Diffusing with Stefan and Maxwell

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In most chemical engineering problems, diffusion is treated as an add-on to forced advection, and the boundary conditions are the Danckwerts conditions in order to maintain conservation. If we treat problems in which there is no applied advection or chemical reaction for a steady-state situation and with an ideal gas, it is an equi-molar process. Because it is considered the natural movement of molecules moving down a concentration gradient, this requires the Stefan-Maxwell equations. In the standard 1-D two-component boundary value problem, analogous to the Dirichlet problem, the solution is direct and is probably the only one there is. In a ternary system, the solution is already not direct and can only be obtained by numerical means, which is not severe. In a quaternary system, it does not appear feasible to obtain a simple procedure like that obtained for the ternary system. A different numerical scheme developed is robust with rapid convergence and works well with an arbitrary number of components, 60 having been used in one problem. As the number of components increases, the solution profiles tend to become linear and the dependence on particular diffusivities is less important. This manifests itself when using diffusivities from a random collection. The problem using a continuous distribution of components is solved, and computationally and theoretically the profiles are probably linear and with a single pairwise diffusion coefficient.

Introduction

The purpose of this article is to present some manipulations of the Stefan-Maxwell equations as applied to the simple one-dimensional (1-D) diffusion problem in the steady state for an ideal gas with an arbitrary number of components. Anyone who has examined these equations becomes frustrated by their backward presentation which manifests itself in some way in almost every application of their use. In addition, they are nonlinear in the two important sets of variables although linear in each set singly. The two sets of variables are the mol fraction of each component and the corresponding flux of each. Manipulation of these equations reveals that their inversion to produce the fluxes in terms of the gradient for a two-component system is trivial. For a three-component system, it is doable and builds one's confidence, while for a four-component system the problem is a character builder; for a five-component system, it seems impassable and impossible in an analytical way. Some of the earliest attempts at using the equations were carried out by Toor (1964) and Stewart and Prober (1964) who linearized the equations to cast them into a usable form. This is a successful procedure since the system is very benign, and, as will be shown later, many of the solutions turn out to be close to linear. Later workers developed many other schemes, and these are discussed by Taylor and Krishna (1993) whose book is required reading. The numerical scheme devised by Krishna and Standart (1976) was and still is the method of choice.

Our first effort will be to invert the Stefan-Maxwell equations for three and four component systems, and to attempt to simplify these equations to make their use easier. For a three-component system, this is relatively easy, but for a four-component system, this is a trial and requires the introduction of two sets of simple functions to present the inversion in a relatively simple way. Some small surprises result here and make its perusal worth the effort.

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A different numerical scheme for the 1-D diffusion problem is presented, and its application to several different problems is illustrated for a wide range of components. The equations for the diffusion problems with a continuous distribution of components are presented, and the 1-D diffusion problem is solved although the numerical solution is obtained by a lumping procedure as for a finite distribution. For some of these problems, it is shown by direct computation that the final solutions for the mol fraction profiles are relatively independent of the choice of diffusion coefficients.

Ternary Inversion

The basic set of equations for 1-D diffusion in matrix form is, for an n component system,

$$c\frac{d\boldsymbol{x}}{dz} = \boldsymbol{B}\boldsymbol{x} \tag{1}$$

where c is the total molar local concentration, $\boldsymbol{x}$ is the vector of mol fractions, z is the axial space variable, N_j is the molar flux of species j, and the D_{ij} represent the pairwise diffusion coefficients. With

$$\boldsymbol{B} = [\mu_{ij}] \quad (i \text{ row}; j \text{ column})$$

then

$$\mu_{ij} = -\frac{N_i}{D_{ij}},\ i \neq j,\ \mu_{ii} = \sum_{\substack{k=1\\k\neq i}}^{n} \frac{N_k}{D_{ik}}$$

which shows the linearity in x_i for known values of N_j. These equations will also be used in the form

$$c\frac{d\boldsymbol{x}}{dz} = \beta \boldsymbol{N} \tag{2}$$

where

$$\beta = [\nu_{ij}]$$

with

$$\nu_{ij} = \frac{x_i}{D_{ij}},\ i \neq j,\ \nu_{ii} = -\sum_{\substack{k=1\\k\neq i}}^{n} \frac{x_k}{\mathfrak{D}_{ik}}.$$

These matrices are singular since each column will sum to zero, and, hence, the sets of differential equations are also singular. Since we are dealing with 1-D steady-state diffusion, the singularity may be circumvented by using either the fact that diffusion must be equimolar

$$\sum_{j=1}^{n} N_j = 0,$$

or

$$\sum_{i=1}^{n} x_i = 1,$$

since motion of molecules must be balanced, that is, movement of one molecule must be balanced by the motion of another molecule. Thus, any one of the differential equations can be replaced by one of the two conditions above.

For the ternary system, we will use the set of equations (Eq. 2),

$$\begin{aligned} c\frac{dx_1}{dz} &= -\left(\frac{x_2}{D_{12}} + \frac{x_3}{D_{13}}\right)N_1 + \frac{x_1}{D_{12}}N_2 + \frac{x_1}{D_{13}}N_3, \\ c\frac{dx_2}{dz} &= \frac{x_2}{D_{21}}N_1 - \left(\frac{x_1}{D_{21}} + \frac{x_3}{D_{23}}\right)N_2 + \frac{x_2}{D_{23}}N_3, \\ 0 &= N_1 + N_2 + N_3. \end{aligned} \tag{3}$$

In order to invert the system we will treat this as a set of linear simultaneous algebraic equations in N_1, N_2, and N_3 and simply solve using Cramer's rule on Eq. 3. This procedure gives solutions for N_1, N_2, and N_3 in terms of dx_1/dz and dx_2/dz which are linear in these variables and clumsy, and we must cast them into relations which are independent of the species numbering and also quasi symmetric as occurs in the original Stefan-Maxwell equations. To do this, we add to the three relations quantities like

$$\alpha \sum_{i=1}^{3} \frac{dx_i}{dz} = 0$$

with α appropriately chosen to each equation to produce the species independent property, and this is much easier to do than it sounds. The Cramer denominator turns out to be

$$\frac{x_1}{D_{13}D_{12}} + \frac{x_2}{D_{12}D_{23}} + \frac{x_3}{D_{13}D_{23}}$$

which we will use in the form, on multiplying through $D_{12}D_{13}D_{23}$, as

$$\phi(\boldsymbol{x}) = D_{23}x_1 + D_{13}x_2 + D_{12}x_3. \tag{4}$$

After some juggling, we obtain the matrix form of the inverse

$$N = -\frac{c}{\phi(\boldsymbol{x})} \times \begin{bmatrix} (1-x_1)D_{13}D_{12} & -x_1D_{23}D_{12} & -x_1D_{23}D_{13} \\ -x_2D_{13}D_{12} & (1-x_2)D_{23}D_{12} & -x_2D_{23}D_{13} \\ -x_3D_{13}D_{12} & -x_3D_{23}D_{12} & (1-x_3)D_{23}D_{13} \end{bmatrix} \frac{d\boldsymbol{x}}{dz}. \tag{5}$$

In this form it is evident that the flux N_i depends on a sum of terms with a net single diffusivity as it should.

Since our main interest is in the solution of the 1-D diffusion equations, we consider diffusion in a 1-D conduit which is adjoined at its ends by infinitely large reservoirs, each at a fixed molar concentration and each at a fixed and the same temperature and same pressure. In one dimension the concentration equations are, where l is the conduit length

$$\frac{dN_i}{dz} = 0,\ 0 < z < l,\ i = 1, 2, 3$$

and boundary conditions are, with $\boldsymbol{x}_0$ and $\boldsymbol{x}_l$ specified

$$\boldsymbol{x}(0) = \boldsymbol{x}_0,\ \boldsymbol{x}(l) = \boldsymbol{x}_l.$$

This simple problem will be cast in dimensionless form later, since now the occurrence of the diffusivities is revealing. From the conservation equation, N_i is a constant for all x and

$$\sum_{i=1}^{n} N_i = 0$$

since this diffusion movement of molecules only means that they replace each other.

In an effort to simplify Eq. 5 by removing the unity in each row, we multiply it by the diagonal matrix

$$\begin{bmatrix} D_{23} & 0 & 0 \\ 0 & D_{13} & 0 \\ 0 & 0 & D_{12} \end{bmatrix}$$

and then add the rows to obtain

$$-\frac{c}{\phi(\boldsymbol{x})}\Bigg[D_{13}D_{12}(-x_1D_{23} - x_2D_{13} - x_3D_{12})\frac{dx_1}{dz} + D_{23}D_{12}(-x_1D_{23} - x_2D_{13} - x_3D_{12})\frac{dx_2}{dz} + D_{23}D_{13}(-x_1D_{23} - x_2D_{13} - x_3D_{12})\frac{dx_3}{dz}\Bigg] = D_{23}N_1 + D_{13}N_2 + D_{12}N_3.$$

We see that, fortuitously, the three quantities within the parentheses are $\phi(\boldsymbol{x})$ so that from Eq. 4

$$c\left[D_{13}D_{12}\frac{dx_1}{dz} + D_{23}D_{12}\frac{dx_2}{dz} + D_{23}D_{13}\frac{dx_3}{dz}\right] = D_{23}N_1 + D_{13}N_2 + D_{12}N_3.$$

Integration between zero and l gives

$$c\left[\frac{x_{1l} - x_{10}}{D_{23}} + \frac{x_{2l} - x_{20}}{D_{13}} + \frac{x_{3l} - x_{30}}{D_{12}}\right] = \left(\frac{N_1}{D_{13}D_{12}} + \frac{N_2}{D_{12}D_{23}} + \frac{N_3}{D_{13}D_{23}}\right)l$$

after dividing through by $D_{12}D_{13}D_{23}$. Integrating from 0 to z, gives

$$c\left[\frac{x_1 - x_{10}}{D_{23}} + \frac{x_2 - x_{20}}{D_{13}} + \frac{x_3 - x_{30}}{D_{12}}\right] = \left(\frac{N_1}{D_{13}D_{12}} + \frac{N_2}{D_{12}D_{23}} + \frac{N_3}{D_{13}D_{23}}\right)z$$

so

$$\frac{1}{D_{23}}\frac{dx_1}{dz} + \frac{1}{D_{13}}\frac{dx_2}{dz} + \frac{1}{D_{12}}\frac{dx_3}{dz} = \left[\frac{x_{1l} - x_{10}}{D_{23}} + \frac{x_{2l} - x_{20}}{D_{13}} + \frac{x_{3l} - x_{30}}{D_{12}}\right]\frac{1}{l} = \frac{K}{l} \qquad (6)$$

and also

$$\frac{x_1 - x_{10}}{D_{23}} + \frac{x_2 - x_{20}}{D_{13}} + \frac{x_3 - x_{30}}{D_{12}} = \left(\frac{x_{1l} - x_{10}}{D_{23}} + \frac{x_{2l} - x_{20}}{D_{13}} + \frac{x_{3l} - x_{30}}{D_{12}}\right)\frac{z}{l}$$

which is not a relation one might expect for three components.

In order to use these equations, particularly Eq. 6, let us consider the expression for N_1, and write it in the form

$$N_1 = -\frac{c}{\phi(\boldsymbol{x})}(D_{12}D_{13}D_{23}) \times \left[\frac{1}{D_{23}}\frac{dx_1}{dz} - x_1\left(\frac{1}{D_{23}}\frac{dx_1}{dz} + \frac{1}{D_{13}}\frac{dx_2}{dz} + \frac{1}{D_{12}}\frac{dx_3}{dz}\right)\right]$$

which reduces to an expression with a single derivative

$$N_1 = -\frac{c}{\phi(\boldsymbol{x})}(D_{12}D_{13}D_{23})\left[\frac{1}{D_{23}}\frac{dx_1}{dz} - x_1\frac{K}{l}\right]$$

If we now cast this in dimensionless form, using the Cramer denominator (Eq. 4), we obtain

$$-\frac{dx_1}{d\xi} + x_1K_{23} = Z_1[c_{23}x_1 + c_{13}x_2 + c_{12}x_3]K_1$$

with

$$\xi = \frac{z}{l},\ c_{ij} = \frac{D_{ij}}{D},\ K_{23} = D_{23}K,\ K_{13} = D_{13}K,\ K_{12} = D_{12}K,$$

$$Z_1 = \frac{N_1 l}{D_c},\ Z_2 = \frac{N_2 l}{D_c},\ Z_3 = \frac{N_3 l}{D_c},\ K_1 = \frac{D^2}{D_{12}D_{13}},$$

$$K_2 = \frac{D^2}{D_{12}D_{23}},\ K_3 = \frac{D^2}{D_{13}D_{23}}$$

and in a similar way

$$-\frac{dx_2}{d\xi}+x_2K_{13}=Z_2[c_{23}x_1+c_{13}x_2+c_{12}x_3]K_2,$$

$$-\frac{dx_3}{d\xi}+x_3K_{12}=Z_3[c_{23}x_1+c_{13}x_2+c_{12}x_3]K_3.$$

These last three equations should be simpler to apply to the numerical problem than the original ones, but one needs to have a good estimate of Z_1, Z_2, Z_3 to initiate that solution. One can find such a solution by assuming that an approximate solution is a straight line connecting the appropriate boundary points and using the values of $\boldsymbol{x}_0$ (at $z=0$) to obtain

$$-\frac{x_{1l}-x_{10}}{l}+x_{10}K_{23}=Z_1^0(c_{23}x_{10}+c_{13}x_{20}+c_{12}x_{30})K_1$$

$$-\frac{x_{2l}-x_{20}}{l}+x_{20}K_{13}=Z_2^0(c_{23}x_{10}+c_{13}x_{20}+c_{12}x_{30})K_2$$

from which a reasonable guess should ensue. (Note that $\sum Z_i=0$.)

We stress that the advantage to these equations is the fact that the lefthand sides are linear first-order operators since K_{ij} is a predetermined constant. If we write the original Stefan-Maxwell equations in the form

$$-c\frac{dx_i}{dz}+x_i\sum\frac{N_j}{D_{ij}}=N_i\sum\frac{x_j}{D_{ij}}$$

the left-hand side is a linear operator in x_i, but its coefficient contains the unknown N_j for all j except $j=i$. It is evident of course that these equations for constant values of N_i and $\sum x_i=1$ have an analytical solution which is not of great use since the boundary conditions must be used to eventually determine the N_i, which is a tortuous exercise, but doable.

It may be interesting to consider the structure of the solution profiles $x_i=x_i(\xi)$, not because the solutions are rich with pathology, but rather in order to show their simplicity. Diffusional processes are normally very benign (as long as they are not coupled with exothermic chemical reactions), since molecular motion tends to smear things out.

If we consider a ternary system, there are three equations of which only two are linearly independent in pairs. If, for example, $dx_3/d\xi=0$ at a point, then it follows that

$$\frac{dx_2}{d\xi}+\frac{dx_1}{d\xi}=0$$

which is impossible since the functions defined by the corresponding two SM equations are linearly independent. If we differentiate the equation for x_1, we obtain

$$c\frac{d^2x_1}{d\xi^2}=-\left(\frac{1}{D_{12}}\frac{dx_2}{d\xi}+\frac{1}{D_{13}}\frac{dx_3}{d\xi}\right)N_1+\frac{dx_1}{d\xi}\left(\frac{N_2}{D_{12}}+\frac{N_3}{D_{13}}\right).$$

If we assume this is zero, then, using

$$\sum_i\frac{dx_i}{d\xi}=0$$

we have

$$\left(-\frac{1}{D_{12}}+\frac{1}{D_{13}}\right)\left(N_1\frac{dx_2}{d\xi}-N_2\frac{dx_1}{d\xi}\right)=0$$

which gives

$$N_1\frac{dx_2}{d\xi}=N_2\frac{dx_1}{d\xi}$$

which is also impossible because of the linear independence. Thus, the profiles of the components are strictly monotonic between the boundaries and we shall illustrate some of these later. The above may be generalized to higher-order equations.

Toor (1957) in the early 1950s solved the ternary diffusion problem by obtaining the analytical solution for fixed fluxes, and then solved for the fluxes by trial and error. Hsu and Bird (1960) published a massive paper for three-component chemical reaction problems in which the catalytic reaction occurred at one of the boundaries. These were solved in an analytical way with computations on an IBM 650.

Quaternary Systems

In order to realize the inversion we must solve the following set of linear simultaneous equations in N_1, N_2, N_3, and N_4, where we use Eq. 2

$$\begin{bmatrix} c\dfrac{dx_1}{dz}\\ c\dfrac{dx_2}{dz}\\ c\dfrac{dx_3}{dz}\\ 0\end{bmatrix}=\begin{bmatrix} \dfrac{-x_2}{D_{12}}-\dfrac{x_3}{D_{13}}-\dfrac{x_4}{D_{14}} & \dfrac{x_1}{D_{12}} & \dfrac{x_1}{D_{13}} & \dfrac{x_1}{D_{14}}\\ \dfrac{x_2}{D_{21}} & \dfrac{-x_1}{D_{21}}-\dfrac{x_3}{D_{23}}-\dfrac{x_4}{D_{24}} & \dfrac{x_2}{D_{23}} & \dfrac{x_2}{D_{24}}\\ \dfrac{x_3}{D_{31}} & \dfrac{x_3}{D_{32}} & \dfrac{-x_1}{D_{31}}-\dfrac{x_2}{D_{32}}-\dfrac{x_4}{D_{34}} & \dfrac{x_3}{D_{34}}\\ 1 & 1 & 1 & 1\end{bmatrix}N.$$

One could hope that the treatment of quaternary systems might not be substantially different from ternary systems but, of course, the fourth-order manipulations are certainly more tedious in this Cramer solution. The challenging part of the exercise, however, as before, is the casting of the resultant solutions into forms which are independent of the numbering of the species and are quasi-symmetric in the component variables. The Cramer solution first obtained is linear in the three derivatives dx_1/dz, dx_2/dz, and dx_3/dz since the last Stefan-Maxwell equation is replaced by

$$\sum_{i=1}^{4} N_i = 0.$$

The Cramer denominator may be written as a fourth-order quadratic form. This is not readily apparent during the calculation, but it can be written in the form

$$\phi(\boldsymbol{x}) = \boldsymbol{x}^T \begin{bmatrix} d_{12}d_{13}d_{14} & d_{24}d_{13}d_{12} & d_{12}d_{13}d_{34} & d_{12}d_{14}d_{34} \\ d_{12}d_{14}d_{23} & d_{24}d_{23}d_{12} & d_{12}d_{23}d_{34} & d_{24}d_{34}d_{12} \\ d_{13}d_{14}d_{23} & d_{23}d_{13}d_{24} & d_{13}d_{34}d_{23} & d_{24}d_{34}d_{13} \\ d_{13}d_{14}d_{24} & d_{24}d_{14}d_{23} & d_{23}d_{14}d_{34} & d_{24}d_{34}d_{14} \end{bmatrix} \boldsymbol{x}; \quad d_{ij} = d_{ji} \tag{7}$$

where $d_{ij} = D_{ij}^{-1}$, that is, the elements in the matrix are reciprocals of the pairwise diffusion coefficients. There are six pairwise diffusion coefficients in a four component set, and so there are 20 combinations of six things taken three at a time. Clearly, four of these are missing in the above, and, after some scrutiny, it develops that these four are those in which one of the four digits is missing; that is, there is no subscript form like $d_{12}d_{13}d_{23}$. Physically, this makes sense since it means that every chemical component has an effect in each term. Since the quantity obtained as the Cramer determinant was not obviously a quadratic form *a priori*, the placement of the terms in the matrix in a quasi-symmetric form was somewhat arbitrary at the start and might need rearrangement.

The solution obtained can be put into the matrix-vector form given below, and the placement of the functions α_{ij}, defined below, is restricted by the form,

$$A \sum_{i=1}^{4} \frac{dx_i}{dz} = 0$$

where A is chosen and the functions $X_i(\boldsymbol{x})$ and α_{ij} are chosen and are defined below

$$\boldsymbol{N} = -\frac{c}{\phi(\boldsymbol{x})} \boldsymbol{W} \frac{d\boldsymbol{x}}{dz} \tag{8}$$

where the matrix $\boldsymbol{W}$ is

$$\begin{bmatrix} (1-x_1)X_1 + \alpha_1 & -x_1X_2 + \alpha_{13} + \alpha_{14} & -x_1X_3 + \alpha_{12} + \alpha_{41} & -x_1X_4 + \alpha_{21} + \alpha_{31} \\ -x_2X_1 + \alpha_{23} + \alpha_{24} & (1-x_2)X_2 + \alpha_2 & -x_2X_3 + \alpha_{21} + \alpha_{42} & -x_2X_4 + \alpha_{12} + \alpha_{32} \\ -x_3X_1 + \alpha_{32} + \alpha_{34} & -x_3X_2 + \alpha_{31} + \alpha_{43} & (1-x_3)X_3 + \alpha_3 & -x_3X_4 + \alpha_{13} + \alpha_{23} \\ -x_4X_1 + \alpha_{42} + \alpha_{43} & -x_4X_2 + \alpha_{41} + \alpha_{34} & -x_4X_3 + \alpha_{14} + \alpha_{24} & (1-x_4)X_4 + \alpha_4 \end{bmatrix}$$

Table 1. Definition of the Functions in Eqs. 8.

α_{12}	α_{21}	α_{13}	α_{31}	α_{14}	α_{41}	
$\frac{x_1x_2}{D_{13}D_{24}}$	$\frac{x_2x_1}{D_{23}D_{14}}$	$\frac{x_1x_3}{D_{12}D_{34}}$	$\frac{x_3x_1}{D_{32}D_{14}}$	$\frac{x_1x_4}{D_{12}D_{43}}$	$\frac{x_4x_1}{D_{42}D_{13}}$	$[D_{ij} = D_{ji}]$
α_{23}	α_{32}	α_{24}	α_{42}	α_{34}	α_{43}	
$\frac{x_2x_3}{D_{21}D_{34}}$	$\frac{x_3x_2}{D_{31}D_{24}}$	$\frac{x_2x_4}{D_{21}D_{43}}$	$\frac{x_4x_2}{D_{41}D_{23}}$	$\frac{x_3x_4}{D_{31}D_{42}}$	$\frac{x_4x_3}{D_{41}D_{32}}$	

and

$$X_1 = \frac{x_2}{D_{23}D_{24}} + \frac{x_3}{D_{23}D_{34}} + \frac{x_4}{D_{24}D_{34}},$$
$$X_2 = \frac{x_1}{D_{13}D_{14}} + \frac{x_3}{D_{13}D_{34}} + \frac{x_4}{D_{14}D_{34}}$$
$$X_3 = \frac{x_1}{D_{14}D_{12}} + \frac{x_2}{D_{12}D_{24}} + \frac{x_4}{D_{14}D_{24}},$$
$$X_4 = \frac{x_1}{D_{12}D_{13}} + \frac{x_2}{D_{23}D_{12}} + \frac{x_3}{D_{13}D_{23}} \tag{9}$$

(note that these have the same gross form as the ternary Cramer denominator), and

$$\alpha_i = \sum_{\substack{s=1 \\ s \neq i}}^{4} (\alpha_{is} + \alpha_{si}) \tag{10}$$

which is the sum of the six terms in which x_i appears in each term and α_{ij} is defined in Table 1.

It is seen that X_i contains no x_i, and each x_j has $D_{lj}D_{kj}$, $l \neq k \neq i \neq j$ in the denominator in Eq. 9. The X_i's are quasi-symmetric, as are the α_{ij}'s. Note also that every α_{ij} has a 1234 subscript property in some order, and, therefore, there are only three different ones. If one examines the matrix solution carefully, one finds that it is quasi-symmetric, although, in some cases, one must go back to the definitions of the functions. It is readily apparent also that the matrix is singular since the sum of the rows is zero.

The solution matrix can also be written in the form

$$\boldsymbol{N} = -\frac{c}{\phi(\boldsymbol{x})}[w_{ij}]\frac{d\boldsymbol{x}}{dz}$$

with

$$w_{ij} = -x_iX_j + x_i\frac{x_l + x_m}{D_{ij}D_{lm}}; \; i \neq j \neq l \neq m,$$
$$w_{ii} = (1-x_i)X_i + x_i\sum_s \frac{x_l + x_m}{D_{is}D_{lm}}; \; s \neq j \neq l \neq m.$$

If we were to assume that all the diffusivities were the same, then

$$D^2 w_{ij} = -x_i \sum_{s \neq j} x_s + x_i \sum_{\substack{s \neq i \\ s \neq j}} x_s;\; i \neq j,$$

$$= -x_i(1-x_j) + x_i(1-x_i-x_j) = -x_i^2,\; i \neq j,$$

$$D^2 w_{ii} = (1-x_i)(1-x_j) + 2x_i(1-x_i) = 1-x_i^2$$

and, hence, since the Cramer denominator equals D^{-3}

$$N = -cD \begin{bmatrix} 1-x_1^2 & -x_1^2 & -x_1^2 & -x_1^2 \\ -x_2^2 & 1-x_2^2 & -x_2^2 & -x_2^2 \\ -x_3^2 & -x_3^2 & 1-x_3^2 & -x_3^2 \\ -x_4^2 & -x_4^2 & -x_4^2 & 1-x_4^2 \end{bmatrix} \frac{d\boldsymbol{x}}{dz},$$

$$N = -cD\frac{d\boldsymbol{x}}{dz},$$

and so singularity is preserved.

Because we wish to simplify, if possible, the quaternary problem we will spend some time now on the structure of what we have already established. Some surprising solutions will surface. For example, if we examine the Cramer denominator (Eq. 7), we discover that it has the form

$$\begin{aligned}\phi(\boldsymbol{x}) &= \frac{x_1^2}{D_{12}D_{13}D_{14}} + \frac{x_1x_2}{D_{12}D_{13}D_{24}} + \frac{x_1x_3}{D_{12}D_{13}D_{34}} + \frac{x_1x_4}{D_{12}D_{14}D_{34}} \\ &+ \frac{x_2x_1}{D_{14}D_{21}D_{32}} + \frac{x_2^2}{D_{12}D_{24}D_{23}} + \frac{x_2x_3}{D_{12}D_{23}D_{34}} + \frac{x_2x_4}{D_{12}D_{24}D_{34}} \\ &+ \frac{x_3x_1}{D_{13}D_{14}D_{23}} + \frac{x_3x_2}{D_{13}D_{24}D_{32}} + \frac{x_3^2}{D_{13}D_{23}D_{34}} + \frac{x_3x_4}{D_{13}D_{24}D_{34}} \\ &+ \frac{x_4x_1}{D_{13}D_{14}D_{24}} + \frac{x_4x_2}{D_{14}D_{23}D_{24}} + \frac{x_4x_3}{D_{14}D_{23}D_{34}} + \frac{x_4^2}{D_{14}D_{24}D_{34}}\end{aligned} \quad (11)$$

where we use the commonality of some species in each row and each column, and, if we look at this a little more closely, we can, using the α_{ij} functions defined before, write

$$\begin{aligned}\phi(\boldsymbol{x}) = &\frac{x_1^2}{D_{12}D_{13}D_{14}} + \frac{\alpha_{12}}{D_{12}} + \frac{\alpha_{13}}{D_{13}} + \frac{\alpha_{14}}{D_{14}} \\ &+ \frac{\alpha_{21}}{D_{21}} + \frac{x_2^2}{D_{12}D_{23}D_{24}} + \frac{\alpha_{23}}{D_{23}} + \frac{\alpha_{24}}{D_{24}} \\ &+ \frac{\alpha_{31}}{D_{31}} + \frac{\alpha_{32}}{D_{32}} + \frac{x_3^2}{D_{31}D_{32}D_{34}} + \frac{\alpha_{34}}{D_{34}} \\ &+ \frac{\alpha_{41}}{D_{41}} + \frac{\alpha_{42}}{D_{42}} + \frac{\alpha_{43}}{D_{43}} + \frac{x_4^2}{D_{41}D_{42}D_{43}}.\end{aligned} \quad (12)$$

Using the expression for the Cramer denominator given by Eq. 7, we can produce some other interesting results. If we examine $\phi(\boldsymbol{x})$, in particular, the last three rows and the last three columns, we see that row two in the last three elements may be written $(x_2/D_{12})X_1$, while the third and the fourth rows (the last three elements) become

$$\frac{x_3}{D_{13}}X_1 + \frac{x_4}{D_{14}}X_1.$$

It then follows that $\phi(\boldsymbol{x})$ may be written

$$\phi(\boldsymbol{x}) = \left(\frac{x_2}{D_{12}} + \frac{x_3}{D_{13}} + \frac{x_4}{D_{14}}\right)X_1 + \frac{\alpha_{12}+\alpha_{21}}{D_{12}} + \frac{\alpha_{13}+\alpha_{31}}{D_{13}} + \frac{\alpha_{14}+\alpha_{41}}{D_{14}} + \frac{x_1^2}{D_{12}D_{13}D_{14}}. \quad (13)$$

Now, to find a similar representation involving X_2, we look at the first, third, and fourth rows, and first, third, and fourth columns, and, proceeding as above, one obtains

$$\phi(\boldsymbol{x}) = \left(\frac{x_1}{D_{21}} + \frac{x_3}{D_{23}} + \frac{x_4}{D_{24}}\right)X_2 + \frac{\alpha_{21}+\alpha_{12}}{D_{21}} + \frac{\alpha_{23}+\alpha_{32}}{D_{23}} + \frac{\alpha_{24}+\alpha_{42}}{D_{24}} + \frac{x_2^2}{D_{21}D_{23}D_{24}}. \quad (14)$$

The expansion in terms of X_3 follows from the elements of the first, second, and fourth columns, and first, second, and fourth rows. One obtains

$$\phi(\boldsymbol{x}) = \left(\frac{x_1}{D_{31}} + \frac{x_2}{D_{32}} + \frac{x_4}{D_{34}}\right)X_3 + \frac{\alpha_{13}+\alpha_{31}}{D_{31}} + \frac{\alpha_{23}+\alpha_{32}}{D_{32}} + \frac{\alpha_{34}+\alpha_{43}}{D_{34}} + \frac{x_3^2}{D_{31}D_{32}D_{34}}. \quad (15)$$

The expansion in terms of X_4 follows from the elements of the rows and columns in the upper lefthand corner and is

$$\phi(\boldsymbol{x}) = \left(\frac{x_1}{D_{41}} + \frac{x_2}{D_{42}} + \frac{x_3}{D_{43}}\right)X_4 + \frac{\alpha_{14}+\alpha_{41}}{D_{41}} + \frac{\alpha_{24}+\alpha_{42}}{D_{42}} + \frac{\alpha_{34}+\alpha_{43}}{D_{43}} + \frac{x_4^2}{D_{41}D_{42}D_{43}}. \quad (16)$$

We see also that there is a systematic scheme for the above relations. The expansions in terms of X_1 and X_4 are made directly from $\phi(\boldsymbol{x})$. The expansion in terms of X_2 and X_3 requires some minor symmetric juggling, more for X_3 than for X_4.

Simple Quaternary Representation

With the ternary system by some judicious juggling, we were able to reduce the fundamental equations to equations which had a linear operator. This is desirable since the operator determines the form of the solution and should enable one to produce a numerical solution, which is less likely to be unstable and to converge more rapidly. With this in mind, we will try to do the same with the quaternary system written in the form

$$\boldsymbol{N} = -\frac{c}{\phi(\boldsymbol{x})}\left[\boldsymbol{X}\frac{d\boldsymbol{x}}{dz} - \sum_j X_j \frac{dx_j}{dz}\cdot\boldsymbol{x} + \overline{\alpha}\frac{d\boldsymbol{x}}{dz}\right] \tag{17}$$

where $\boldsymbol{X}$ is the diagonal matrix with X_i on the ith term of the diagonal and where we note that the quasi-symmetry in $\overline{\alpha}$ in the second matrix which contains the functions belonging to α_{ij}

$$\overline{\alpha} = \begin{bmatrix} \alpha_1 & \alpha_{13}+\alpha_{14} & \alpha_{12}+\alpha_{41} & \alpha_{21}+\alpha_{31} \\ \alpha_{23}+\alpha_{24} & \alpha_2 & \alpha_{21}+\alpha_{42} & \alpha_{12}+\alpha_{32} \\ \alpha_{32}+\alpha_{34} & \alpha_{31}+\alpha_{43} & \alpha_3 & \alpha_{13}+\alpha_{32} \\ \alpha_{42}+\alpha_{43} & \alpha_{41}+\alpha_{34} & \alpha_{14}+\alpha_{24} & \alpha_4 \end{bmatrix}$$

$$= \begin{bmatrix} \overline{\alpha}_1 \\ \overline{\alpha}_2 \\ \overline{\alpha}_3 \\ \overline{\alpha}_4 \end{bmatrix}, \tag{18}$$

which is singular and

$$\overline{\alpha} = \begin{bmatrix} \alpha_1 & \dfrac{x_1(x_3+x_4)}{1234} & \dfrac{x_1(x_2+x_4)}{1324} & \dfrac{x_1(x_2+x_3)}{1423} \\ \dfrac{x_2(x_3+x_4)}{1234} & \alpha_2 & \dfrac{x_2(x_1+x_4)}{1423} & \dfrac{x_2(x_1+x_3)}{1324} \\ \dfrac{x_3(x_2+x_4)}{1324} & \dfrac{x_3(x_1+x_4)}{1423} & \alpha_3 & \dfrac{x_3(x_1+x_2)}{1234} \\ \dfrac{x_4(x_2+x_3)}{1423} & \dfrac{x_4(x_1+x_3)}{1324} & \dfrac{x_4(x_1+x_2)}{1234} & \alpha_4 \end{bmatrix} \tag{19}$$

where in the denominator we have only written the subscripts of $D_{ij}D_{lm}$.

In an effort to obtain a simpler representation of the inversion given by Eq. 8 we will use Eq. 17 in a form by writing first the representation for N_1

$$-N_1 = \frac{c}{\phi(\boldsymbol{x})}\left[X_1\frac{dx_1}{dz} - x_1\sum_j X_j\frac{dx_j}{dz} + \overline{\alpha}_1\frac{d\boldsymbol{x}}{dz}\right]$$

where $\overline{\alpha}_1$ is the first row of $\overline{\alpha}$. Then

$$\frac{-N_1\phi(\boldsymbol{x})}{c} = [(1-x_1)X_1 + \alpha_1]\frac{dx_1}{dz} - [x_1X_2 - \alpha_{13} - \alpha_{14}]\frac{dx_2}{dz}$$
$$-[x_1X_3 - \alpha_{12} - \alpha_{41}]\frac{dx_3}{dz} - [x_1X_4 - \alpha_{21} - \alpha_{31}]\frac{dx_4}{dz}.$$

This equation is not as mean as it looks for all of the α_{ij}'s and α_{ji}'s contain an x_1. A little juggling with the formula

$$A\sum\frac{dx_j}{dz} = 0$$

will cast it into a form

$$\frac{-N_1\phi(\boldsymbol{x})}{c} = [(1-x_1)X_1]\frac{dx_1}{dz} - (x_1X_2 + \beta_{12})\frac{dx_2}{dz}$$
$$-(x_1X_3 + \beta_{13})\frac{dx_3}{dz} - (x_1X_4 + \beta_{14})\frac{dx_4}{dz}.$$

Notice what one would call $\beta_{11} = 0$ and we have the following for N_1, N_2, N_3, and N_4

$$\beta_{12} = \alpha_{12} + \alpha_{21} + \alpha_{31} + \alpha_{41}, \quad \beta_{21} = \alpha_{21} + \alpha_{12} + \alpha_{32} + \alpha_{42},$$
$$\beta_{13} = \alpha_{13} + \alpha_{31} + \alpha_{14} + \alpha_{21}, \quad \beta_{23} = \alpha_{23} + \alpha_{32} + \alpha_{12} + \alpha_{24},$$
$$\beta_{14} = \alpha_{14} + \alpha_{41} + \alpha_{12} + \alpha_{13}, \quad \beta_{24} = \alpha_{24} + \alpha_{42} + \alpha_{23} + \alpha_{21},$$
$$\beta_{11} = 0, \quad \beta_{22} = 0,$$
$$\beta_{31} = \alpha_{31} + \alpha_{13} + \alpha_{23} + \alpha_{43}, \quad \beta_{41} = \alpha_{41} + \alpha_{14} + \alpha_{34} + \alpha_{24},$$
$$\beta_{32} = \alpha_{32} + \alpha_{23} + \alpha_{34} + \alpha_{13}, \quad \beta_{42} = \alpha_{42} + \alpha_{24} + \alpha_{43} + \alpha_{14},$$
$$\beta_{34} = \alpha_{34} + \alpha_{43} + \alpha_{31} + \alpha_{32}, \quad \beta_{43} = \alpha_{43} + \alpha_{34} + \alpha_{41} + \alpha_{42},$$
$$\beta_{33} = 0, \quad \beta_{44} = 0.$$

and also

$$\frac{-\boldsymbol{N}\phi(\boldsymbol{x})}{c} = \begin{bmatrix} (1-x_1)X_1 & -x_1X_2 - \beta_{12} & -x_1X_3 - \beta_{13} & -x_1X_4 - \beta_{14} \\ -x_2X_1 - \beta_{21} & (1-x_2)X_2 & -x_2X_3 - \beta_{23} & -x_2X_4 - \beta_{24} \\ -x_3X_1 - \beta_{31} & -x_3X_2 - \beta_{32} & (1-x_3)X_3 & -x_3X_4 - \beta_{34} \\ -x_4X_1 - \beta_{41} & -x_4X_2 - \beta_{42} & -x_4X_3 - \beta_{43} & (1-x_4)X_4 \end{bmatrix}\frac{d\boldsymbol{x}}{dz}.$$

The nondiagonal terms have a connection with the Cramer determinant when multiplied by the symmetric matrix

$$\begin{bmatrix} 1 & \frac{1}{D_{12}} & \frac{1}{D_{13}} & \frac{1}{D_{14}} \\ \frac{1}{D_{12}} & 1 & \frac{1}{D_{23}} & \frac{1}{D_{24}} \\ \frac{1}{D_{13}} & \frac{1}{D_{23}} & 1 & \frac{1}{D_{34}} \\ \frac{1}{D_{14}} & \frac{1}{D_{24}} & \frac{1}{D_{34}} & 1 \end{bmatrix}$$

However, taking the sum of the rows in the product does not have the desired result which occurred with the ternary systems because the unity terms on the diagonal do not disappear and so a relation analogous to Eq. 6 does not result. In addition, the above process, which looks so promising, introduces a substantial number of other terms, and, while there is some redundancy which could be removed, the overall result is not much simpler and does not reduce to a simple linear operator as in the ternary system.

Numerical Diffusion Problem

Solutions of the 1-D diffusion problem have been presented for the Stefan-Maxwell equations, the best known, as mentioned earlier, being that developed by Krishna and Standard (1976), which involve the solution of the set of equations treated as ordinary differential equations in the mol fractions x_i for fixed values of the fluxes. To determine the fluxes, this set of equations then must be solved by some numerical procedure. This has apparently produced in some cases instability and some nonconvergence, and has been studied by Taylor (Taylor and Webb, 1981; Taylor, 1982) who has, in addition, developed some interesting and useful results in a series of papers referenced in his book.

The purpose of this section is then to present a numerical solution method for the standard 1-D multicomponent diffusion problem with specified boundary values at $z = 0$ and $z = l$ for all species. The fluxes will be constant and unknown, and we assume that there is equimolar diffusion. While the method is applicable to n species, our illustration will be for four. The equations to be treated are Eq. 1

$$c\frac{d\boldsymbol{x}}{dz} = \boldsymbol{B}\boldsymbol{x}, \quad 0 < z < l,$$

$$\boldsymbol{x}(0) = \boldsymbol{x}_0, \quad \boldsymbol{x}(l) = \boldsymbol{x}_l.$$

$\boldsymbol{B}$ is given in Eq. 1. We cast these equations in dimensionless form using the standard notation; then, we have

$$\frac{dx_i}{d\xi} = \sum_j \frac{Z_j x_i - Z_i X_j}{\beta_{ij}}; \quad i \neq j,$$

$$\beta_{ij} = \frac{D_{ij}}{D}; \quad \beta_{ij} = \beta_{ji}; \quad Z_j = \frac{N_j l}{cD}$$

where D is normally one of the D_{ij}. We write these equations in the form (where $\boldsymbol{A}$ is defined below)

$$\frac{d\boldsymbol{x}}{d\xi} = \boldsymbol{A}\boldsymbol{x}, \quad \boldsymbol{x}(0) = \boldsymbol{x}_0, \tag{20}$$

the formal solution of which is

$$\boldsymbol{x} = \exp(A\xi)\boldsymbol{x}_0 \tag{21}$$

In the matrix $\boldsymbol{A}$ there are n unknown values of Z_i which are constant and $\sum_i Z_i = 0$. Our problem is to determine the set $\{Z_i\}$ from the equation

$$\boldsymbol{x}_l = \exp(\boldsymbol{A})\boldsymbol{x}_0. \tag{22}$$

In order to solve this equation we will develop a different representation for $\boldsymbol{A}$, which follows

$$\boldsymbol{A} = \begin{bmatrix} \frac{Z_2}{\beta_{12}} + \frac{Z_3}{\beta_{13}} + \frac{Z_4}{\beta_{14}} & -\frac{Z_1}{\beta_{12}} & -\frac{Z_1}{\beta_{13}} & -\frac{Z_1}{\beta_{14}} \\ -\frac{Z_2}{\beta_{21}} & \frac{Z_1}{\beta_{21}} + \frac{Z_3}{\beta_{23}} + \frac{Z_4}{\beta_{24}} & -\frac{Z_2}{\beta_{23}} & -\frac{Z_2}{\beta_{24}} \\ -\frac{Z_3}{\beta_{31}} & -\frac{Z_3}{\beta_{32}} & \frac{Z_1}{\beta_{31}} + \frac{Z_2}{\beta_{32}} + \frac{Z_4}{\beta_{34}} & -\frac{Z_3}{\beta_{34}} \\ -\frac{Z_4}{\beta_{41}} & -\frac{Z_4}{\beta_{42}} & -\frac{Z_4}{\beta_{43}} & \frac{Z_1}{\beta_{41}} + \frac{Z_2}{\beta_{42}} + \frac{Z_3}{\beta_{43}} \end{bmatrix} \tag{23}$$

which is different from the form used earlier.

We shall decompose $\boldsymbol{A}$ into a sum of matrices which makes use of the linearity in the $\{Z_i\}$; so

$$\boldsymbol{A} = \begin{bmatrix} 0 & -\frac{1}{\beta_{12}} & -\frac{1}{\beta_{13}} & -\frac{1}{\beta_{14}} \\ 0 & \frac{1}{\beta_{12}} & 0 & 0 \\ 0 & 0 & \frac{1}{\beta_{13}} & 0 \\ 0 & 0 & 0 & \frac{1}{\beta_{14}} \end{bmatrix} Z_1 + \begin{bmatrix} \frac{1}{\beta_{12}} & 0 & 0 & 0 \\ -\frac{1}{\beta_{12}} & 0 & -\frac{1}{\beta_{23}} & -\frac{1}{\beta_{24}} \\ 0 & 0 & \frac{1}{\beta_{23}} & 0 \\ 0 & 0 & 0 & \frac{1}{\beta_{24}} \end{bmatrix} Z_2 + \begin{bmatrix} \frac{1}{\beta_{13}} & 0 & 0 & 0 \\ 0 & \frac{1}{\beta_{23}} & 0 & 0 \\ -\frac{1}{\beta_{13}} & -\frac{1}{\beta_{23}} & 0 & -\frac{1}{\beta_{34}} \\ 0 & 0 & 0 & \frac{1}{\beta_{34}} \end{bmatrix} Z_3 + \begin{bmatrix} \frac{1}{\beta_{14}} & 0 & 0 & 0 \\ 0 & \frac{1}{\beta_{24}} & 0 & 0 \\ 0 & 0 & \frac{1}{\beta_{34}} & 0 \\ -\frac{1}{\beta_{14}} & -\frac{1}{\beta_{24}} & -\frac{1}{\beta_{34}} & 0 \end{bmatrix} Z_4 \quad (24)$$

Such a decomposition exists for any n. We write the above as

$$\boldsymbol{A} = \boldsymbol{A}_1 Z_1 + \boldsymbol{A}_2 Z_2 + \boldsymbol{A}_3 Z_3 + \boldsymbol{A}_4 Z_4$$

Each of the $\boldsymbol{A}_i$ is singular (and each has very simple eigenvalues). We consider now Eq. 20, 21, and 22 and the general procedure will involve a sequence of paired steps. Approximate values for the fluxes Z_i will be found by solving a set of linear simultaneous algebraic equations obtained by keeping only the first term of the exponential solution. This step will be followed by solving the differential equation Eq. 21 with the values of Z_i so obtained. If we keep only the first term of the exponential solution of Eq. 22, we obtain a vector $\boldsymbol{v}$

$$\boldsymbol{v} = \left[\boldsymbol{I} + \sum Z_i \boldsymbol{A}_i \xi \right] \boldsymbol{x}_0 \quad (25)$$

To find the first set of Z_i's we set $\boldsymbol{v} = \boldsymbol{x}_l$ and $\xi = 1$ so

$$\boldsymbol{x}_l - \boldsymbol{x}_0 = \sum Z_i \boldsymbol{A}_i \boldsymbol{x}_0$$

This is a singular set of algebraic equations in the Z_i, so we replace the last equation by $\sum Z_i = 0$. Let us call the solution so obtained $\{Z_i^0\}$. We then consider the set of differential equations

$$\frac{d\boldsymbol{x}_1}{d\xi} = \boldsymbol{A}^0 \boldsymbol{x}_1; \quad \boldsymbol{x}_1(0) = \boldsymbol{x}_0 \quad (26)$$

This set of equations is also singular so that we will substitute $\sum_i x_i = 1$ for the last equation, giving the solution

$$\boldsymbol{x}_1 = \exp(\boldsymbol{A}^0 \xi) \boldsymbol{x}_0$$

which we rewrite as

$$\boldsymbol{x}_0 = \exp(-\boldsymbol{A}^0 \xi) \boldsymbol{x}_1$$

and substitute this into the solution to obtain

$$\boldsymbol{x} = \exp(\boldsymbol{A}\xi)\exp(-\boldsymbol{A}^0 \xi) \boldsymbol{x}_1$$

which we treat as before, keeping only the first-order term in the expansion of the exponential to give

$$\boldsymbol{v} = \left[\boldsymbol{I} + \sum \boldsymbol{A}_i (Z_i - Z_i^0) \xi \right] \boldsymbol{x}_1$$

and at $\xi = 1$, we obtain

$$\boldsymbol{x}_l - \boldsymbol{x}_1 = \sum \boldsymbol{A}_i (Z_i - Z_i^0) \boldsymbol{x}_1 \quad (27)$$

which is a new set of linear simultaneous algebraic equations for $\{Z_i\}$, which we treat as before. Call the solution $\{Z_i^1\}$ which we use in

$$\frac{d\boldsymbol{x}_2}{d\xi} = \boldsymbol{A}^1 \boldsymbol{x}_2; \quad \boldsymbol{x}_2(0) = \boldsymbol{x}_0$$

which has the solution

$$\boldsymbol{x}_2 = \exp(\boldsymbol{A}^1 \xi) \boldsymbol{x}_0$$

and as before

$$\boldsymbol{x}_0 = \exp(-\boldsymbol{A}^1 \xi) \boldsymbol{x}_2$$

Thus

$$\boldsymbol{x} = \exp(\boldsymbol{A}\xi) \boldsymbol{x}_0 = \exp(\boldsymbol{A}\xi)\exp(-\boldsymbol{A}^1 \xi) \boldsymbol{x}_2,$$
$$\boldsymbol{v} - \boldsymbol{x}_2 = \sum \boldsymbol{A}_i \xi (Z_i - Z_i^1) \boldsymbol{x}_2$$

and, with $\xi = 1$, $\boldsymbol{v} = \boldsymbol{x}_l$, we solve for a new set of $\{Z_i^2\}$. The procedure then repeats itself with equations

$$A^k = \sum A_i Z_i^k,$$

$$\frac{d\boldsymbol{x}_{k+1}}{d\xi} = \boldsymbol{A}^k \boldsymbol{x}_{k+1}; \quad \boldsymbol{x}_{k+1}(0) = \boldsymbol{x}_0,$$

$$\boldsymbol{x}_l - \boldsymbol{x}_{k+1} = \sum \boldsymbol{A}_i \left(Z_i^{k+1} - Z_i^k\right) \boldsymbol{x}_{k+1}$$

with the hope that

$$\lim_{k \to \infty} \boldsymbol{x}_k(1) = \boldsymbol{x}_l.$$

The scheme described above can best be thought of as a quasi-Newton scheme for the nonlinear equation

$$\boldsymbol{F}(\boldsymbol{Z}) = \exp(\boldsymbol{AZ})\boldsymbol{x}_0; \quad \boldsymbol{F}: \mathbb{R}^4 \to \mathbb{R} =^4$$

Returning to Eq. 27, we see that our wish is to solve $\boldsymbol{F}(\boldsymbol{Z}_\infty) = \boldsymbol{x}_l$. If we apply Newton's method with an initial estimate $\boldsymbol{Z}_0 = \boldsymbol{0}$, we find that

$$\boldsymbol{F}'(\boldsymbol{0}) = [\boldsymbol{A}_1\boldsymbol{x}_0 \;\; \boldsymbol{A}_2\boldsymbol{x}_0 \;\; \boldsymbol{A}_3\boldsymbol{x}_0 \;\; \boldsymbol{A}_4\boldsymbol{x}_0]$$

Forgetting for the moment the problem of invertability, we see that the next approximation to $\boldsymbol{Z}_\infty$ is

$$\boldsymbol{Z}_1 = \boldsymbol{F}(\boldsymbol{0})^{-1}(\boldsymbol{x}_l - \boldsymbol{x}_0)$$

yielding $\boldsymbol{x}_1 = \boldsymbol{F}(\boldsymbol{Z}_1)$. At the next step in Newton's method, one needs to compute $\boldsymbol{F}'(\boldsymbol{Z}_1)$. Our method approximates $\boldsymbol{F}'(\boldsymbol{Z}_n)$ by

$$[\boldsymbol{A}_1\boldsymbol{x}_n \;\; \boldsymbol{A}_2\boldsymbol{x}_n \;\; \boldsymbol{A}_3\boldsymbol{x}_n \;\; \boldsymbol{A}_4\boldsymbol{x}_n].$$

How well this latter approximates $\boldsymbol{F}'(\boldsymbol{Z}_n)$ can be shown to depend on how well

$$\exp(\boldsymbol{A}(\boldsymbol{Z} + \boldsymbol{Z}_n))\boldsymbol{x}_0$$

is approximated by

$$\exp(\boldsymbol{AZ})\exp(\boldsymbol{AZ}_n)\boldsymbol{x}_0$$

for small $\boldsymbol{Z}$. Since matrix exponentials do not commute unless the respective matrices commute, we would expect that how well this approximation works depends on the size of commutators of $\boldsymbol{AZ}_{n+1}$ and $\boldsymbol{AZ}_n$.

In the implementation of the quasi-Newton method we have applied the Runge-Kutta-Fehlberg method, described in Burden and Faires (2001), to solve the set of equations

$$\frac{d\boldsymbol{x}_{k+1}}{d\xi} = \boldsymbol{A}^k \boldsymbol{x}_{k+1}, \quad 0 < \xi < 1,$$

$$\boldsymbol{x}_{k+1}(0) = \boldsymbol{x}_0$$

for each k, $k = 1, 2, 3, \ldots$. This method adapts the number and position of the nodes used in the approximation to ensure that the local truncation error is kept within a specified bound. It consists of using a Runge-Kutta method with local truncation error of order five to estimate the local error in a Runge-Kutta method of order four and then adjusting the step size to keep the local error within a specified bound; in our examples the tolerance was 10^{-5}. In the examples to follow it took less than 20 iterations to have a convergent result. The scheme is very robust.

Numerical Examples

Example 1

This is taken directly from Taylor and Krishna (1993, p. 103). Components are hydrogen (1), nitrogen (2), and carbon dioxide (3).

Diffusion path length $l = 85.9$ mm
Temperature = 35.2°C

At $z = 0$,	$x_{10} = 0.00000$	At $z = l$,	$x_{1l} = 0.50121$
	$x_{20} = 0.50086$		$x_{2l} = 0.49879$
	$x_{30} = 0.49914$		$x_{3l} = 0.00000$

Pairwise diffusion coefficients

$$D_{12} = 83.3 \text{ m}^2/\text{s} \times 10^{-6} \quad \beta_{12} = 1$$

$$D_{13} = 48.0 \text{ m}^2/\text{s} \times 10^{-6} \quad \beta_{13} = 0.8163$$

$$D_{23} = 16.8 \text{ m}^2/\text{s} \times 10^{-6} \quad \beta_{23} = 0.20168$$

Total concentration $c = 39.513$ mol/m^3

$$Z_i = 26.087\, N_i$$

Figure 1 shows the composition profiles, and, as stated by Taylor and Krishna, the nitrogen flux is substantially higher

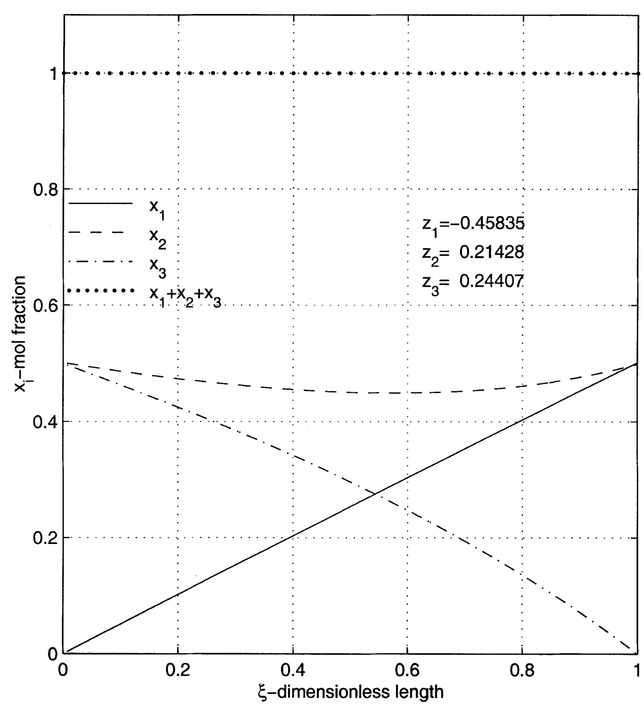

Figure 1. Composition profiles with abnormal fluxes.

Table 2. Boundary Conditions in Examples 2a, 2b, and 2c.

Fig.	x_{10}	x_{20}	x_{30}	x_{1l}	x_{2l}	x_{3l}
2a	0.55	0.05	0.40	0.01	0.45	0.54
2b	0.55	0.05	0.40	0.10	0.72	0.18
2c	0.55	0.05	0.40	0.01	0.98	0.01

than one would anticipate from the gross gradient. In fact, the flux of nitrogen approaches that of the flux of carbon dioxide. The profiles show some curvature and are strictly monotonic. Here we had to solve Eq. 26 reversely by starting at $\xi = 1$.

Example 2

This is also chosen from Example 4.2.4 of Taylor and Krishna and illustrates the effect on the solution of changes in boundary compositions with hydrogen (1), nitrogen (2), and carbon dichloride difluoride (3). The pairwise diffusion coefficients are

$$D_{12} = 77.0 \text{ m}^2/\text{s} \times 10^{-6} \quad \beta_{12} = 2.3293$$

$$D_{13} = 33.1 \text{ m}^2/\text{s} \times 10^{-6} \quad \beta_{13} = 1.00000$$

$$D_{23} = 8.1 \text{ m}^2/\text{s} \times 10^{-6} \quad \beta_{23} = 0.24482$$

The different cases considered are given in Table 2.

While Figure 2a is a normal case in the sense that the fluxes are in the directions expected, they are somewhat different than expected. Figure 2b is an abnormal case since it appears that the flux of component three is the reverse of the direction. Figure 2c is a really abnormal case since it shows that component three, in spite of having a large superficial gradient, has almost no flux and substantial profile curvature.

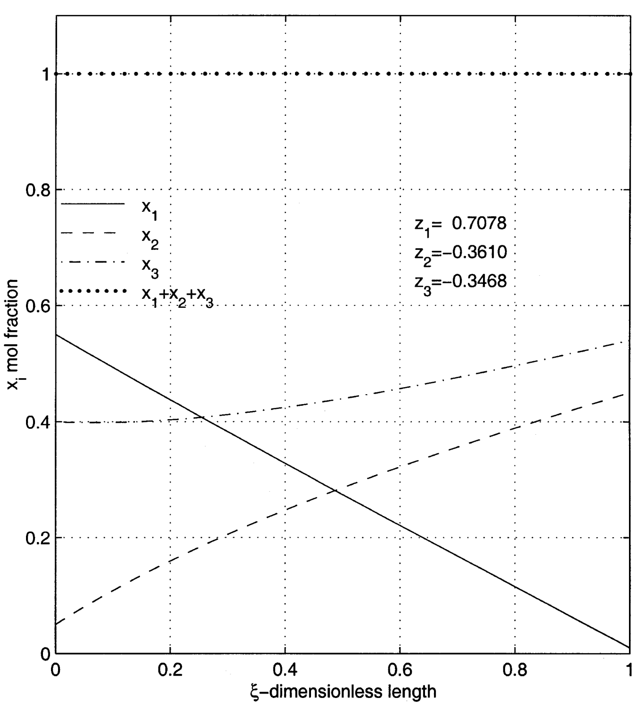

Figure 2a. Fluxes that are normal, but with surprising values.

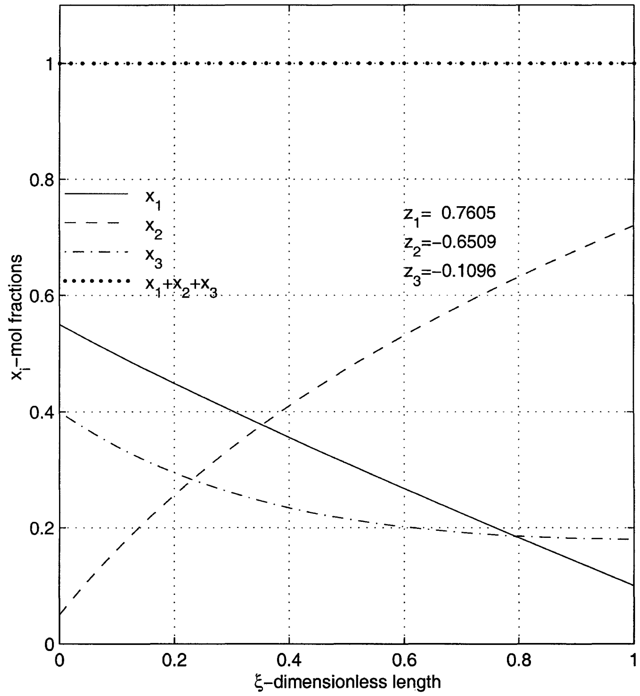

Figure 2b. Abnormal flux in component three.

Example 3

This is an eight component case in which the relative pairwise diffusivities vary by about a factor of seven and there are 28 of them. The boundary values are given in Table 3 and the numerical results are in Figure 3.

This is a relatively normal case since the fluxes are in the same direction as their superficial values. It may be said,

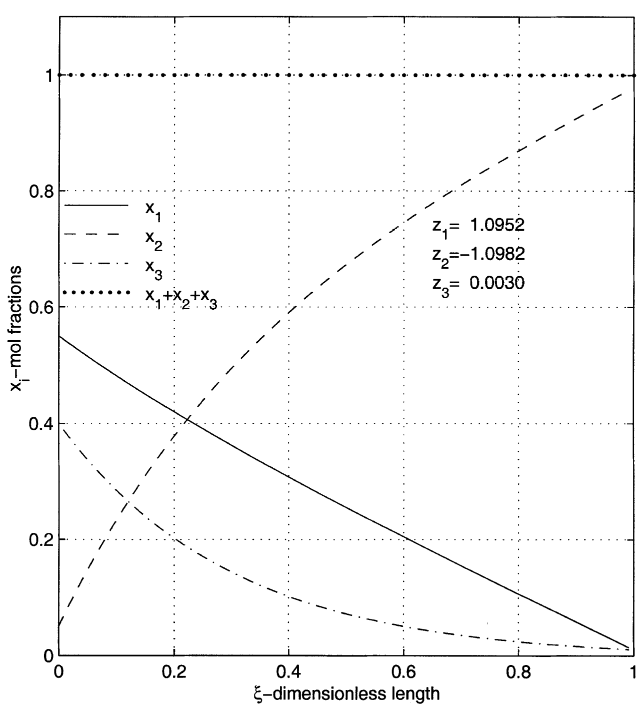

Figure 2c. Very abnormal flux in component three.

Table 3. Boundary Conditions in the Eight Components in Example 3 and Figure 3.

ξ, x_i	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8
$\xi = 0$	0.30	0.35	0.05	0.05	0.10	0.15	0.00	0.00
$\xi = 1$	0.05	0.00	0.00	0.10	0.00	0.25	0.10	0.50

however, that while the superficial flux of x_8 is greater in absolute value than that of x_1, the actual flux is less. The profiles show some curvature, but most appear to be relatively straight lines between boundary values, except that of x_8. The chemical species used in these calculations were H_2 (1), O_2 (2), N_2 (3), CO (4), CO_2 (5), CH_4 (6), C_2H_4 (7), and C_2H_6 (8). Many of the pairwise coefficients were calculated using the Fuller-Schettler-Giddings (Fuller et al., 1966) scheme or were those listed in the same source.

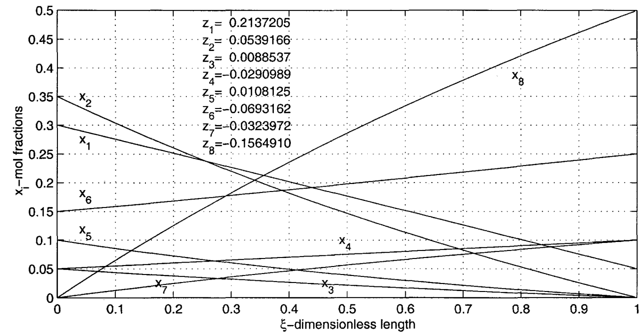

Figure 3. Eight-component case with tendency toward straight line profiles.

Example 4

This is a six component case with H_2 (1), O_2 (2), N_2 (3), CO (4), CO_2 (5), and CH_4 (6), so there are 15 pairwise diffusion coefficients with a spread of values of over 11. There are no real surprises here with the possible exception that the flux of x_5 is negative, as seen in Figure 4. Otherwise, curvature in minimal.

Continuous Distribution of Components

We will now consider a slightly different approach in which we assume that the number of components is very large and, in fact, that there is a continuous distribution of components. In order to do this it is easier and, perhaps, even necessary, to change the procedure. With a large number of components, say 60, in order to proceed as earlier, it could be necessary to introduce 1,770 pairwise diffusion coefficients, all of which probably must be estimated by the methods of Fuller et al. (1966). Let us now consider the problem in which there is a continuous distribution of components, first, in which no species is present in finite amount, and, second, in which some species are present in the finite amount, but the remainder as a continuous distribution.

To start this effort, we write the Stefan-Maxwell equations in the form

$$-c\frac{dx_i}{dz} = N_i \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{x_j}{D_{ij}} - x_i \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{N_j}{D_{ij}}, \quad 0 < z < l, \quad i = 1,\ldots,N. \tag{28}$$

If we suppose that p is a component designating variable and $x(p)dp$ is the mol fraction of that component in the mixture, then

$$\int_{p_l}^{p_g} x(p)dp = 1$$

where p_l is the lowest p and p_g is the greatest p of the continuous variable, $p_l \le p \le p_g$. The total fluxes of these variables will be $N(p)dp$ where

$$\int_{p_l}^{p_g} N(p)dp = 0$$

if we assume equimolarity of diffusion. The pairwise diffusion coefficients will be $D(p,q)$ where D is a function of two variables p and q, $p_l \le q \le p_g$. If $c(p)dp$ is the concentration of component p, then

$$\int_{p_l}^{p_g} c(p)dp = c$$

and $c(p)dp/c = x(p)dp$, and c is a constant. The Stefan-Maxwell equations now become

$$-c\frac{\partial x(p)}{\partial z} = N(p)\int_{p_l}^{p_g}\frac{x(q)}{D(p,q)}dq - x(p)\int_{p_l}^{p_g}\frac{N(q)}{D(p,q)}dq.$$

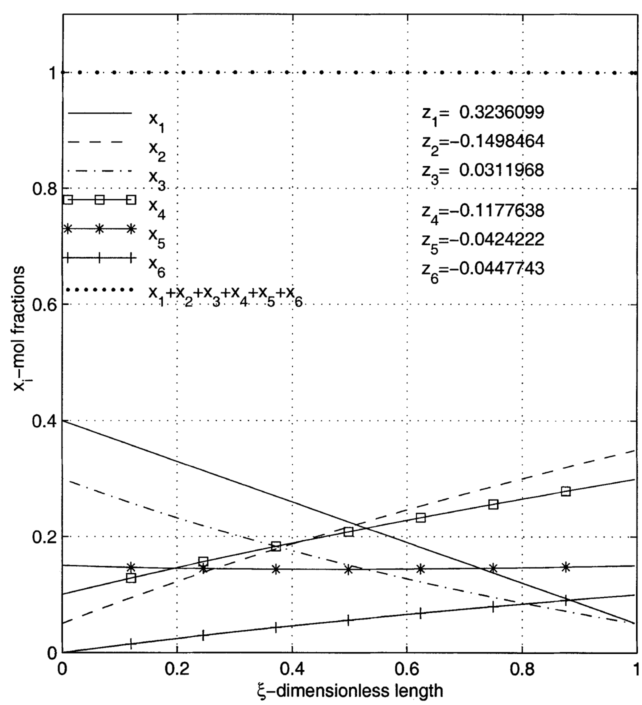

Figure 4. Component five with a flat profile and a negative flux.

If we make the change of variables by normalizing $D(p,q)$ as before, then

$$\frac{N(p)}{D(p_l,p_l)}\frac{l}{c}=Z(p);\quad \beta(p,q)=\frac{D(p,q)}{D(p_l,p_l)};\quad \xi=\frac{z}{l},$$

then Eq. 28 becomes

$$-\frac{\partial x(p)}{\partial \xi}=Z(p)\int_{p_l}^{p_g}\frac{x(q)}{\beta(p,q)}dq-x(p)\int_{p_l}^{p_g}\frac{Z(q)}{\beta(p,q)}dq, \tag{29}$$

and, if we assume that we have 1-D steady-state diffusion at constant pressure, we must specify the mol fraction distribution at $z=0$ and $z=l$, or at $\xi=0$ and $\xi=1$. At $\xi=0$ $x(p)=x^0(p)$ and at $\xi=1$, $x(p)=x^l(p)$.

Having a continuous distribution of components implies that we must have a scheme for determining the pairwise diffusion coefficients for that infinite distribution. One probably would only be interested in such a problem when the mixture has some organized system in its composition. One that comes to mind immediately, of course, is that of a continuous distribution of hydrocarbons. The building blocks of hydrocarbons, in general, vary from C to CH to CH_2 with a few CH_3's added on. Trying to compute the average $CH_\times$ is a problem. For saturated hydrocarbons $CH_\times$ is $CH_{2\pm}$. For unsaturated hydrocarbons $CH_\times$ will be $CH_{2\mp}$ or $CH_{1\pm}$. If we use the Fuller formula (Taylor and Krishna, 1993, p. 68) for pairwise diffusion constants we have

$$D_{ij}=c\frac{T^{7/4}}{P}\frac{\sqrt{\frac{1}{M_i}+\frac{1}{M_j}}}{\left(\sqrt[3]{V_i}+\sqrt[3]{V_j}\right)^2}$$

where M_i and M_j are the molecular weights and V_i and V_j are the partial molecular diffusion volumes. For carbon, the appropriate partial diffusion volume is 15.9 and, for hydrogen, it is 2.31. These values come from Taylor and Krishna (1993, p. 69). For CH_2, the appropriate partial diffusion volume is 20.53. For the average, we would take 20 and for the molecular weight 13.8 p and 20 p for the approximate V_i. The Fuller formula for a hydrocarbon mixture then will be

$$D(p_i,p_j)=c\frac{T^{1.75}}{P}\frac{\sqrt{\frac{1}{p_i}+\frac{1}{p_j}}}{\left(\sqrt[3]{p_i}+\sqrt[3]{p_j}\right)^2}\frac{1}{\sqrt{13.8}\,(20)^{2/3}}$$

and, if we choose $T=500$ K, $P=500{,}000$ Pa and with $c=1.013\times10^{-2}$, D will be in meters squared per second (multiply the above by 10^{-6}),

$$D(p_i,p_j)=36.8\frac{\sqrt{\frac{1}{p_i}+\frac{1}{p_j}}}{\left(\sqrt[3]{p_i}+\sqrt[3]{p_j}\right)^2}\times10^{-6}(\mathrm{m^2/s})$$

Now, with a little manipulation, one can discover a different form for this relation with which it is easier to compute. While we will not show a number of possibilities, let us consider one that seems like the best and easiest. If we write

$$\frac{\sqrt{\frac{1}{p}+\frac{1}{q}}}{\left(\sqrt[3]{p}+\sqrt[3]{q}\right)^2}=\frac{1}{p^{7/12}q^{7/12}}\frac{\sqrt{\frac{1}{p^{7/6}q^{1/6}}+\frac{1}{q^{7/6}p^{1/6}}}}{\left(\frac{1}{p^{1/3}}+\frac{1}{q^{1/3}}\right)^2}$$

$$=\frac{1}{p^{7/12}q^{7/12}}w$$

and, if we compute w for values of p and q from $p=q=5$ to $p=q=20$ in various increments of p and q separately, we will find that the average value of w will be 0.3567 with a standard deviation of 0.0053 and the value of w for $p=q$ is $\sqrt{2}/4\approx0.3536$. If in addition we normalize the $D(p,q)$ by $D(p_l,p_l)$ then (with $p_l=6$)

$$\beta_{pq}=\frac{8.09}{p^{7/12}q^{7/12}} \tag{30}$$

In cases where we make calculations for a large number of chemical species we will use the above formula for the computation with the pairwise normalized diffusivities. The normalization factor used above is specific to the numerical solutions which will follow where we have used D (6,6).

More Examples

We are now in position to compute with the Stefan-Maxwell equations for the continuous distribution case. We will use a lumped constant model for all of these.

Example 5

This is a problem in which the continuous distribution is described at the two endpoints by

$$x_0(p,0)=\begin{cases}\frac{1}{2{,}365}(p-2)(p-16)^2; & 6\le p\le16,\\ 0; & 16\le p\le20,\end{cases}$$

$$x_l(p,l)=\begin{cases}\frac{1}{444}(p-12)(30-p); & 12\le p\le20,\\ 0; & 6\le p\le12\end{cases} \tag{31}$$

where we think of p as a continuous variable. We will use only integers in [6, 20] for p

$$x_i=x(p_i,\xi),\quad i=1,2,3,\ldots,15,$$
$$p_1=6,\ p_2=7,\ldots,p_i=i+5,\ldots,p_{15}=20.$$

The normalization factors above are for fifteen components. For the diffusivities, we use Eq. 30. The boundary values are listed in Table 4 and are computed from the definitions in the problem. The calculations in Figure 5a show what appear to be almost straight lines. If one calculates the difference between these solution curves and the corresponding straight lines, one obtains Figure 5b which shows that this difference

Table 4. Boundary Conditions for the 15 Components in Example 5 and Figure 5a.

i	1	2	3	4	5	6	7	8
$x_i(0)$	.1691	.1712	.1624	.1450	.1218	.0951	.0677	.0419
$x_i(l)$	0	0	0	0	0	0	0	.0383
p_i	6	7	8	9	10	11	12	13
i	9	10	11	12	13	14	15	
$x_i(0)$	.0203	.0055	0	0	0	0	0	
$x_i(l)$	.0721	.1014	.1261	.1464	.1622	.1734	.1802	
p_i	14	15	16	17	18	19	20	

for curves with positive slopes are concave negative while those with negative slopes are concave positive, but not by much. It is interesting to determine what happens if one uses random diffusivities between 0.25 and 1.25. The profiles are not discernibly different from those in Figure 5a and the comparison of the fluxes given in Figure 5c with the dots representing the formula diffusivities and the asterisks the random diffusivities case. The random diffusivities range is well outside the physical range of β_{ij}.

Example 6

This example is the same as Example 5. However, instead of using 15 components as integers, we will now use 57, but with the same distribution from $p=6$ to $p=20$ so now

$$p_i = 6 + \frac{i-1}{4},\ i = 1,2,\ldots,57.$$

We must make it known that the normalizations must now be different since in Example 5 we had 15 rectangles over which to sum where now we will have 57. To accommodate this, we will replace 2,365 in Eq. 31 with 8,866 and 444 by 1,661. Note that these have the common ratio of 3.75. The profile structure is given in Figure 6a. In Figure 6b we plot the fluxes vs. the component number. We do this problem primarily to show in Figure 6c that what appear to be straight lines are beginning to look more and more like straight lines when the straight line comparison is made; however, comparison of Figures 5b and 6c shows that the convergence may be slow. In Figure 6d is the plot of flux vs. straight line slope and it appears that k is close to 2/5 so

$$N(p) = -\frac{2}{5}D\frac{c}{l}\frac{dx}{dz} = -\frac{2}{5}cD[x(p,l) - x(p,0)];$$

so that the coefficient of diffusion coefficient for this case is $2/5D$ where D was the normalizing diffusivity in β_{ij}. We will show in the Theoretical section that this is a natural consequence of the continuous distribution case. Figure 6d also indicates that the convergence to straight line profiles may be

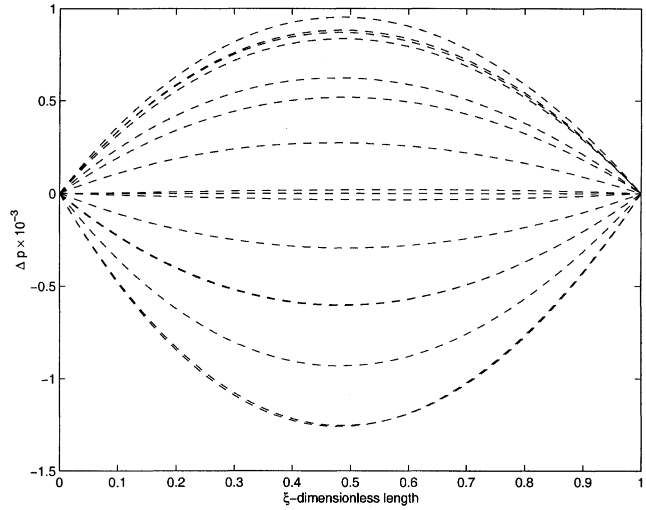

Figure 5b. Local difference Δp between computational profiles and straight line profiles.

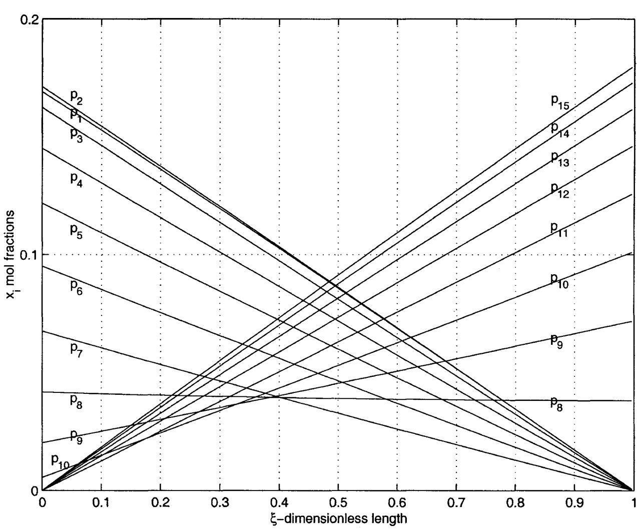

Figure 5a. Fifteen-component case with essentially straight line profiles.

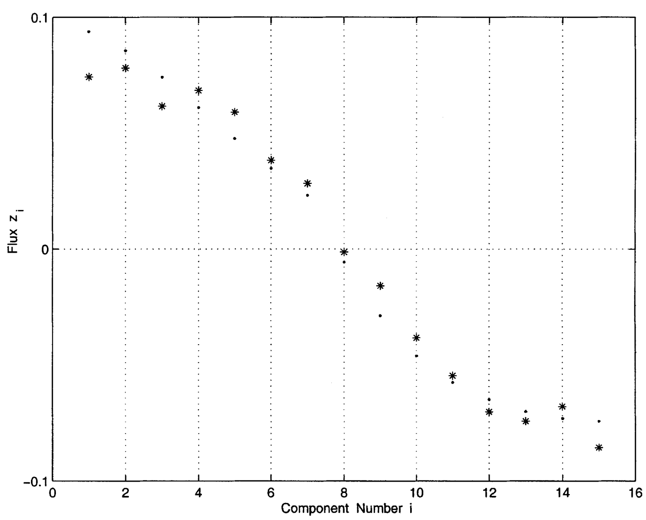

Figure 5c. Fluxes for Example 5: formula diffusivities (●) and randomly chosen diffusivities (*).

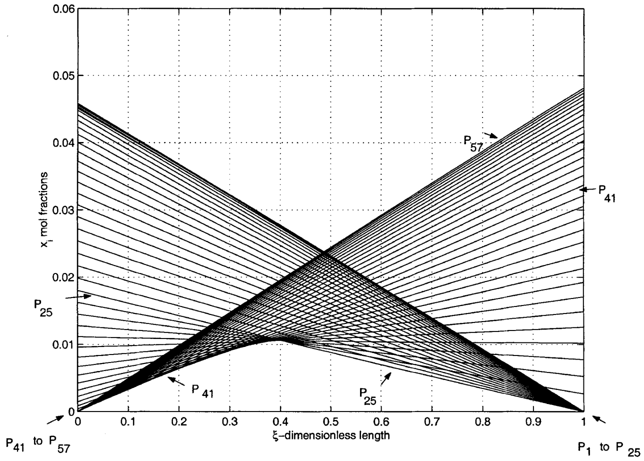

Figure 6a. Case with 57 components and three different sets of profiles.

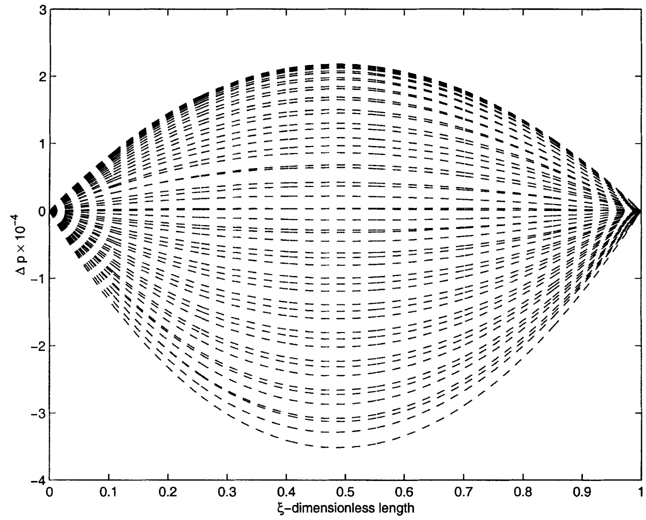

Figure 6c. Local difference between calculated profiles and linear profiles.

The difference is less, but changing slowly.

slow. Figure 6a is a little confusing since the profiles for $12 \leq p \leq 16$ do not emanate from the corners and in fact there is a profile among $26 < i < 40$ for which it will be almost flat.

Example 7

This example is presented to illustrate the case where continuous distribution is augmented by three components which have a finite contribution. With our lumping procedure, this is no more difficult than the others. This time, for the lumping, the continuous distribution will contain 57 species and, with the finite three, we have

$$p_i = 6 + \frac{i-1}{4},\ i = 1,2,\ldots,57,$$

$$p_{58} = 3,\ p_{59} = 4,\ p_{60} = 5.$$

In this case rather than using integers we will again be using jumps of one-quarter unit from $p = 6$ to $p = 20$, hence, approximating the continuous distribution by a finer set of rectangles. We will use the same distribution, but we must modify its application somewhat. At $\xi = 0$, we will write

$$y(p_i,0) = \begin{cases} (p_i - 2)(p_i - 16)^2; & 6 \leq p_i \leq 16, \\ 0; & 16 \leq p_i \leq 20, \end{cases}$$

$$y(p_i,l) = \begin{cases} (p_i - 12)(30 - p_i); & 12 \leq p_i \leq 20, \\ 0; & 6 \leq p_i \leq 12. \end{cases}$$

We set $Sum^l = \sum_{i=1}^{57} y(p_i,l)$; $Sum^0 = \sum_{i=1}^{57} y(p_i,0)$ and let

$$x(p_i,0) = 0.8y(p_i,0)/Sum^0, \quad i = 1,2,\ldots,57,$$

$$x(p_i,l) = 0.8y(p_i,l)/Sum^l, \quad i = 1,2,\ldots,57,$$

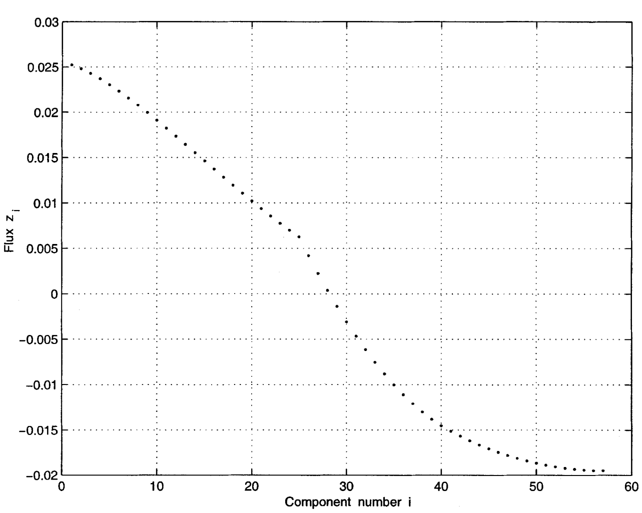

Figure 6b. Fluxes for 57-component case.

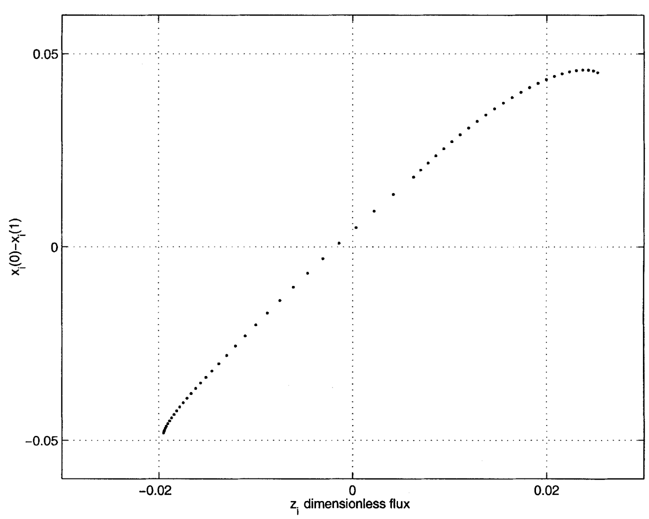

Figure 6d. Dimensionless slope vs. dimensionless flux showing tendency toward linearity.

and with

$$x(p_{58},0)=0.04;\quad x(p_{58},l)=0.12,$$
$$x(p_{59},0)=0.06;\quad x(p_{59},l)=0.02,$$
$$x(p_{60},0)=0.10;\quad x(p_{60},l)=0.06.$$

Also

$$\beta_{ij}=\frac{8.09}{p_i^{7/12}p_j^{7/12}};\quad .25\le\beta_{ij}\le 1.$$

The results of the calculations are presented in Figure 7a, and one immediately notices that the profiles are again straight lines or approximately so. If one makes the same calculations, but this time using diffusivities taken from a random number generator in the interval $0.15<\beta_{ij}<1.25$, one obtains what appear to be the same profiles. The fluxes vary obviously, depending upon the field of random numbers selected. The dots are the diffusivities chosen from the Fuller formula, while the pluses and asterisks are the two results from different domains of random numbers. The comparison of the three is in Figure 7b.

Calculations were also made in order to determine the effect of the continuous domain on the solution profiles for the discrete domain, if any. For a very small continuous domain, the solution for the discrete domain is similar in shape to Figure 7a with slightly curved profiles as before. Changing the diffusion coefficients, such as β_{ij}, $58\le i<j\le 60$, from these values determined by the above formula to strongly different coefficients (such as, the ones used in Example 2) produces a strong effect on the solution profiles for the discrete domain with little or no effect on the solution profiles for the continuous domain.

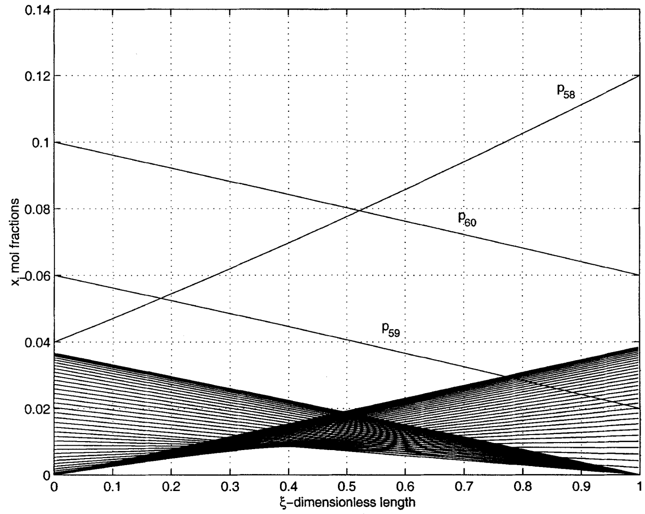

Figure 7a. Concentration vs. mol fraction with 57 components in the distributed section and three finite compositions.

Theoretical Justification

We have seen in the numerical solutions for the continuous distribution cases that the concentration profiles are straight lines or at least very close to straight lines. This seems like something that should be evident from the equations. Suppose we write Eq. 29 in the form

$$Z(p)=\left(-\frac{\partial x(p,\xi)}{\partial\xi}+x(p,\xi)\int_{p_l}^{p_g}\frac{Z(q)}{\beta(p,q)}dq\right)\left(\int_{p_l}^{p_g}\frac{x(q,\xi)}{\beta(p,q)}dq\right)^{-1}.$$

The lefthand side is not dependent upon ξ, so the derivative of the righthand side with respect to ξ must be zero giving

$$0=-\frac{\partial^2 x}{\partial\xi^2}\int_{p_l}^{p_g}\frac{x}{\beta}dq+\frac{\partial x}{\partial\xi}\int_{p_l}^{p_g}\frac{\frac{\partial x}{\partial\xi}}{\beta}dq+\frac{\partial x}{\partial\xi}\int_{p_l}^{p_g}\frac{x}{\beta}dq\int_{p_l}^{p_g}\frac{Z}{\beta}dq-x\int_{p_l}^{p_g}\frac{\frac{\partial x}{\partial\xi}}{\beta}dq\int_{p_l}^{p_g}\frac{Z}{\beta}dq$$

which can be written as

$$\int_{p_l}^{p_g}\frac{Z}{\beta}dq=\frac{\frac{\partial^2 x}{\partial\xi^2}\int_{p_l}^{p_g}\frac{x}{\beta}dq-\frac{\partial x}{\partial\xi}\int_{p_l}^{p_g}\frac{\frac{\partial x}{\partial\xi}}{\beta}dq}{\frac{\partial x}{\partial\xi}\int_{p_l}^{p_g}\frac{x}{\beta}dq-x\int_{p_l}^{p_g}\frac{\frac{\partial x}{\partial\xi}}{\beta}dq}$$

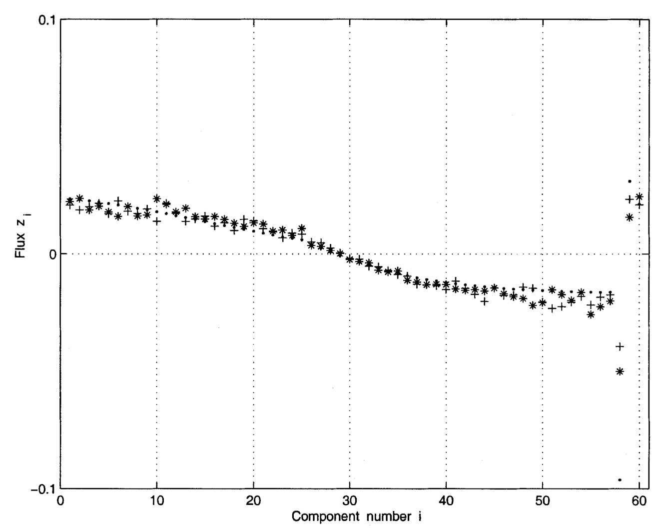

Figure 7b. Dimensionless flux vs. component number with formula based diffusivities and vs. two sets of randomly chosen ones with total of 60 components.

The left hand side is independent of ξ so that differentiation with respect to ξ, and, after some manipulation, using

$$A = \int_{p_l}^{p_g} \frac{x}{\beta} dq; \quad \frac{\partial A}{\partial \xi} = \int_{p_l}^{p_g} \frac{\frac{\partial x}{\partial \xi}}{\beta} dq,$$

we obtain

$$\left(A\frac{\partial x}{\partial \xi} - x\frac{\partial A}{\partial \xi} \right) \left[\frac{\partial A}{\partial \xi}\frac{\partial^2 x}{\partial \xi^2} + A\frac{\partial^3 x}{\partial \xi^3} - \frac{\partial^2 x}{\partial \xi^2}\frac{\partial A}{\partial \xi} - \frac{\partial x}{\partial \xi}\frac{\partial^2 A}{\partial \xi^2} \right] - \left[A\frac{\partial^2 x}{\partial \xi^2} - x\frac{\partial^2 A}{\partial \xi^2} \right] \left[A\frac{\partial^2 x}{\partial \xi^2} - \frac{\partial x}{\partial \xi}\frac{\partial A}{\partial \xi} \right] = 0$$

which will certainly be equal to zero if x is a linear function of ξ. So, we choose as that linear function

$$x(p,\xi) = [x(p,1) - x(p,0)]\xi + x(p,0).$$

Since now the solution profiles are established, one must check on the fluxes. Substitution of the linear solution in the Stefan-Maxwell equations gives

$$-[x(p,1) - x(p,0)] = Z(p)\int_{p_l}^{p_g} \frac{[x(q,1) - x(q,0)]\xi + x(q,0)}{\beta} dq - [(x(p,1) - x(p,0))\xi + x(p,0)]\int_{p_1}^{p_g} \frac{Z(q)}{\beta} dq.$$

Again, the lefthand side is independent of ξ, so differentiation gives

$$Z(p)\int_{p_l}^{p_g} \frac{[x(q,1) - x(q,0)]}{\beta} dq - [x(p,1) - x(p,0)]\int_{p_1}^{p_g} \frac{Z(q)}{\beta} dq = 0$$

Thus

$$Z(p) = -k[x(p,1) - x(p,0)]$$

and because the profiles are straight lines, we must have

$$Z(p) = -k\frac{dx(p,\xi)}{d\xi}, \quad k > 0.$$

Now, since Z and the derivative are both dimensionless, k must be dimensionless and so, reverting to dimensions again

$$N = -\frac{kcD}{l}\frac{dx}{d\xi} = -kcD\frac{dx}{dz},$$

where D is the normalizing diffusivity; for this to be valid, k must be a constant since otherwise the integral sum of the fluxes will not be zero.

We see now that the continuous distribution case for the one-dimension diffusion will be

$$-\frac{\partial x(p,\xi)}{\partial \xi} = Z\int_{p_l}^{p_g} \frac{x(q,\xi)}{\beta(p,q)} dq - x(p,\xi)\int_{p_l}^{p_g} \frac{Z(q)}{\beta(p,q)} dq$$

which holds for $0 < \xi < 1$; and $x(p,0) = f_0(p)$ and $x(p,1) = f_1(p)$ where f_0 and f_1 are prescribed functions of p where each is always non-negative and

$$\int_{p_l}^{p_g} f_0(q)dq = 1, \text{ and } \int_{p_l}^{p_g} f_1(q)dq = 1$$

where $f_i(q)dq$ stands for the mol fraction of component q. We know also that

$$\int_{p_l}^{p_g} Z(q)dq = 0$$

which follows from the basic assumption of component balancing. We also know that $\beta(p,q) > 0$. The sort of problem in which we are interested is in which the number of molecules per unit of volume is always fixed and constant, and that the reservoirs at $\xi = 0$ and $\xi = 1$ are of fixed composition.

Because of the fact that the profiles of concentration are straight lines, the problem may be considered to fall into two cases. If f_0 and f_1 have no components in common, then all of the profiles pass through either $\xi = 0$ or $\xi = 1$ and have their termini on $\xi = 1$ or $\xi = 0$, respectively. On the other hand, if f_0 and f_1 have components in common, the corresponding profile will run from the mol fractions on $\xi = 0$ to the mol fraction on $\xi = 1$. The profile will have slope zero if the corresponding mol fractions are also equal as it should be.

Conclusions

Some of the following problems have been faced in this article successfully and others somewhat less so:

(1) The ternary case for the Stefan-Maxwell equations has resulted in a successful inversion and has produced a simpler presentation than might have been expected because of Eq. 6.

(2) The quaternary case resulted in the inversion in a quasi-symmetric form and a simpler presentation was not very simple.

(3) A numerical scheme was presented which seems to be very robust for an arbitrary number of components with reasonable convergence speed and was used on all examples presented.

(4) The case with a continuous distribution of components was solved, and the character of the solution profiles satisfactorily explained. With several components, the solution profiles are very nearly straight lines. The lumping scheme will always give slightly curved solutions.

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