999).

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