Use of Fick's Law and Maxwell–Stefan Equations in Computation of Multicomponent Diffusion

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Introduction

Multicomponent diffusion has attracted the attention of chemical engineers both in view of its practical importance and complexity. Maxwell–Stefan equations (MSE) and generalized Fick's law (GFL) forms are used to describe multicomponent diffusion. A component has to be excluded to write a GFL form for a multicomponent system, and hence GFL cannot be defined in a unique way.[1] The choice of the component to be excluded is arbitrary and can be difficult if all the components are present in approximately similar amounts. Solutions of mass balance equations in binary systems, where MSE and GFL become identical, are well known and conform to expectations. However, multicomponent systems do throw up surprises. One such, raised by Nauman and Savoca[2] and reinforced by Price and Romdhane,[3] is the difficulty of consistently combining mass balances with GFL forms where a component has to be excluded arbitrarily. Price and Romdhane[3] refer to the instances where negative values are obtained for mass fractions when mass balances combined with GFL form were solved numerically. Their work pertains to polymer–solvent systems, and they attribute the physically unrealistic results mainly to inconsistencies in the approximations used to get away with measurement of fewer diffusivities than the theoretical minimum. Nauman and Savoca[2] suggest that neglect of concentration dependency of diffusion coefficients could also be an important source of error, and physically unrealistic results can be obtained for the "balancing" component, that is the component excluded in defining GFL. However, they also claim that numerical solution of unsteady-state mass balance equations in gas mixtures, where the composition dependency of GFL diffusion coefficients is exactly known, also results in negative mole fractions. What ever might be the source of the physically unrealistic results, these instances point to the convenience of defining GFL forms without having to arbitrarily exclude a component. It is also relevant to point out two advantages of GFL forms. One is that they are easily combined with mass balances and require lesser number of equations to be solved than when MSE are used. That GFL can be directly used with standard CFD routines is the other advantage.

Bird and Curtiss,[4] based on work of Curtiss[5] and Merk,[6] proposed a form of GFL, which is equivalent to inverted MSE. This form does not require a particular component to be excluded for inversion, ensures symmetric coefficients and nonzero values for diagonal coefficients. They give the equations for diffusive mass flux with respect to mass average velocity. In the absence of thermal diffusion, however, they are equivalent to

$$\mathbf{J}_i^* = -C_i \sum_j \bar{D}_{ij}\mathbf{d}_j, \qquad \sum_i y_i \bar{D}_{ij} = 0, \quad i,j = 1,2,\ldots v \quad (1)$$

where v is the number of components in the mixture, C_i and y_i, respectively, are the molar concentration and mole fraction of ith species, $\mathbf{d}_i$ is its driving force, and the diffusive flux is with respect to molar average velocity. Only $v(v-1)/2$ diffusion coefficients appear in the above equations. They are independent and can be expressed in terms of the diffusion (or friction) coefficients that appear in MSE.

In this communication, we use the formulation of Bird and Curtiss[4] to show that only positive values are obtained for mole fractions for the case specified by Nauman and Savoca.[2] We also obtain results published by Newman[7] using MSE and, as expected, GFL method requires solution of lesser number of equations.

Diffusion Through a Stagnant Component

Newman[7] used film model to solve for steady-state composition profiles, when a mixture of acetone and methanol vaporizes into "stagnant" air, and diffusion in gas phase controls mass transfer. Air was treated as a single component, and conditions were such that the total molar concentration could be treated as constant. Denote acetone by 1, methanol by 2, and air by 3. The properties and boundary conditions are shown in Table 1, where x is the film coordinate, and δ is the film thickness. $\mathcal{D}_{ij}$ are binary diffusivities and are same as MSE diffusivities for mixtures of ideal gases. The total molar concentration in the system is constant, and hence, the total molar flux N_t is a constant. As the third component is stagnant, it follows that

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Table 1. Properties and Boundary Conditions for Film Model

	Acetone	Methanol	Air
$y(x = 0)$	0.319	0.528	0.153
$y(x = \delta)$	0.0001	0.0001	0.9998
Diffusion	$\mathcal{D}_{13}$	$\mathcal{D}_{23}$	$\mathcal{D}_{12}$
coefficient × 10^4, (m^2/s)	0.1372	0.1991	0.0848

$$0 = N_3 = J_3^* + y_3 N_t, \quad \text{or} \quad N_t = -\frac{J_3^*}{y_3} \tag{2}$$

This relationship allows the mass balances for the other two components to be written in terms of diffusive fluxes

$$0 = \frac{dN_i}{dx} = \frac{dJ_i^*}{dx} - \frac{d}{dx} y_i \frac{J_3^*}{y_3} \tag{3}$$

Substituting Eq. 1 into Eq. 3, we get

$$0 = \frac{d}{dx}\left(y_i \sum_{j=1}^{j=3} (\bar{D}_{ij} - \bar{D}_{3j}) \frac{dy_j}{dx} \right), \quad i = 1, 2 \tag{4}$$

Note that Eq. 4 is in the classical conservative form and can be solved by any CFD routine. The above equations contain $\overline{D}_{ij}$ and have to be expressed in terms of $\mathcal{D}_{ij}$. Bird and Curtiss[4] give the "algebraic" relationships for systems containing up to four components. We reproduce them for three component system that are used in this communication.

$$C_{ij} \equiv \frac{y_i y_j}{\mathcal{D}_{ij}} \tag{5a}$$

$$\Delta_3 = C_{12}C_{13} + C_{12}C_{23} + C_{13}C_{23} \tag{5b}$$

$$\bar{D}_{11} = [y_3^2 C_{12} + y_2^2 C_{13} + (y_2 + y_3)^2 C_{23}]/\Delta_3 \tag{5c}$$

$$\bar{D}_{12} = [y_3^2 C_{12} - y_2(y_1 + y_3)C_{13} - y_1(y_2 + y_3)C_{23}]/\Delta_3 \tag{5d}$$

Other coefficients can be obtained by permutation of indices. Bird and Curtiss[4] mention that these relationships were generated using a computer, and we could also do so using Mathematica. It is possible that other approaches[8] may also be useful. Equivalent of Eqs. 5 would be essential for efficient computer solution of mass balance equations when the number of components is large.

Three mole fractions are the unknowns in the two Eq. 4. After replacing y_3 by $1 - y_1 - y_2$, they can be solved to determine y_1 and y_2. However, in general, it is easier[7] to solve the two mass balance equations along with

$$\sum_{i=1}^{3} y_i = 1.0 \tag{6}$$

Equations 4 and 6 were solved in this way using the boundary conditions given in Table 1. $\overline{D}_{ii}$ become infinitely large when $y_i = 0$. However, it is always the product $y_i\overline{D}_{ii}$ that appears in the equations, and it remains finite[9] when $y_i = 0$. This can be used in programming to handle $\overline{D}_{ii}$ at all values of mole fractions. For the sake of convenience, however, instead of zero, very small values were taken for mole fractions in boundary conditions. Results remain unaffected when values smaller than those shown in Table 1 were used. Finite volume method[10] was used to discretize equations, and BAND approach[11] was used to solve the simultaneous algebraic equations of the boundary value problem. Results are identical to those obtained by Newman[7] and are shown in Figure 1.

Newman[7] also used the penetration model to solve the above problem. The physical properties remain the same. Mass balance equations are given by

$$\frac{\partial (Cy_i)}{\partial t} = -\frac{\partial N_i}{\partial x}, \quad i = 1, 2, 3, \quad 0 \le x < \infty$$

As the total molar concentration is constant, the total molar flux is not a function of x. Hence, we can use stagnancy of air at $x = 0$ to express N_t as

$$0 = N_3(x = 0) = J_3^*(x = 0) + y_3(x = 0)N_t, \quad \text{or}$$

$$N_t = -\frac{J_3^*(x = 0)}{y_3(x = 0)} \tag{7}$$

After using this relationship, the mass balances can be rewritten as

$$C\frac{\partial y_i}{\partial t} = -\frac{\partial J_i^*}{\partial x} - \frac{J_3^*(x = 0)}{y_3(x = 0)} \frac{\partial y_i}{\partial x}, \quad i = 1, 2, \quad 0 \le x < \infty$$

Newman[7] points out that similarity transformation variable can be used

$$\eta = \frac{x}{2\sqrt{\mathcal{D}_{13} t}}$$

where any diffusion coefficient could have been used in the definition and $\mathcal{D}_{13}$ was chosen. In terms of the similarity variable, the unsteady mass balance becomes

$$\frac{d}{d\eta} y_i \sum_{j=1}^{j=3} \left(\bar{D}_{ij}^* \frac{dy_j}{d\eta} - \left(\bar{D}_{3j}^* \frac{dy_j}{d\eta}\right)\Big|_{\eta=0} \right) + 2\eta \frac{dy_i}{d\eta} = 0, \quad i = 1, 2 \tag{8}$$

where the starred diffusivities are values nondimensionalized with $\mathcal{D}_{13}$. The boundary conditions of Table 1 at $x = \delta$ were also the initial conditions and are applied as $\eta \to \infty$. Condition at $x = 0$ holds at $\eta = 0$. As the mass balance is in conservative form, it can be solved by any CFD routine. Procedure of the previous section was used to solve Eq. 8 along with Eq. 6. The

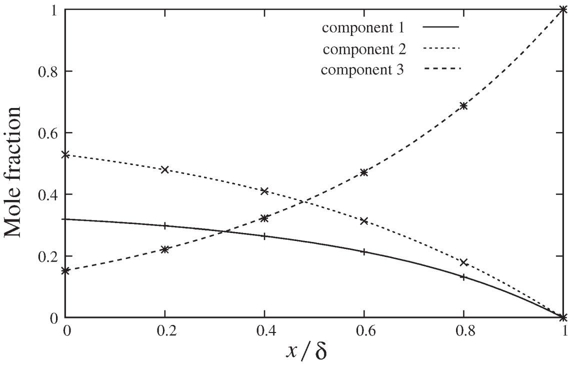

Figure 1. Results for film model.

Points are results from Newman.[7]

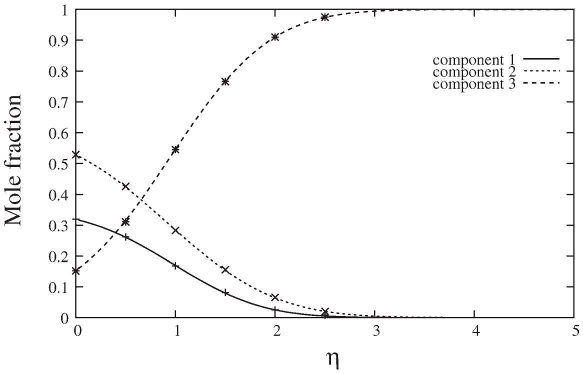

Figure 2. Concentration profiles as a function of similarity variable for diffusion in a semi-infinite medium with one component stagnant.

Points are results from Newman.[7]

results are indistinguishable from those obtained by Newman[7] and are shown in Figure 2. Newman[7] also used boundary layer model for this problem, and it can also be solved using the GFL and procedure similar to what we presented.

Equimolar Counter Diffusion

Nauman and Savoca[2] give an example of unsteady diffusion in a ternary mixture of ideal gases. The total molar concentration is constant and the total molar flux was set to zero, and they use the mass balances

$$C\frac{\partial y_i}{\partial t} = -\frac{\partial J_i^*}{\partial x}, \quad i = 1,2$$

They report that with the initial conditions $y_1 = 0.8$, $y_2 = 0.1$, $y_3 = 0.1$ for $x < L/2$ and $y_1 = 0.1$, $y_2 = 0.8$, $y_3 = 0.1$ for $x > L/2$, their calculations give negative values for y_3 (i.e., mole fraction of the excluded component) at small times when $\mathcal{D}_{12}$, $= 1.0$, $\mathcal{D}_{13} = 0.25$, and $\mathcal{D}_{23} = 0.25$. As problematic results were obtained at "initial times," and as L is not specified, the problem can be treated as diffusion in two semi-infinite slabs of different compositions brought into contact with each other at $t = 0$. Thus

$$C\frac{\partial y_i}{\partial t} = -\frac{\partial J_i^*}{\partial x}, \quad i = 1,2; \quad -\infty < x < \infty$$

Nauman and Savoca[2] specified initial condition for Component 1 that is a reflection (on the midplane) of that for Component 2 and uniform mole fraction of Component 3. Further $\mathcal{D}_{13} = \mathcal{D}_{23}$. Under these conditions, this is effectively a problem in binary diffusion and has an analytical solution given by $y_3 = 0.1$ and

$$\begin{aligned} y_1 &= 0.1 + 0.35\left(1 - \mathrm{erf}\left(\frac{x}{2\sqrt{\mathcal{D}_{\mathrm{eff}}t}}\right)\right) \\ y_2 &= 0.1 + 0.35\left(1 + \mathrm{erf}\left(\frac{x}{2\sqrt{\mathcal{D}_{\mathrm{eff}}t}}\right)\right) \end{aligned} \qquad (9a)$$

$$\frac{1}{\mathcal{D}_{\mathrm{eff}}} = \frac{1 - y_3}{\mathcal{D}_{12}} + \frac{y_3}{\mathcal{D}_{13}} \qquad (9b)$$

The mass balances were numerically solved with the earlier approach. The similarity variable of the previous section was used here as well, and the mass balances are given by

$$\frac{d}{d\eta} y_i \sum_{j=1}^{j=3}\left(\bar{D}_{ij}^*\frac{dy_j}{d\eta}\right) + 2\eta\frac{dy_i}{d\eta} = 0, \quad i = 1,2 \qquad (10)$$

The boundary conditions are given by $y_1 \to 0.8$, y_2, and $y_3 \to 0.1$ as $\eta \to -\infty$ and $y_2 \to 0.8$, y_1, and $y_3 \to 0.1$ as $\eta \to \infty$. The results obtained are shown in Figure 3. Small times correspond to large values of η, and negative values were not obtained in our calculation. The results are indistinguishable from the analytical solution given earlier. While the stagnancy of one component forced solution of mass balance for the other two components in the previous two problems, any two of the three mass balances can be solved in this problem. Identical results were obtained by solving mass balances for Components 2 and 3 instead of 1 and 2, indicating that exclusion of a component is not a source of error when correct number of diffusivities along with their composition dependencies is used. A step discontinuity in the mole fraction has to be handled in this problem. Here, similarity variable was used, while Nauman and Savoca[2] employed finite differences and the discrepancy between their and our results may be attributed to this.

The ratio of diffusion coefficients is large in the case just considered. While retaining this aspect and symmetry of the boundary conditions, it is interesting to observe results when $\mathcal{D}_{13}$ and $\mathcal{D}_{23}$ are made unequal. The problem was solved with the following values of diffusion coefficients

$$\mathcal{D}_{12} = 1.0, \quad \mathcal{D}_{13} = 0.25, \quad \mathcal{D}_{23} = 0.1$$

Concentration profiles are shown in the top panel of Figure 4. It is seen that the concentration of the third component does not remain constant. The far away boundary conditions are satisfied but the profile shows a maximum and a minimum. Values of fluxes are shown in the bottom panel. As expected, fluxes of all components decay to zero far away. In between, flux of the first component is found to be in the positive x direction, and this is in accordance with the overall driving force. Flux of the second component is in the negative direction, and this is also in accordance with the overall driving force. The third component, however, diffuses in the negative x direction. This is diffusion in the absence of an overall driving force and is referred[12] to as osmotic diffusion. It occurs because of the coupling of fluxes, and the values are dictated by the relative magnitudes of diffusion coefficients. As driving force for Component 2 is expected to be large in the

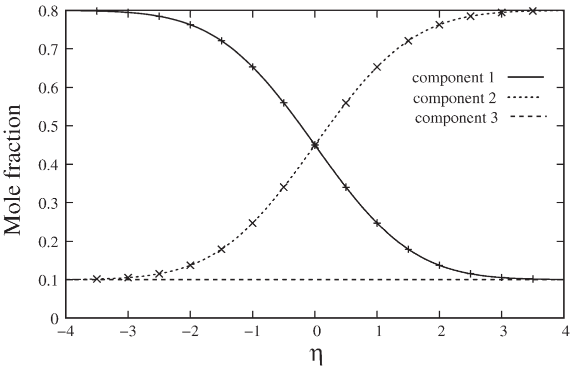

Figure 3. Concentration profiles as a function of similarity variable for equimolar counter diffusion for the conditions of Nauman and Savoca.[2]

Points are calculated from Eq. 9.

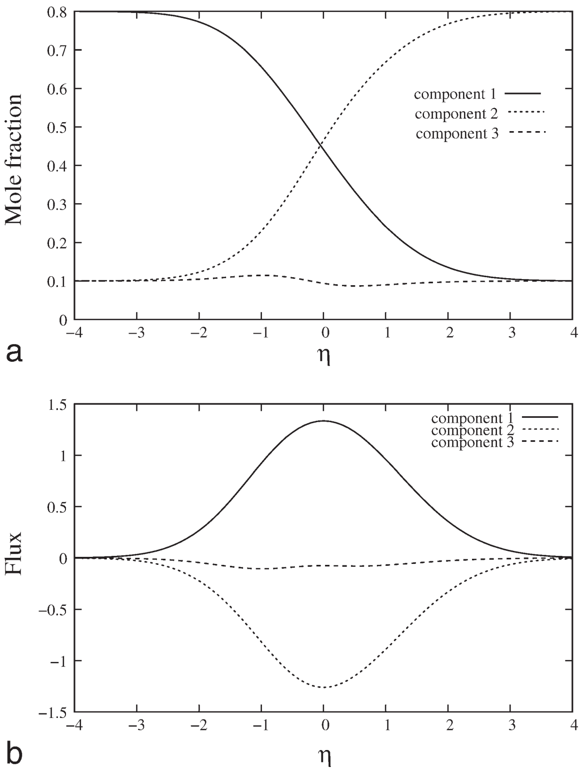

Figure 4. Top panel shows concentration profiles as a function of similarity variable for equimolar counter diffusion for the boundary conditions of Nauman and Savoca[2] but with all diffusion coefficients being different.

The bottom panel shows fluxes (J_i^*/C).

right half of the x-plane but as $\mathcal{D}_{23}$ is small, the osmotic flux there is small. As $\mathcal{D}_{13}$ is larger than $\mathcal{D}_{23}$, and driving force for Component 1 is expected to be large in the left half of the plane, osmotic flux of the third component is larger there. As $\mathcal{D}_{13}$ is larger than $\mathcal{D}_{23}$, flux of Component 2 can be expected to be smaller than that of Component 1 given that the overall driving force for both the components is the same. Hence, Component 3 has to diffuse in the same direction as Component 2 to keep the total molar flux at zero level.

About Negative Mole Fractions

Nauman and Savoca[2] give an illustrative example where negative mass fractions are obtained when GFL that exclude a component are used. Here, the third component is excluded, cross diffusion coefficients are set to zero, $\overline{D}_{11} = 1.0$, $\overline{D}_{22} = 0.25$, and boundary conditions are same as in the example of equimolar counter diffusion. As a system is not specified, one can only speculate about the causes leading to physically unrealistic results. If the system was to be composed of ideal gases, the values chosen for diffusion coefficients are incorrect as cross diffusion coefficients can be zero only when the diagonal coefficients are equal. In liquid systems, the diffusion coefficients will be functions of concentrations and it is unlikely that the cross coefficients will be zero over the entire concentration range. One can, therefore, argue that the values specified for diffusion coefficients will not conform to restrictions placed by Onsager's reciprocal relationships (ORR) and, hence, are unrealistic in liquid systems as well. However, for this example, it can be shown that

$$y_3 = 0.1 - 0.35\left(\operatorname{erf}\left(\frac{x}{2\sqrt{\overline{D}_{22}t}}\right) - \operatorname{erf}\left(\frac{x}{2\sqrt{\overline{D}_{11}t}}\right)\right)$$

and, y_3 will not become negative if $\overline{D}_{22}/\overline{D}_{11}$ is greater than about 0.3. Thus, one can only conclude that while physically unrealistic values may not be obtained in some fortuitous conditions, experimentally realizable values can be obtained only on the basis of a sound physicochemical theory of diffusion coefficients. Price and Romdhane[3] present a detailed analysis of a case of diffusion in polymer solutions containing two solvents where mass fractions were calculated to be negative. In this particular case, they could get rid of physically unrealistic results by correcting some inconsistencies in the model of diffusion coefficients used. However, to achieve consistency with ORR, corrective measures required very restrictive assumptions on the nature of friction coefficients. This also points toward development of better theories of diffusion coefficients as the way to avoid unphysical results.

Conclusions

The GFL form proposed by Bird and Curtiss,[4] which does not exclude a component arbitrarily and is equivalent to the inverse of MSE, was used to solve some problems in multicomponent diffusion. This approach can directly be incorporated into CFD routines and would be of value when the number of components become large, for example, in multicomponent distillation or absorption. It was also shown that, unlike observed earlier,[2] when the theoretical number of diffusion coefficients along with their dependencies on concentration are used, physically unrealistic negative values for mole fractions were not obtained. The approach suggested here also points to the value of models[3,13,14] of friction coefficients of MSE.

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