SOLUTION OF THE LINEARIZED EQUATIONS OF MULTICOMPONENT MASS TRANSFER WITH CHEMICAL REACTION BY MATRIX METHODS

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ABSTRACT

The linearized equations of multicomponent mass transfer with chemical reaction are solved by matrix methods for a film model. The molar flux of each component at the film boundary and the concentration profile of each component across the film are calculated. The general solution obtained is also applied to two variations of the mass transfer problem; the case when there is no reaction and the case when there is reaction but no convection. The method of solution is applied to the cyclopropane-propene-argon-neon and the iodine-hydrogen-hydrogen iodide-argon quaternary reacting systems. The homogeneous reactions in both cases occur isothermally in the gas phase. The results of the computations show that as the reaction rates increase or as the diffusive fluxes decrease, the enhancement factors increase. The lower fluxes obtained in the cases when the convective terms are equated to zero shows that the convective mechanism of mass transfer is just as important as the diffusive and reactive mechanisms in the film.

Ö Z E T

Çok bileşenli ve kimyasal reaksiyonlu kütle transferinin linearize edilmiş denklemleri matris metoduyla bir film modeli için çözülmüştür. Film sınırında hirbir bileşinin molal akışı ve film boyunca herbir bileşenin konsantrasyon değişim eğrisi hesaplanmıştır. Bulunan genel çözüm aynı zamanda kütle transferi probleminin 2 değişik durumuna; reaksiyon olmadığı duruma ve reaksiyonun olduğu fakat konveksiyonun olmadığı duruma uygulanmıştır. Çözüm metodu siklopropan-propin-argon-neon ve iyot-hidrojen-hidrojen iyodür-argon dörtlü reaksiyon oluşan sistemlere uygulanmıştır. Her iki durumda da homojen reaksiyonlar sabit derecede gaz fazında oluşur. Hesapların sonucuna göre reaksiyon akışları çoğaldığında veya diffüz eden akış azaldığında, artma katsayısı çoğalır. Konveksiyon teriminin sıfıra eşitlendiği durumda elde edilen düşük akılar, kütle transferindeki konveksiyon mekanizmasının, diffüzyon ve reaksiyon mekanizmaları kadar önemli olduğunu göstermektedir.

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I. INTRODUCTION

Many industrial separation processes involve multicomponent mixtures that have finite rates of mass transfer probably, with chemical reaction, and the real model would have to be different from the equilibrium stage model. In multicomponent mass transfer with chemical reaction dual coupling occurs; one is the simultaneous reaction coupling depending on the local contentrations and the other is diffusion coupling depending on the local concentration gradients. Accordingly, a particular species may transfer in opposite direction to its own concentration gradient, may not transfer at all even though a gradient for it exists, or it may be transferred through the medium even if it has no concentration gradients since the rate of diffusion of each species is dependent on all the concentration gradients.

Even though multicomponent mass transfer can appreciably couple with chemical reaction, these effects have not been fully studied experimentally. Also, there is a lack of general solution of the problems having coupled diffusion and homogenous reactions in literature.

In this study, first, the solution of the linearized equations of of multicomponent mass transfer by matrix methods developed by earlier

workers is studied and applied. Finally, the linearized equations of multicomponent mass transfer with chemical reaction is solved by matrix methods. Starting from the linearized continuity equations, the second order differential equations are reduced to first order differential equations and the solution is obtained in matrizants. Through a trial and error procedure the finite rates of individual molar fluxes, total molar fluxes and concentration profiles are evaluated for a film model. As applications cyclopropane-propene-argon-neon and iodine-hydrogen-hydrogen iodide- argon quaternary reacting systems are studied.

II. THEORETICAL BACKGROUND

II.A - SOLUTION OF THE LINEARIZED EQUATIONS OF MULTICOMPONENT MASS TRANSFER BY THE UNCOUPLING METHOD.

The starting point for the linearized theory is the so-called continuity equation in which Fick's law for diffusion is inserted. For an n+1 component system

$$\frac{\partial C_i}{\partial t} + \underline{\nabla}\cdot\{\underline{V}\, C_i\} = -\underline{\nabla}\cdot j_i + r_i \qquad i = 1,2,\ldots,n \quad \text{(II.A.1)}$$

$$j = -\sum_{j=1}^{n} D_{ij}\, \underline{\nabla}\, C_j \qquad i = 1,2,\ldots,n \quad \text{(II.A.2)}$$

These n independent differential equations can be represented in n dimensional matrix notation as

$$\frac{\partial (C)}{\partial t} + \underline{\nabla}\cdot\{\underline{V}\,(C)\} = -\underline{\nabla}\cdot(j) + (r) \quad \text{(II.A.3)}$$

$$(\underline{j}) = -[D]\ (\underline{\nabla} C) \quad \text{(II.A.4)}$$

where (C) is the concentration vector, (j) flux vector, (r) reaction

vector and [D] multicomponent diffusion coefficient matrix. The D_{ij} are cross diffusion coefficients if $i \neq j$ and main diffusion coefficients if $i=j$.

In multicomponent mixtures, the diffusion rate of one species is dependent not only on its own concentration gradient but on all the other concentration gradients as well. Hence a coupling exists between the individual gradients which makes the calculations a great deal more complicated than the binary systems. A possible result of the coupling is that a particular species may diffuse in opposition to its own concentration gradient, or may not transfer at all even it has a concentration gradient, or diffuse significantly with no concentration gradient. If all the cross diffusion coefficients go to zero, there will be no coupling. Therefore the cross coefficients in eqtn(II.A.4)may be considered to represent the coupling.

As explained in Chapter II.C, the concentration dependent multicomponent diffusion coefficients for fluids can be predicted from the concentration independent binary diffusion coefficients by making use of the Generalized Maxwell-Stefan equations. Cussler (1976) points out that the concentration dependence of the D_{ik} in liquid systems is often small. Also, for liquid mixtures, the computation of D_{ik} from the Generalized Maxwell-Stefan equations requires complete knowledge on D_{ik} and the activity coefficients γ_i. So, usually, measurement of D_{ik}'s experimentally are preferred for liquid systems. As for the gas mixtures, the D_{ik} vary with concentration more significantly and the Maxwell-Stefan equations are utilized preferably for the computation of these coefficients.

The kinetic theory of gases require that the main diffusion coefficients are always individually positive, i.e

$$D_{ii} > 0 \qquad i = 1,2,\ldots,n \qquad \text{(II.A.5)}$$

Moreover, the D_{ik} measured experimentally suggest the validity of eqtn (II.A.5). The cross diffusion coefficients D_{ik} ($i \neq k$) can be either negative or positive. In addition, the sign of these cross coefficients can be changed by altering the numbering of the components.

The matrix eqtn (III.A.3) in which eqtn (II.A.4) is substituted can be partially linearized if the matrix [D] is assumed to be independent of concentration through the diffusion path as shown by Toor (1964) and Stewart and Prober (1964). The matrix [D] of this linearized matrix eqtn. is usually calculated at the average concentrations in between the boundaries. The reaction term can also be linearized was explained Delancey (1974).

Hence, by taking [D] outside of gradient vector the matrix eqtn. becomes

$$\frac{\partial(C)}{\partial t} + \underline{\nabla}\cdot\{\ \underline{V}\ (C)\ \} = [D]\ \underline{\nabla}\cdot(\underline{\nabla}C) + (r) \qquad \text{(II.A.6)}$$

Uncoupling is accomplished by a similarity transformation as shown by Toor (1964). In this method, the modal matrix [t] is found by diagonalizing [D] such that

$$[t]^{-1}\,[D]\,[t] = \begin{bmatrix} \hat{D}_1 & & & \\ & \hat{D}_2 & & \\ & & \ddots & \\ & & & \hat{D}_n \end{bmatrix} = \begin{bmatrix} \hat{D} \end{bmatrix} \qquad \text{(II.A.7)}$$

where $\hat{D}_1, \hat{D}_2, \ldots, \hat{D}_n$ are the eigenvalues of the matrix [D] that are obtained by solving the characteristic equation of [D]. There are n roots of the characteristic equation of which some of them may be repeated. The real parts of the roots must be positive for this method to be valid.

For ternary gas mixtures, if the components are chosen so that the binary diffusion coefficient D_{12} is the smallest of three D_{ij}, then the D_i will always be real, positive and distinct for all but trivial solutions. Furthermore, if the cross diffusion coefficients in liquids are much less than the main coefficients and the difference between the main coefficients is small, Toor (1964 a) indicates that the D_i will never be negative. They may be complex, but the real parts will always be positive. So far in all systems, in which the D_{ij} have been measured it is seen that the D_i are real, positive and distinct.

If there are repeated roots D_i, it may or may not be possible to find a nonsingular [t] which diagonalizes [D] since [D] is nonsymmetrical. In all situations studied so far (ternary liquids and gases) the roots are distinct, so [t] is nonsingular.

If reaction exists, since (r) = [k] (C), [D] and [k] matrices must commute in order to have both matrices in diagonalized form. The commutation property of [D] and [k] covers only special

cases of real multicomponent systems.

When there is no reaction and for a steady-state unidirectional film model, eqtn (II.A.7) becomes

$$\frac{d}{dz}\{ V(C) \} = [D] \frac{d^2}{dz^2}(C) \qquad \text{(II.A.8)}$$

Or, in molar fractions, when the total concentration is constant

$$\frac{d}{dz}\{ V(x) \} = [D] \frac{d^2(x)}{dz^2} \qquad \text{(II.A.9)}$$

If eqtn (II.A.9) is multiplied by $[t]^{-1}$ from the left; and $[t]\,[t]^{-1}$ multiplication is introduced after the [D] matrix

$$[t]^{-1}\frac{d}{dz}\{V(X)\} = [t]^{-1}\,[D]\,[t]\,[t]^{-1}\,\frac{d^2(x)}{dz^2} \qquad \text{(II.A.10)}$$

one can obtain the following equation

$$\underline{\hat{D}}\frac{d^2(\hat{x})}{dz^2} - V\frac{d(\hat{x})}{dz} = 0 \qquad \text{(II.A.11)}$$

where $(\hat{x}) = [t]^{-1}(x)$. Using the indical notation, eqtn (II.A.11) is written as

$$\hat{D}_i \frac{d^2\hat{x}_i}{dz^2} - V\frac{d\hat{x}_i}{dz} = 0 \qquad i = 1,2,\ldots,n \qquad \text{(II.A.12)}$$

The $\hat{x}_i$ are defined as pseudo compositions.

The second order differential equation is now in the uncoupled form, since the pseudo variables play the role of variables of a binary mixture with the diffusion coefficient $\hat{D}_i$. The boundary conditions are $\hat{x}_i = \hat{x}_{io}$ at $z=0$ and $\hat{x}_i = x_{iL}$ at $z = L$. If nondimensional variables are used such that

$$\psi_i = \frac{\hat{x}_i - \hat{x}_{io}}{\hat{x}_{iL} - \hat{x}_{io}} \qquad \text{and} \qquad z^* = \frac{z}{L}$$

equation (II.A.12) becomes

$$\frac{D_j}{L} \frac{d^2 \psi_2}{dz^{*2}} - V \frac{d \psi_i}{dz^*} = 0 \quad i = 1,2,\ldots,n \qquad \text{(II.A.13)}$$

while the boundary conditions are at $z^* = 0$ $\psi_i = 0$, and at $z^* = 1$ $\psi_i = 1$.

Accordingly, the solution is obtained as

$$\psi_i = \frac{\exp (V z^* / \hat{D}_j) - 1}{\exp (V / \hat{D}_i) - 1} \qquad i = 1,2,\ldots,n \qquad \text{(II.A.14)}$$

Finally, the real component mole fractions can be reached through back transformation by the following equation.

$$(x) = [t] (\hat{x}) \qquad \text{(II.A.15)}$$

The constituent flux equation is composed of diffusive and convective terms.

$$(N) = (j) + V\,(C) \qquad \text{(II.A.16)}$$

Or,

$$(N) = \frac{[D]}{L}\,\frac{d\,(C)}{d\,z^*} + V\,(C) \qquad \text{(II.A.17)}$$

In the same way, the pseudo fluxes (n) are obtained by premultiplying the relevant equation by $[t]^{-1}$ and inserting $[t]\,[t]^{-1}$ after the [D] matrix.

$$(n) = \frac{[D]}{L}\,\frac{d\,(\hat{C})}{d\,z^*} + V\,(\hat{C}) \qquad \text{(II.A.18)}$$

Or,

$$(n) = \frac{[D]}{L}\,C\,\frac{d\,(\hat{x})}{d\,z^*} + V\,C\,(\hat{x}) \qquad \text{(II.A.19)}$$

where $(\hat{x})$ is replaced by the solution of eqtn (II.A.12). Then, the real fluxes are determined by back transformation such that

$$(N) = [t]\,(n) \qquad \text{(II.A.20)}$$

Finally, the total flux is obtained by summing the individual fluxes. In order to find the total flux N_t, a trial and error procedure is needed since the reference velocity $V = N_t/C$ and for that reason eqtn (II.A.19) is implicit.

The linear dependence among the mole fraction gradients means that an additional relationship, called the determinancy condition, is required before the n N_i can be computed. For isothermal and isobaric conditions, the determinancy conditions can be equimolar counter transfer

or diffusion through a stagnant n^{th} species. In the former case no iteration is needed to find the constituent fluxes, since N_t is known.

The outline of the iteration procedure is as follows:

STEP I. Calculate the multicomponent diffusion coefficients D_{ij} at the arithmetic average composition between the boundary concentrations X_{io} and X_{iL}.

STEP II. Find the eigenvalues $\tilde{D}_i$ of the matrix [D] and the elements of the modal matrix [t].

STEP III. Find the pseudo compositions at the boundaries by multiplying the inverse of [t] matrix with the composition column vector (x) at the boundaries.

STEP IV. Initialize total flux by multiplying the n dimensional multicomponent diffusion matrix with the column vector of the real composition differences at the boundaries.

STEP V. Find the pseudo constituent fluxes at $z^* = 0$ by using eqtn. (II.A.19)

STEP VI. Calculate the real constituent fluxes at $z^* = 0$ through back transformation by using eqtn. (II.A.20).

STEP VII. Find the total constituent flux by summing the individual constituent fluxes.

STEP VIII. Check whether the difference between the calculated total flux and the used total flux is less than a predetermined error factor, ε. If it is so, the procedure ends. If not, a new total flux is guessed

i.e using the Newton Raphson method and all the calculations are repeated starting from STEP V. till convergence occurs.

II.B - SOLUTION OF THE LINEARIZED EQUATIONS OF MULTICOMPONENT MASS TRANSFER WITHOUT THE UNCOUPLING METHOD

Multicomponent mass transfer for a nonreacting mixture can be examined by solving the continuity equations of species

$$\frac{\partial C_i}{\partial t} + \underline{\nabla}\cdot\underline{N}_i = 0 \qquad i = 1,2,\ldots,n \quad \text{(II.B.1)}$$

where there exist only n independent differential equations for an n+1 component system. The N_i are the constituent molar fluxes that are composed of a diffusive flux and a convective flux.

$$\underline{N}_i = J_i + \underline{X}_i \underline{N}_t \qquad i = 1,2,\ldots,n \quad \text{(II.B.2)}$$

The J_i are the diffusive fluxes that can be expressed by the generalized form of Fick's law

$$\underline{J}_i = -\sum_{k=1}^{n} D_{ik} \underline{\nabla} C_k \qquad i = 1,2,\ldots,n \quad \text{(II.B.3)}$$

Or it is written as

$$\underline{J}_i = -C \sum_{k=1}^{n} D_{ik} \underline{\nabla} X_k \qquad i = 1,2,\ldots,n \quad \text{(II.B.4)}$$

if a gas mixture is of concern instead of a liquid mixture.

Introducing eqtn (II.B.4) into (II.B.2) and eqtn (II.B.2) into (II.B.1) and writing each term in column matrix form yields

$$\frac{\partial (C)}{\partial t} + \underline{\nabla}.(N_t(x)) = \underline{\nabla}.\{ C\,[D]\,\underline{\nabla}\,(x) \} \qquad \text{(II.B.5)}$$

The matrix [D] represents the concentration dependent multicomponent diffusion coefficients. According to the linearized theory of multicomponent mass transfer (Toor, 1964, and Stewart and Prober, 1964), the total concentration C and the matrix C [D] are assumed to be constant along the mass transfer path. Consequently, the linearized matrix differential equation is

$$C\,\frac{\partial (x)}{\partial t} + \underline{\nabla}\,(\underline{N}t\,(x)) = C\,[D]\,\nabla^2\,(x) \qquad \text{(II.B.6)}$$

Here, it could be satisfactory to calculate the multicomponent diffusion coefficient matrix [D] at the avarage concentration in between the boundaries of the diffusion path. If the concentration gradients are small, the change of [D] matrix with distance won't be of significance. The multicomponent diffusion coefficients can be found accurately for gas mixtures from binary diffusion coefficients by making use of the Maxwell-Stefan equations. For liquid mixtures theoretical prediction of the D_{ik} are less developed and hence experimentel value of these coefficients are preferred (Cussler, 1976).

As shown by Taylor (1982); if the linearized differential mass balance can be reduced to the first order matrix differential eqtn.

$$\frac{d\,(y)}{d\,\eta} = [\,A(\eta)\,]\,(y) + (a\,(\eta)) \qquad \text{(II.B.7)}$$

then that eqtn can be solved without using the uncoupling procedure.

The most general method for solving this eqtn. is explained by Amundson (1960) and also emphasized by Taylor (1982) in which the solution is obtained in terms of matrizants where the matrizant represents an m-fold iterated integral. The advantage of this method is that the tiresome computation of the eigenvalues of the [D] matrix is avoided. Furthermore, this method is utilized if [D] can not be diagonalized or the modal matrix can not be found.

For steady-state and one-dimensional mass transfer, which is called the film model, eqtn. (II.B.6) becomes

$$N_t \frac{d\,(x)}{d\,z} = C\,[D] \frac{d^2\,(x)}{d\,z^2} \qquad \text{(II.B.8)}$$

where N_t, C and [D] are constant. By integrating eqtn. (II.B.8) once,

$$N_t(x) = C\,[D] \frac{d\,(x)}{d\,z} + (\text{constants}) \qquad \text{(II.B.9)}$$

From the form of the solution, it can be concluded that the constants in eqtn. (II.B.9) are the constituent molar fluxes, N_i. Then ψ_i are introduced where $\psi_i = N_i / N_t$

$$(x) = \frac{C\,[D]}{N_t} \frac{d\,(x)}{d\,z} + (\psi) \qquad \text{(II.B.10)}$$

Having the ψ_i's as constants, the eqtn. is made homogeneous by subtracting the (ψ) from each concentration column.

$$(x-\psi) = \frac{C\,[D]}{N_t} \frac{d\,(x-\psi)}{d\,z} \qquad \text{(II.B.11)}$$

Eqtn. (II.B.11) is rearranged and dimensionless distance η, and matrix

of rate factors $[\Psi]$ are introduced such that $\eta=Z/\delta$

$$[\Psi] = \frac{N_t\ \delta}{C}\ [D]^{-1} \qquad \text{(II.B.12)}$$

where δ is the film thickness for diffusion.

$$\frac{d\ (x-\psi)}{d\ \eta} = [\Psi]\ (x-\psi) \qquad \text{(II.B.13)}$$

Eqtn. (II.B.13) is the reduced form of the continuity equation. Since $[\Psi]$ is constant, the solution is

$$(x-\psi) = \exp\ \{\ [\ \Psi]\ \ \eta\ \}\ (x_o-\psi) \qquad \text{(II.B.14)}$$

which can also be obtained using the m folded iterated integral method of solution as proposed by Taylor (1982). Subtracting $(x_o-\psi)$ from each side

$$(x-x_o) = \{\ \exp\ [\Psi]\ \eta - [I]\ \}\ (x_o-\psi) \qquad \text{(II.B.15)}$$

Then, by applying the boundary condition such that at $\eta=1$ $x=x_\delta$,

$$(x_\delta - x_o) = \{\ \exp\ [\Psi] - [I]\ \}\ (x_o-\psi) \qquad \text{(II.B.16)}$$

From eqtn. (II.B.16),

$$(x_o-\psi) = \{\ \exp\ [\Psi] - [I]\ \}^{-1}\ (x_\delta-x_o) \qquad \text{(II.B.17)}$$

Substituting eqtn. (II.B.17) into eqtn (II.B.15), the concentration profile expression is obtained.

$$(x-x_o) = \{\exp[\Psi]\,\eta - [I]\}\,\{\exp[\Psi] - [I]\}^{-1}(x_\delta - x_o) \quad \text{(II.B.18)}$$

Here, exp [Ψ] can be calculated first by finding the characteristic roots of the [Ψ] matrix and then by applying the Chayley-Hamilton theorem (Bronson, 1972). In an other way, exp [Ψ] can be obtained as a series of matrices (Bronson, 1972),i.e.

$$\exp[\Psi] = \sum_{k=o}^{\infty} \frac{[\Psi]^k}{k!} \quad \text{(II.B.19)}$$

If eqtn.(II.B.4), the diffusion flux eqtn., is written in matrix form,

$$(J) = -\frac{C}{\delta}\,[D]\,\frac{d\,(x)}{d\,\eta} \quad \text{(II.B.20)}$$

Taking the derivative of eqtn (II.B.18),

$$\frac{d\,(x)}{d\,\eta} = \{\,[\Psi]\exp[\Psi]\eta\,\}\,\{\exp[\Psi] - [I]\}^{-1}(x_\delta - x_o) \quad \text{(II.B.21)}$$

The change of concentration at η = 0 is

$$\left.\frac{d\,(x)}{d\,\eta}\right|_{\eta=0} = [\Psi]\,\{\exp[\Psi] - [I]\}^{-1}\,(x_\delta - x_o) \quad \text{(II.B.22)}$$

So, the diffusion fluxes at η = 0 are found by the following eqtn.

$$(J_o) = \frac{C}{\delta}\,[D]\,[\Psi]\,\{\exp[\Psi] - [I]\}^{-1}(x_o - x_\delta) \quad \text{(II.B.23)}$$

Furthermore, the constituent molar fluxes are found from eqtn.

$$(N) = (J) + N_t\,(x) \qquad \text{(II.B.24)}$$

and the total flux is found by the summation of individual fluxes. Since eqtn. (II.B.24) is implicite in N_t, a trial and error procedure is required for the calculation of the total flux.

Since $\Sigma\, J_i = 0$ when the molar averaged reference velocity is used, there is a linear dependence among the concentration gradients. Therefore an extra relation, which is called the determinancy condition is required before the constituent flux calculations. At constant temperature and pressure, the determinancy conditions can be equimolar counter transfer or diffusion through a stagnant n^{th} species. For the former case, since $N_t = 0$ is known, no iteration is needed to find the constituent fluxes. Instead, the diffusive fluxes are found by the formula

$$(J) = \frac{C}{\delta}\,[D]\,(x_o - x_\delta)$$

which has been derived for this case starting from the continuity eqtn.

The trial and error procedure to find the total constituent flux N_t and the individual constituent fluxes N_i is as follows :

STEP I. Calculate the multicomponent mass transfer coefficients at the mean concentrations between the boundaries.

STEP II. Initialize total flux by multiplying the matrix [D] by the differences of boundary concentrations vector and summing the elements of the resultant vector.

STEP III. Find exp [Ψ] where [Ψ] is identified in eqtn. (II.B.12).

STEP IV. Calculate the diffusive fluxes and the constituent fluxes by using eqtns (II.B.23) and (II.B.24).

STEP V. Calculate the total flux by summing the individual constituent fluxes and check whether it stays constant or not. If it is, the procedure ends; if not guess a new N_t by Newton Raphson or successive approximation method and reevaluate the terms starting from STEP III, till convergence occurs.

II.C - ESTIMATION OF MULTICOMPONENT DIFFUSION COEFFICIENTS FROM THE GENERALIZED MAXWELL-STEFAN EQUATIONS FOR FLUIDS.

If the chemical potential gradients are linear functions of diffusion velocities, the generalized Maxwell-Stefan equations for an n+1 component system can be written as (Krishna, 1979)

$$\frac{1}{RT} \underline{\nabla} \mu_i = \sum_{\substack{k=1 \\ k\neq i}}^{n+1} \frac{x_k (\underline{U}_k - \underline{U}_i)}{Đ_{ik}} \qquad i = 1,2,\ldots,n \qquad \text{(II.C.1)}$$

where only n independent equations are dealt with since the chemical potential gradients at isothermal and isobaric conditions are related by the Gibbs-Duhem equation such that

$$\sum_{i=1}^{n+1} x_i \underline{\nabla} \mu_i = 0 \qquad \text{(II.C.2)}$$

The $Đ_{ik}$ are the generalized Maxwell-Stefan diffusion coefficients which are symmetrical,

$$Đ_{ik} = Đ_{ki} \qquad i,k = 1,2,\ldots, n+1 \quad (i\neq k) \qquad \text{(II.C.3)}$$

whereas the $Đ_{ii}$ are undefined.

If eqtn. (II.C.1) is multiplied by x_i from both sides and the constituent fluxes.

$$\underline{N}_i = C_i \underline{U}_i \qquad i = 1,2,\ldots,n+1 \qquad \text{(II.C.4)}$$

are inserted,

$$\frac{1}{RT} x_i \underline{\nabla} \mu_i = \sum_{\substack{k=1 \\ k \neq i}}^{n+1} \frac{x_i \underline{N}_k - x_k \underline{N}_i}{C \mathcal{D}_{ik}} \qquad i = 1,2,\ldots,n \qquad (II.C.5)$$

Moreover, as the constituent fluxes are made up of diffusive and convective terms,

$$\underline{N}_i = J_i + C_i \underline{U} = \underline{J}_i + x_i \underline{N}_t \qquad i = 1,2,\ldots,n+1 \qquad (II.C.6)$$

Substituting eqtn(II.C.6) into (II.C.5) yields

$$\frac{1}{RT} x_i \underline{\nabla} \mu_i = \sum_{\substack{k=1 \\ k \neq i}}^{n+1} \frac{x_i J_k - x_k \underline{J}_i}{C \mathcal{D}_{ik}} \qquad i = 1,2,\ldots,n \qquad (II.C.7)$$

Also, at constant temperature and pressure, the chemical potential gradients can be written as

$$\nabla \mu_i = \sum_{k=1}^{n} \frac{\partial \mu_i}{\partial x_k} \nabla x_k \qquad i = 1,2,\ldots,n \qquad (II.C.8)$$

The chemical potentials are given by the eqtn.

$$\mu_i = R\,T \ \ell n\, \gamma_i x_i \qquad i = 1,2,\ldots,n \qquad (II.C.9)$$

Then, composition derivatives of the chemical potential are taken.

$$\frac{\partial \mu_i}{\partial x_j} = R\,T \frac{\partial \ell n\,(\gamma_i x_i)}{\partial x_j}$$

$$= \frac{R\,T}{x_i} \left(\delta_{ij} + \frac{x_i}{x_j} \frac{\partial\, \ell n\, \gamma_i}{\partial\, \ell n\, x_j} \right)$$

$$= \frac{R\,T}{x_i}\, \Gamma_{ij} \qquad i,j = 1,2,\ldots,n \qquad \text{(II.C.10)}$$

The Γ_{ij} are the thermodynamic factors that are given by

$$\Gamma_{ij} = \delta_{ij} + \frac{x_i \partial \ell n\, \gamma_i}{x_j \partial \ell n\, x_j} \qquad i,j = 1,2,\ldots,n \qquad \text{(II.C.11)}$$

If eqtn. (II.C.10) is inserted into eqtn. (II.C.7),

$$\sum_{k=1}^{n} \Gamma_{ik}\, \underline{\nabla}\, x_k = \sum_{\substack{k=1 \\ k \neq i}}^{n+1} \frac{x_i\, \underline{J}_k - x_k\, \underline{J}_i}{C\, \mathcal{D}_{ik}} \qquad i = 1,2,\ldots,n \qquad \text{(II.C.12)}$$

This formula can be written in matrix notation as (Taylor, 1982 a; and Krishna, 1979)

$$C\, [\Gamma]\, (\underline{\nabla}\, x) = -\, [B]\, (J) \qquad \text{(II.C.13)}$$

where the elements of the matrix [B] are given by

$$B_{ii} = \frac{x_i}{\mathcal{D}_{in}} + \sum_{k=1}^{n} \frac{x_k}{\mathcal{D}_{ik}} \qquad i = 1,2,\ldots,n \qquad \text{(II.C.14)}$$

$$B_{ij} = -\, x_i \left[\frac{1}{\mathcal{D}_{ij}} - \frac{1}{\mathcal{D}_{in}} \right] \qquad \substack{i,j = 1,2,\ldots,n \\ i \neq k} \qquad \text{(II.C.15)}$$

The Maxwell-Stefan diffusion coefficients are equal to the

binary molecular diffusion coefficients for ideal gas mixtures, i.e.

$$\mathcal{D}_{ik} = D_{ik} \qquad \begin{matrix} i,k = 1,2,\ldots, n+1 \\ i \neq k \end{matrix} \qquad \text{(II.C.16)}$$

Since the $[\Gamma]$ matrix reduces to the identity matrix for ideal gases, the generalized Maxwell-Stefan diffusion equations become

$$\underline{\nabla} x_i = \sum_{\substack{k=1 \\ k \neq i}}^{n+1} \frac{x_i \underline{N}_k - x_k \underline{N}_i}{C D_{ik}}$$

$$= \sum_{\substack{k=1 \\ k \neq i}}^{n+1} \frac{x_i \underline{J}_k - x_k \underline{J}_i}{C D_{ik}} \qquad i = 1,2,\ldots,n \qquad \text{(II.C.17)}$$

which can be written in n dimensional matrix notation as

$$C (\underline{\nabla} x) = - [B] (J) \qquad \text{(II.C.18)}$$

Here, the elements of the matrix [B] are identified by eqtns. (II.C.14) and (II.C.15) by replacing $\mathcal{D}_{ik}$ by the binary diffusion coefficients D_{ik}.

If both sides of eqtn. (II.C.18) is multipled by $[B]^{-1}$, diffusion flux eqtn. will be obtained as

$$(\underline{J}) = C [B]^{-1} (\underline{\nabla} x) \qquad \text{(II.C.19)}$$

Also, for the multicomponent mixtures, the diffusion flux formula in terms of the multicomponent diffusion coefficients represents Fick's law.

$$(J) = C\,[D]\,(\underline{\nabla} x) \qquad \text{(II.C.20)}$$

Equating eqtn (II.C.19) with eqtn. (II.C.20), it is found out that multicomponent diffusion coefficient matrix is equal to the inverse of the matrix [B].

$$[D] = [B]^{-1} \qquad \text{(II.C.21)}$$

So, in order to determine the multicomponent diffusion coefficients using binary diffusion coefficients, elements of the matrix [D] are required to be found in terms of the elements of the matrix $[B]^{-1}$. In this way, the multicomponent diffusion coefficients of 3,4,5,...,or n components systems can be found.

Following this procedure where the reference velocity is taken as the molar avarage velocity, multicomponent diffusion coefficients for a ternary ideal gas system are obtained as

$$D_{ii} = D_{i3}\,[\,(1-x_i)\,D_{ij} + x_i\,D_{j3}\,]\,/\,S \qquad \text{(II.C.22)}$$

$$D_{ij} = x_i\,D_{i3}\,(D_{i3} - D_{ij})\,/\,S \qquad \text{(II.C.23)}$$

$$S = x_1\,D_{23} + x_2\,D_{13} + x_3\,D_{12} \qquad \text{(II.C.24)}$$

For liquid mixtures, the evaluation of the elements D_{ij} from eqtn $[D] = [B]^{-1}\,[\Gamma]$ needs complete information on the Maxwell-Stefan diffusivities $Đ_{ik}$ and the activity coefficient γ_i. Hence, the experimental measurements of [D] are necessary in most cases.

III. SOLUTION OF THE LINEARIZED EQUATIONS OF MULTICOMPONENT MASS TRANSFER WITH CHEMICAL REACTION

In multicomponent mixtures, when mass transfer with chemical reaction occurs, dual coupling takes place where one is the simultaneous reaction coupling and the other diffusion coupling. Here, the former coupling depends on the local concentrations, while the latter coupling depends on the local concentration gradients. The linearized continuity equations for n+1 components in which the generalized Fick's law is inserted are as follows

$$\frac{\partial (C)}{\partial t} + \underline{\nabla} \cdot \{ \underline{V} (C) \} = [D] \nabla^2 (C) + [k] (C) \qquad (III.1)$$

where [k] is the n dimensional square matrix of the reaction rate constants. For simplicity, the reaction is considered as first order and homogenous under isothermal and isobaric conditions.

Cussler (1976) indicates that these equations can be solved analytically only for two special cases. The first case occurs at ste-

ady state with no convection

$$0 = \nabla^2 (C) + [D]^{-1} [k] (C) \qquad \text{(III.2)}$$

of which the solution was obtained by Toor (1965) and by Delancey and Chiang (1970) through the uncoupling method. The second case of eqtn. (III.1) is the mass transfer without convection.

$$\frac{\partial (C)}{\partial t} = [D] \nabla^2 (C) + [k] (C) \qquad \text{(III.3)}$$

where a solution is given by Toor (1965) for the one-dimensional case by a separation-of-variables matrix technique.

Furthermore, Cussler (1976) points out that the theory about the multicomponent mass transfer with chemical reaction and with convective term is approximate and limited. This lack of generality results from the situation that both the diffusion coefficients matrix and reaction rate constants matrix can not be simultaneously diagonalized except in special cases. In addition, only first order isothermal mechanisms can be dealed with since the second or higher order reversible mechanisms creates nonlinearity.

In this thesis, the linearized equations of multicomponent mass transfer with chemical reaction and convective term are solved. For steady-state and unidirectional case with constant total concentration the continuity equations become.

$$C [D] \frac{d^2 (x)}{d z^2} - N_t \frac{d (x)}{d z} + C [k] (x) = 0 \qquad \text{(III.4)}$$

Multiplying each term by the matrix $[D]^{-1}$ and dividing by C,

$$\frac{d^2(x)}{dz^2} - \frac{N_t [D]^{-1}}{C} \frac{d(x)}{dz} + [D]^{-1} [k] (x) = 0 \qquad \text{(III.5)}$$

or,

$$\frac{d^2(x)}{dz^2} - [A] \frac{d(x)}{dz} + [B] (x) = 0 \qquad \text{(III.6)}$$

where

$$[A] = \frac{N_t}{C} [D]^{-1} \qquad \text{(III.7)}$$

$$[B] = [D]^{-1} [k] \qquad \text{(III.8)}$$

Eqtn. (III.6) can also be written in simpler form,

$$\ddot{\bar{X}} - A \dot{\bar{X}} + B \bar{X} = 0 \qquad \text{(III.9)}$$

The capital letters with double lines represent the matrices, the other letters with arrows above them represent the vector columns. Choosing new variables Y,

$$\bar{Y} = \begin{bmatrix} \bar{X} \\ \dot{\bar{X}} \end{bmatrix} = \begin{bmatrix} \bar{X} \\ \bar{V} \end{bmatrix} \qquad \text{(III.10)}$$

$\bar{Y}$, being of 2n dimensions such that for n components

$$Y_i = X_i \qquad i = 1,2,\ldots,n \qquad \text{(III.11)}$$

after the n^{th} component,

$$Y_i = \frac{d\,X_i}{d\,z} \qquad i = n+1,\ldots,2n \qquad \text{(III.12)}$$

Combining eqtns. (III.9) and (III.10), eqtn (III.9) is reduced into a first order matrix differential equations

$$\frac{d\,\overline{Y}}{d\,z} = \mathbb{A}\,\overline{Y} \qquad \text{(III.13)}$$

where

$$\mathbb{A} = \begin{bmatrix} \mathbb{O} & \mathbb{I} \\ \mathbb{B} & \mathbb{A} \end{bmatrix} \qquad \text{(III.14)}$$

The solution, Beker (1984), is

$$\overline{Y} = e^{\mathbb{A}z}\,\overline{C} \qquad \text{(III.15)}$$

Defining $\mathbb{F} = e^{\mathbb{A}z}$ (III.16)

$$\overline{Y} = \mathbb{F}\,\overline{C} \qquad \text{(III.17)}$$

The boundary conditions,

$$\overline{X}\,(0) = \overline{X}_o \quad \text{and} \quad \overline{X}\,(L) = \overline{X}_L \qquad \text{(III.18)}$$

are used to evaluate the constant vector $\bar{C}$. If eqtn (III.17) is written in partitioned form such that

$$\mathbb{F} = \begin{bmatrix} \mathbb{F}_{11} & \mathbb{F}_{12} \\ \mathbb{F}_{21} & \mathbb{F}_{22} \end{bmatrix} \tag{III.19}$$

and

$$\bar{\bar{C}} = \begin{bmatrix} \bar{C}_1 \\ \bar{C}_2 \end{bmatrix} \tag{III.20}$$

then,

$$\begin{bmatrix} \bar{X}(Z) \\ \bar{V}(Z) \end{bmatrix} = \begin{bmatrix} \mathbb{F}_{11}(Z) & \mathbb{F}_{12}(Z) \\ \mathbb{F}_{21}(Z) & F_{22}(Z) \end{bmatrix} \begin{bmatrix} \bar{C}_1 \\ \bar{C}_2 \end{bmatrix} \tag{III.21}$$

By applying the boundary conditions,

$$\begin{bmatrix} \bar{X}_o \\ \bar{V}_o \end{bmatrix} = \begin{bmatrix} \mathbb{F}_{11}(0) & \mathbb{F}_{12}(0) \\ \mathbb{F}_{21}(0) & \mathbb{F}_{22}(0) \end{bmatrix} \begin{bmatrix} \bar{C}_1 \\ \bar{C}_2 \end{bmatrix} \tag{III.22}$$

$$\begin{bmatrix} \bar{X}_L \\ V_L \end{bmatrix} \quad \begin{bmatrix} \mathbb{F}_{11}(L) & \mathbb{F}_{12}(L) \\ \mathbb{F}_{21}(L) & \mathbb{F}_{22}(L) \end{bmatrix} \begin{bmatrix} \bar{C}_1 \\ \bar{C}_2 \end{bmatrix} \tag{III.23}$$

From eqtns (III.22) and (III.23),

$$\bar{X}_o = \mathbb{F}_{11}(0)\,\bar{C}_1 + \mathbb{F}_{12}(0)\,\bar{C}_2 \qquad \text{(III.24)}$$

$$\bar{X}_L = \mathbb{F}_{11}(L)\,\bar{C}_1 + \mathbb{F}_{12}(L)\,\bar{C}_2 \qquad \text{(III.25)}$$

From eqtn (III.24)

$$\bar{C}_1 = \mathbb{F}_{11}^{-1}(0)\,\bar{X}_o - \mathbb{F}_{11}^{-1}(0)\,\mathbb{F}_{12}(0)\,\bar{C}_2$$

Substituting into eqtn. (III.25)

$$\bar{X}_L = \mathbb{F}_{11}(L)\,\mathbb{F}_{11}^{-1}(0)\,\bar{X}_o - F_{11}(L)\,\mathbb{F}_{11}^{-1}(0)\,\mathbb{F}_{12}(0)\,\bar{C}_2 + \mathbb{F}_{12}(L)\,\bar{C}_2 \qquad \text{(III.27)}$$

$\bar{C}_2$ is obtained,

$$\bar{C}_2 = [\,\mathbb{F}_{11}(L)\,\mathbb{F}_{11}^{-1}(0)\,\mathbb{F}_{12}(0) - \mathbb{F}_{12}(L)]^{-1}\,[\,\mathbb{F}_{11}(L)\,\mathbb{F}_{11}^{-1}(0)\,\bar{X}_o - \bar{X}_L] \qquad \text{(III.28)}$$

Similarly, from eqtn. (III.24)

$$\bar{C}_2 = \mathbb{F}_{12}^{-1}(0)\,\bar{X}_o - \mathbb{F}_{12}^{-1}(0)\,\mathbb{F}_{11}(0)\,\bar{C}_1 \qquad \text{(III.29)}$$

Substituting this eqtn into (III.25)

$$\bar{X}_L = \mathbb{F}_{11}(L)\,\bar{C}_1 + \mathbb{F}_{12}(L)\,\mathbb{F}_{12}^{-1}(0)\,\bar{X}_o - \mathbb{F}_{12}(L)\,\mathbb{F}_{12}^{-1}(0)\,\mathbb{F}_{11}(0)\,\bar{C}_1 \qquad \text{(III.30)}$$

$\bar{C}_1$ is found as

$$\bar{C}_1 = [\,\mathbb{F}_{12}(L)\,\mathbb{F}_{12}^{-1}(0)\,\mathbb{F}_{11}(0) - \mathbb{F}_{11}(L)]^{-1}\,[\,\mathbb{F}_{12}(L)\,\mathbb{F}_{12}^{-1}(0)\,\bar{X}_o - \bar{X}_L] \qquad \text{(III.31)}$$

Finally, the general solution is obtained as

$$\bar{Y}_{(z)} = e^{\begin{vmatrix} 0 & I \\ -B & A \end{vmatrix} z} \begin{vmatrix} [F_{11}(L) - F_{12}(L) F_{12}^{-1}(0) F_{11}(0)]^{-1} [\bar{X}_L - F_{12}(L) F_{12}^{-1}(0) \bar{X}_o] \\ [F_{12}(L) - F_{11}(L) F_{11}^{-1}(0) F_{12}(0)]^{-1} [\bar{X}_L - F_{11}(L) F_{11}^{-1}(0) \bar{X}_o] \end{vmatrix}$$

Having assumed the total flux as constant, (III.32)

$$N_i = J_i + x_i N_t + r_i \qquad i = 1,2,\ldots,n \qquad \text{(III.33)}$$

and, $$J_i = - C \sum_{j=1}^{n} D_{ij} \frac{d X_i}{d z} \qquad i = 1,2,\ldots,n \qquad \text{(III.34)}$$

where the concentration gradients are found out as y_i from eqtn. (III-32) as

$$\frac{d X_i}{d z} = y_k \qquad \begin{matrix} i = 1,2,\ldots,n \\ k = n+1,\ldots,2n \end{matrix} \qquad \text{(III.35)}$$

So, $$J_i = - \sum_{\substack{j=1 \\ k=n+1}}^{\substack{j=n \\ k=2n}} D_{ij} y_k \qquad \begin{matrix} i = 1,2,\ldots,n \\ k = n+1,\ldots,2n \end{matrix} \qquad \text{(III.36)}$$

respectively. Substituting eqtn. (III.36) into (III.33) with X_{io} and y_{ko}, constituent fluxes are found at Z=0. Then summing constituent fluxes N_i, the total flux is obtained.

$$N_t = \sum_{i=1}^{n} N_i \qquad \text{(III.37)}$$

where N_{n+1} is zero is the determinancy condition.

In order to calculate total flux N_t, eqtn. (III.37) where eqtn (III.33) is introduced is to be solved together with eqtn (III.32) the resulting equation is implicit in N_t. Therefore an iterative computation is required. The iteration procedure is as follows

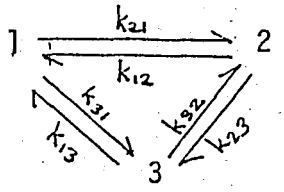
STEP I. Calculate the [D] matrix at the mean compositions between the boundaries. Then, calculate [B] and [A] matrices

STEP II. Initialize N_t.

STEP III. Find Y_k, J_i, r_i, N_i and then N_t.

STEP IV. Check whether the total flux stays constant or not. If it stays constant procedure ends, if not assume a new N_t, i.e, by the secant method and recalculate the values starting from STEP III, till convergence occurs.

As an illustration, the quarternary reacting system of Toor (1965) can be studied. Three reacting components plus 1 inert can be considered.



+ (4)

Since $\sum_{i}^{n+1} r_i = 0$, only n of r_i are independent. Therefore, the fourth component that which is inert is not included into the eqtns. Consequently,

$$(r) = C \begin{bmatrix} k_{21} + k_{31} & -k_{12} & -k_{13} \\ -k_{21} & k_{12} + k_{32} & -k_{23} \\ -k_{31} & -k_{32} & k_{13} + k_{23} \end{bmatrix} \begin{bmatrix} y_1 \\ y_2 \\ y_3 \end{bmatrix}$$

The continuity eqtns with these reactions can be solved according to

the above calculation procedure.

Although first order systems with no inerts present are likely to show little diffusion coupling because of the similarity among reacting species, the presence of inerts can cause significant diffusion coupling. Furthermore, near equilibrium one may treat higher order reactions as approximately first order. Also, multicomponent mass transfer with second or higher order reactions can be solved by this method by linearizing the reactive terms as shown by Lee and Delancey (1974) and taking mass average velocity with constant total mass flux if necessary.

IV. COMPUTATIONS AND DISCUSSION OF RESULTS

In this thesis, a computer program was developed in order to study the general solution of multicomponent mass transfer with chemical reaction, the solution without chemical reaction, and the solution without convective terms respectively. In addition for the nonreacting case two smaller computer programs were developed one of which computes the mass rates by solution of the linearized equations with the uncoupling method (Toor, 1964) and the other without the uncoupling method (Taylor,1982)

In the main program (Appendix F), binary diffusion coefficients of the mixtures are calculated by calling a subroutine program using the formula given in Appendix B. Later on multicomponent diffusion coefficients are calculated through the formulas given in Chapter II.C. by another subroutine program. Moreover, the matrices are multiplied and their inverses are taken by calling separate subroutines for each. Another subroutine exists for linearizing the nonlinear reactions and these are explained in Appendix D.

First the constituent fluxes for the reacting case are found and then the concentration profiles for this case are calculated. Then, the constituent flux calculations and concentration profiles for the unreacting case are calculated. Finally the same calculations are carried out for the case where the convective term is zero.

In order to find out the constituent fluxes a trial and error procedure is carried out by use of the secant method for the reacting and unreacting cases whereas for the case where the convective term is zero and for finding the concentration profiles of the three cases no iterations are needed. The trial and error computations are stopped when the total flux stays constant, where the calculation procedure written in Chapter III is followed. The iteration procedure was found to converge rapidly without oscillations. Also, even if the successive approximation method is used in the trial and error calculations, again rapid convergences are observed.

For the other two small computer programs where calculations are carried out for the nonreacting case the convergences are also rapid. In the first one where the uncoupling method is used, a subroutine program is used in order to find out the eigenvalues of the multicomponent diffusion matrix and the modal matrix. The calculation steps are explained in Appendix E. Also, another subroutine program is used in order to apply the Newton-Raphson method for the iteration procedure. In the second program where no uncoupling is made the successive approximation method was used and was found to give rapid convergences as well. The calculation procedures for these two programs are also outlined in Chapter II.A and II.B respectively.

For the multicomponent mass transfer without chemical reaction, Smith and Taylor (1982,1983) calculated rates of mass transfer for quite a large number of systems in order to determine the range of validity of the linearized equations for steady diffusion in gas mixtures. In these examples mixtures of high concentration and the high rates of mass transfer were included as well low concentration and low mass transfer rates. The average deviation from the results found by the Stefan-Maxwell equations for the calculated consituent N_i was found to be only 1.4 %. After these studies, it was concluded that for the purposes of calculating rates of mass transfer rather than composition profiles, the linearized equations are almost always adequate for design purposes.

In this thesis, for the nonreacting case, mass transfer of carbon-dioxide-water vapor-hydrogen ternary gas mixture was studied. The mass transfer rates found either by the uncoupling or without uncoupling methods were almost the same as can be seen from Table 1. The advantage of the uncoupling method is that the tiresome computation of the eigenvalues of [D] matrix is avoided. Furthermore the uncoupling method must be utilized if [D] can not be diagonalized or the modal matrix can not be found The average discrepancy of the calculated mass transfer rates (Table 1) from the results found by the Stefan-Maxwell equations (Wilke, 1950) is 3.99 %. The multicomponent diffusion coefficients were calculated by the use of the Stefan-Maxwell eqtns. It was seen that the main diffusion coefficients are positive as expected. Also, the main diffusion coefficients came out to be greater than the cross diffusion coefficients. Since the relative value of the cross diffusion coefficients show coupling degree, the fact that they are smaller than the main diffusion coefficients indicate small diffusion coupling for the system

TABLE 1.- CONSTITUENT MOLAR FLUX CALCULATIONS FOR CARBON DIOXIDE(C)-WATER VAPOR (HO)-HYDROGEN(H) TERNARY SYSTEM*

	Mole Fractions at Points 1 and 2		Calculated Multicomponent Diffusion Coefficients† ($sq.cm.sec^{-1}$)		Calculated Constituent Molar Fluxes ($g\ moles\ sec^{-1}\ sq\ cm^{-}$) x 10^5		
					Method 1	Method 2	Method 3
C	.4029	.0000	2.2035	0.7063	4.8600	4.8730	4.8730
HO	.0000	.3666	0.7148	2.4542	-4.6500	-4.6590	-4.6590
C	.3400	.3266	2.0250	0.8707	0.1310	0.1331	0.1330
HO	.3270	.3396	9.9684	2.2205	-0.1080	-0.1063	-0.1063
C	.3366	.3300	2.0250	0.8707	0.0663	0.0657	0.0657
HO	.3302	.3364	0.9684	2.2205	-0.0528	0.0521	-0.0521
C	.4029	.0000	2.6954	0.8640	10.6200	10.6100	10.6100
HO	.0000	.0066	0.0157	2.2301	-0.0441	-0.0343	-0.0343
C	.4029	.0000	2.6516	0.8499	10.2100	10.1700	10.1700
HO	.0000	.0333	0.0782	2.2501	-0.2250	-0.1893	-0.1894
H	.4029	.0000	2.7183	-0.0476	10.6800	10.7000	10.7000
HO	.0000	.0333	-0.0389	1.0833	-0.2310	-0.2528	-5.2530
C	.5333	.0000	2.6865	1.0219	16.0900	16.1000	16.0900
HO	.0133	.0000	0.0283	2.0056	0.4340	0.4423	0.4422

Method 1 - Solution by the Stefan-Maxwell eqtns.(Nilke,1950)

Method 2 - Solution of the linearized continuity eqtns. with uncoupling.

Mathod 3 - Solution of the linearized continuity eqtns without uncoupling

* For all examples
Diffusion distance = 1. mm.
Temperature = 40.°C
Pressure = 150.mm Hg

† D_{ij} matrix

CO_2 - H_2O - H_2.

For the application of the solution of the linearized eqations of multicomponent mass transfer with chemical reaction by matrix methods, first the quaternary system cyclopropane (C)-propene(P)-argon-neon was chosen. The homogeneous gas phase isomerization reaction is first order (Chambers, 1934; Benson 1960; and Robinson, 1972)

$$C \rightarrow P$$

The isothermal reaction is irreversible and the rate expression is

$$r = k\, C_c$$

The reaction rate constants at different temperatures were computed by the Arrhenius equation using the high pressure activation energy and constants written in Appendix C.

In diffusion with chemical reaction an important design parameter is called the enhancement factor. The enhancement factor is defined as the ratio of the mass transfer rate with chemical reaction to the mass transfer rate without reaction. If the enhancement factors found at 823 C and 60 atm. (Table 2) are compared with the ones found at 865°K and 60 atm (Table 3), it is seen that the enhancement factors of the high temperature system deviate from unity in greater extents. In Tables 4 and 5 the reaction takes place at 865°K and 70 atm. The deviations from unity in these examples are much greater. So it can be concluded that the higher the temperature and/or pressure, the greater is the enhancement factor. At higher temperatures the reaction rate constants are higher as a result of which the rates of reactions are also higher. Also at higher pressure the concentration increases which also increases the reaction rate. In these eaxamples concentrations are calculated using the ideal gas law.

TABLE 2 - CONSTITUENT MOLAR FLUX CALCULATIONS FOR CYCLOPROPANE(C)-PROPENCE(P)-ARGON(A)-NEON QUATERNARY SYSTEM*

	Mole Fractions at Points 1 and 2		Calculated Milticomponent Diffusion Coefficients† ($sq.cm.sec^{-1}$) x 10			Calculated Constituent Molar Fluxes ($gmoles\ sec^{-1}\ sqcm^{-1}$) x 10^4			Enhancement Factors
						General Solution	Case 1	Case 2	
C	.1112	.0995	0.4373	0.1319	0.0994	0.0315	0.0307	0.0230	1.026
P	.1725	.1689	0.2141	0.5210	0.1610	0.0283	0.0290	0.0144	0.976
A	.2645	.2705	0.3347	.3341	0.8662	0.0213	0.0213	-0.0035	1.000
C	.2112	.1995	0.4778	0.2183	0.1645	0.0467	0.0452	0.0252	1.033
P	.1823	.1789	0.1923	0.4529	0.1447	0.0304	0.0318	0.0115	0.956
A	.2645	.2705	0.2843	0.2838	0.7358	0.0274	0.0274	-0.0055	1.000
C	.3112	.2995	0.5050	0.2806	0.2115	0.3591	0.3572	0.0745	1.005
P	.2142	.1999	0.1906	0.4158	0.1434	0.2473	0.2491	0.0533	0.993
A	.2505	.2205	0.2164	0.2161	0.6140	0.3274	0.3274	0.1068	1.000
C	.4271	.3597	0.5470	0.3374	0.2544	0.8862	0.8841	0.2225	1.002
P	.2278	.1981	0.1830	0.3931	0.1377	0.4688	0.4709	0.1099	0.996
A	.1505	.1405	0.1248	0.1246	0.5150	0.3196	0.3196	0.0767	1.000
C	.5560	.5400	0.6309	0.4362	0.3289	0.4904	0.4871	0.0785	1.007
P	.1277	.1199	0.0987	0.2938	0.0743	0.1106	0.1139	0.0166	0.971
A	.1605	.1505	0.1238	0.1236	0.4840	0.1518	0.1518	0.0346	1.000

Case 1 - Solution for nonreacting case

Case 2 - Solution when convective term is zero

* For all examples

Diffusion distance = .2 cm
Total Pressure = 60.0 atm
Temperature = 823.0°K
Reaction rate constant = $8.0844 \times 10^{-3}\ sec^{-1}$

† D_{ij} matrix

TABLE 3. - CONSTITUENT MOLAR FLUX CALCULATIONS FOR CYCLOPROPANE(C)-PROPENE(P)-ARGON(A)-NEON QUATERNARY SYSTEM*

	Mole Fractions at Points 1 and 2		Calculated Multicomponent Diffusion Coefficients† $(sq.cm.sec^{-1}).10$			Calculated Constituent Molar Fluxes ($g\ moles\ sec^{-1}\ sqcm^{-1}$) x 10^4 General Solution	Case 1	Case 2	Enhancement Factors
C	.1555	.1501	0.8287	0.3193	0.2403	0.0427	0.0384	0.0341	1.112
P	.0095	.0015	0.0115	0.5239	0.0009	0.0143	0.0185	0.0140	0.773
A	.0033	.0036	0.0007	0.0007	1.0290	-0.0007	-0.0007	-0.0009	1.000
C	.1745	.1698	0.6901	0.2856	0.2151	0.0449	0.0402	0.0290	1.117
P	.0915	0.899	0.1507	0.5573	0.1133	0.0149	0.0197	0.0065	0.756
A	.0099	.0008	0.0009	0.0008	0.8197	0.0327	0.0327	0.0322	1.000
C	.2700	.2688	0.6177	0.3241	0.2443	0.0152	0.0077	0.0120	1.974
P	.1815	.1798	0.2177	0.5124	0.1638	-0.0011	0.0063	0.0033	0.175
A	.0200	.0210	0.0247	0.0246	0.6087	-0.0021	-0.0021	-0.0023	1.000
C	.2546	.2495	0.5976	0.3036	0.2288	0.0431	0.0362	0.0243	1.191
P	.1610	.1585	0.1928	0.4880	0.1450	0.0151	0.0220	0.0031	0.686
A	.1200	.1190	0.1439	0.1437	0.6994	0.0166	0.0166	0.0077	1.000
C	.1473	.1000	0.5036	0.1694	0.1276	0.2814	0.2781	0.1619	1.012
P	.2276	.1295	0.2450	0.5808	0.1843	0.4435	0.4468	0.2685	0.993
A	.1735	.2010	0.2564	0.2560	0.8651	0.2357	0.2357	0.0576	1.000

Case 1 - Solution for nonreacting case

Case 2 - Solution when convective term is zero

* For all examples
Diffusion distance = .2 cm
Total pressure = 60.atm
Temperature = 853. K
Reaction rate constant = $3.2716 \times 10^{-2}\ sec^{-1}$

† D_{ij} matrix

TABLE 4. - CONSTITUENT MOLAR FLUX CALCULATIONS FOR CYCLOPROPANE(C)-PROPENE(P)-ARGON(A)-NEON QUATERNARY SYSTEM *

	Mole Fractions at Points 1 and 2		Calculated Multicomponent Diffusion Coefficients † (sq.cm sec^{-1}) x 10			Calculated Constituent Molar Fluxes (gmoles sec^{-1} sg cm^{-1}) x 10^5			Enhancement Factors
						General Solution	Case 1	Case 2	
C	.1555	.1501		0.7339	0.2128	0.5161	0.3913	0.4291	1.319
P	.0095	.0015	0.0101	0.4660	0.0077	0.0641	0.1888	0.0604	0.340
A	.0033	.0036	0.0064	0.0064	0.9111	-0.0073	-0.0073	-0.0093	1.000
C	.2112	.1995	0.4600	0.2102	0.1584	0.6486	0.4829	0.4218	1.343
P	.1823	.1789	0.1852	0.4360	0.1393	0.1746	0.3402	-0.0294	0.513
A	.2645	.2705	0.2737	0.2733	0.7084	0.2926	0.2926	-0.0059	1.000
C	.1112	.0995	0.4210	0.1270	0.0957	0.4148	0.3284	0.3243	1.263
P	.1725	.1689	0.2061	0.5016	0.1550	0.2237	0.3100	0.0749	0.722
A	.2645	.2705	0.3222	0.3217	0.8339	0.2281	0.2281	-0.0037	1.000
C	.2700	.2688	0.5470	0.2870	0.2163	0.2970	0.0786	0.2645	3.779
P	.1815	.1798	0.1928	0.4538	0.1451	-0.1540	0.0643	-0.1764	-2.395
A	.0200	0.210	0.0218	0.0218	0.5391	-0.0210	-0.0210	0.0235	1.000

Case 1 - Solution for nonreacting case

Case 2 - Solution when convective term is zero

*For all examples

Diffusion distance = .2 cm

Total pressure = 70. atm

Temperature = 865. °K

Reaction rate constant = 0.083988 sec^{-1}

† D_{ij} matrix

TABLE 5. -CONSTITUENT MOLAR FLUX CALCULATIONS FOR CYCLOPROPANE(C)-PROPENE(P)-ARGON(A)-NEON QUATERNARY SYSTEM*

	Mole Fractions At Points 1 and 2		Calculated Milticomponent Diffusion Coefficients† (sq.cm.sec^{-1}) x 10			Calculated Constituent Molar Fluxes (g.moles sec^{-1} sq cm^{-1}) x 10^5			Enhancement Factors
						General Solution	Case 1	Case 2	
C	.1000	.0950	0.5924	0.1692	0.1274	1.6280	1.5520	1.0500	1.0489
P	.1000	.0050	0.0913	0.5170	0.0686	2.7120	2.7880	2.3810	0.9727
A	.1000	.0950	0.1690	0.1687	0.9776	1.6560	1.6560	1.0730	1.0000
C	.3700	.3688	0.5720	0.3443	0.2596	0.4057	0.1070	0.3493	3.792
P	.1815	.1798	0.1687	0.3970	0.1269	-0.2338	0.0649	-0.2624	-3.603
A	.0200	.0210	0.0019	0.0019	0.4717	-0.0174	-0.0174	-0.0205	1.000
C	.5000	.4950	0.7116	0.4771	0.3597	1.8780	1.4860	0.8743	1.264
P	.0050	.0000	0.0024	0.2376	0.0018	-0.3266	0.0653	-0.3438	-5.002
A	.0950	.0850	0.0863	0.0862	0.5356	0.4906	0.4906	0.3066	1.000
C	.7000	.6965	0.7437	0.5507	0.4152	2.1190	1.5720	0.9314	1.348
P	.0050	.0000	0.0020	0.1954	0.0015	-0.4944	0.0533	-0.5160	-9.276
A	.0050	.0000	0.0020	0.0020	0.3885	0.1010	0.1010	0.0966	1.000

Case 1- Solution for nonreacting case

Case 2- Solution when convective term is zero

*For all examples

Diffusion distance = .2 cm

Total pressure = 70. atm

Temperature = 865. °K

Reaction rate constant = 0.083988 sec^{-1}

† D_{ij} matrix

The diffusion coefficients are smaller at high pressures so the diffusive fluxes are also lowered.

As the 2 nd and 4th examples of Table 4 are compared with each other, the former has greater concentration gradient and smaller enhancement factor. This could be due to the fact that higher concentration gradient creates higher diffusive flux. Also as the 1st and 4th examples of Table 5 are compared with each other, it is seen that the enhancement factor of the 4th example having greater ratio of reactant is greater than the enhancement factor of the 1st one. This is probable since at higher concentrations the reaction rate is higher.

As the constituent fluxes of the case where convective term is taken as zero are examined, it is seen that they are smaller than that found for the general solution and for the unreacting case. So this seems to indicate that the convective mechanism is just as important as the diffusive and reactive mechanisms in the system. Again for this system the main diffusion coefficients are greater than zero and greater than the cross diffusion coefficients. Since the molecular weights of the molecules do not differ much from each other, diffusion coupling is not so great in this system.

Secondly, the quaternary system iodine-hydrogen-hydrogen iodine-argon was studied where the homogeneous and 2nd order reversible gas phase reaction (Benson, 1960; and Graven, 1956) takes place at 781°K and 60 atm.

$$H_2 + I_2 \rightleftharpoons 2\,HI$$

The rate expression is

TABLE 6. - CONSTITUENT MOLAR FLUX CALCULATIONS FOR IODINE(I)-HYDROCEN(H)-HYDROGEN IODINE(HI)-ARGON QUATERNARY SYSTEM *

	Mole Fractions at Points 1 and 2		Calculated Multicomponent Diffusion Coefficients† (sq cm.sec^{-1}) x 10			Calculated Constituent Molar Fluxes (g moles. sec^{-1} sq.cm^{-1}) x 10^4			Enhancement Factors
						General Solution	Case 1	Case 2	
I	.1525	.1242	0.1226	-0.1917	0.0323	-0.0743	0.0713	-0.1431	-1.042
H	.1525	.1242	0.0241	1.5770	0.0196	0.1459	0.2884	0.0748	0.506
HI	.3050	.2484	0.0761	-0.3806	0.1918	0.4422	0.1537	0.2955	2.877
I	.0500	.0050	0.1261	-0.0488	0.0091	0.0148	0.0560	-0.0171	0.264
H	.1000	.0500	0.0167	2.0160	0.0135	0.5220	0.5623	0.4472	0.928
HI	.3000	.1000	0.0781	-0.3519	0.2399	0.4510	0.3693	0.2401	1.221
I	.1055	.0674	0.1290	-0.1409	0.0248	0.0224	0.1022	-0.7020	0.219
H	.1124	.0545	0.0171	1.8370	0.0139	0.5252	0.6027	0.4360	0.871
HI	.3137	.1199	0.0733	-0.3507	0.2124	0.5129	0.3592	0.2655	1.439
I	.1455	.1242	0.1259	-0.2020	0.0336	-0.0511	0.0517	-0.0930	0.988
H	.1137	.1001	0.0201	1.6530	0.0164	0.0442	0.1457	0.2361	0.303
HI	.3050	.2498	0.0815	-0.4127	0.1991	0.3268	0.1224	0.2361	2.676
I	.1057	.0545	0.1282	-0.1312	0.0232	0.0349	0.1055	-0.0483	0.331
H	.1057	.0523	0.0160	1.8550	0.0130	0.4693	0.5379	0.3907	0.872
HI	.3132	.1188	0.0737	-0.3511	0.2144	0.5002	0.3606	0.6086	1.387

Case 1- Solution for nonreacting case

Case 2- Solution when convective term is zero

† D_{ij} matrix

* For all examples
Diffusion distance = .2
Total pressure = 60.0 atm
Temperature = 781.0 K
Forward reaction rate constant = 1.5368 x10^3 cm^{3}mole^{-1}sec^{-1}
Backward reaction rate constant= 3.8679 x10 cm^3 mole^{-1}sec^{-1}

$$r = k_f C_{HI}^2 - k_b C_{H_2} C_{I_2}$$

The forward and backward reaction rate constants at different temperatures were found by the Arrhenius equation using the activation energy and constant as shown in Appendix C. Since one mole of iodine reacting with one mole of hydrogen produces 2 moles of hydrogen iodine, the total flux of the system stays constant. The reaction rate was linarized by the linearization procedure of Delancey (1974) as outlined in Appendix D. The linearized rate expression is of the form

$$r = k_{H_2} C_{H2} + k_{I_2} C_{I_2} + k_{HI} C_{HI}$$

It is seen from Table 6 that the enhancement factors for this second order reaction are also of appreciable extent. These figures are expected to diverge from unity more, since due to linearization, the reaction rates found may be less than the actual case. The constituent fluxes found for the case 2, where the solutions are obtained with no convective term, are less than the other cases. This seems to indicate again the relative importance of convective mass transfer in the system.

The multicomponent diffusion coefficients found are greater for this system than the other systems studied which could be seen as Table 6, and Table 4 or are compared. This could be due to the molecular weight differences between the molecules. The main diffusion coefficients are greater than zero and the cross diffusion coefficients which are either positive or negative are smaller than the main diffusion coefficients.

As the concentration profiles are examined for the two reacting systems using the data of Table 5 and 6, Figure 2 and 3 show that there

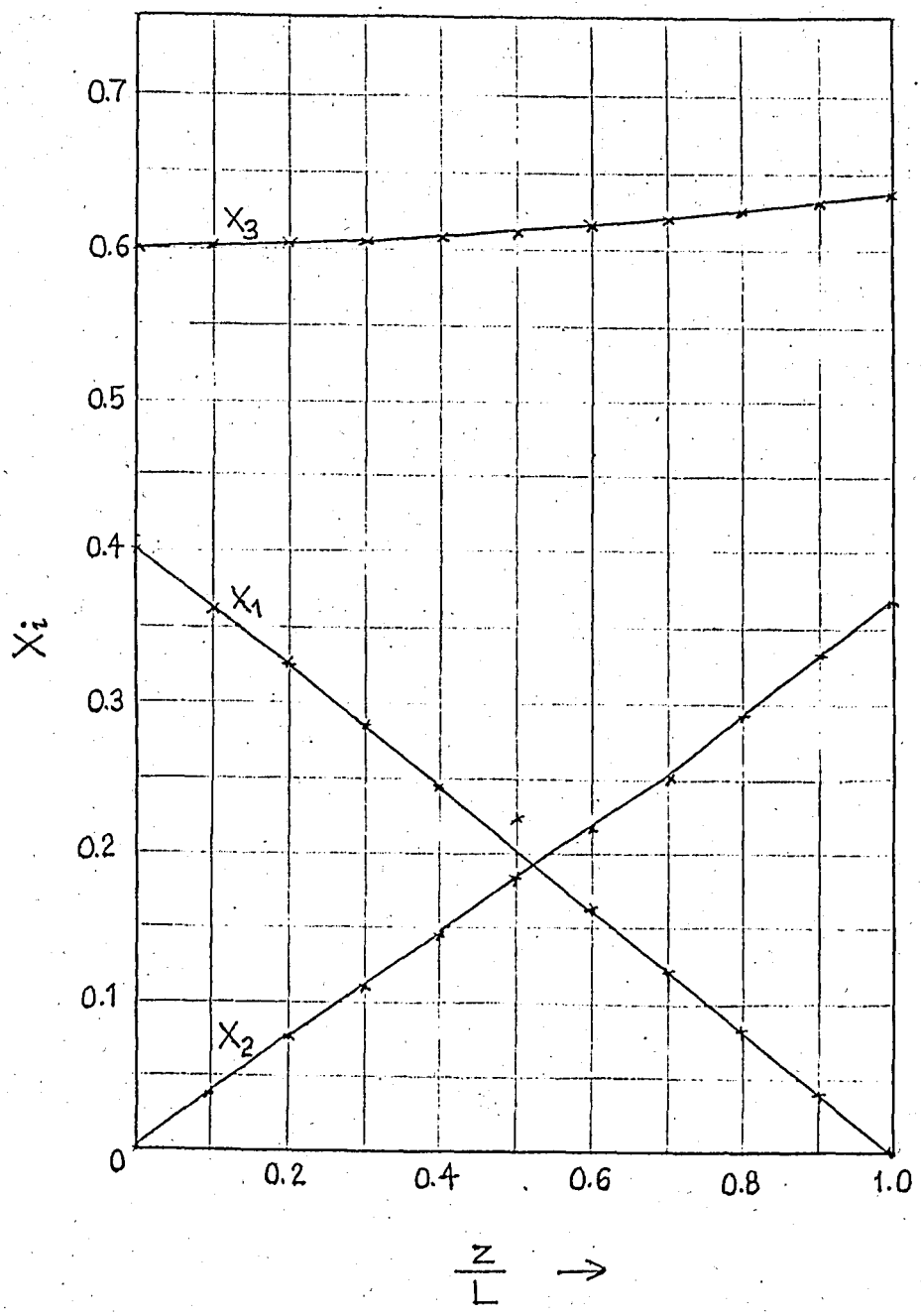


Fig 1 Concentration profiles

I=CO_2, 2=H_2O , 3=H_2

$X_1(o)$= .4029 $X_1(L)$=.0000

$X_2(o)$= .0000 $X_2(L)$=.3666

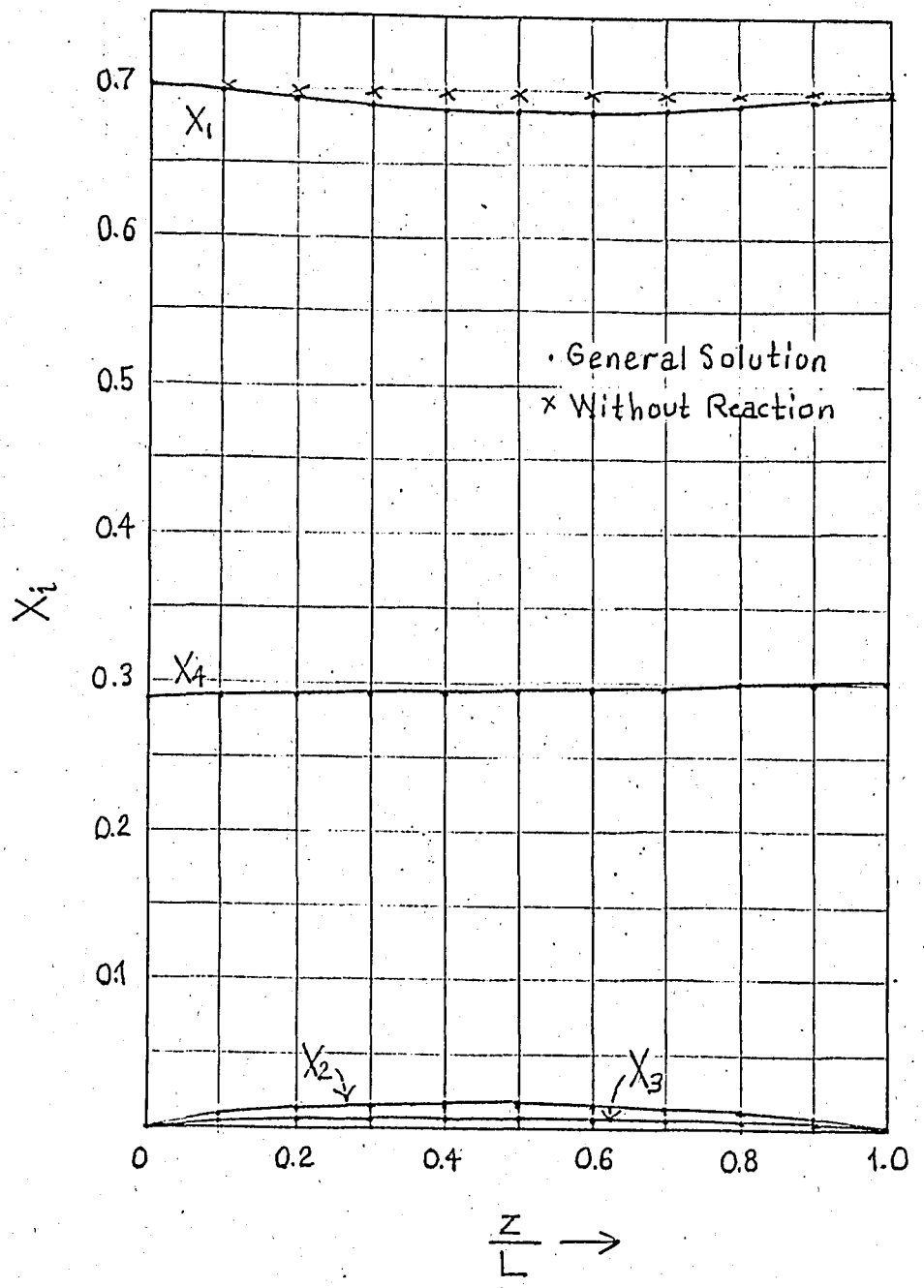


Fig 2. Comparison of concentration profiles

I=Cyclopropane, 2=Propene, 3=Argon, 4=Neon

$X_1(o)=.7000$ $X_1(L)=.6965$

$X_2(o)=.0050$ $X_2(L)=.0000$

$X_3(o)=.0050$ $X_3(L)=.0000$

Conditions given in Table 5.

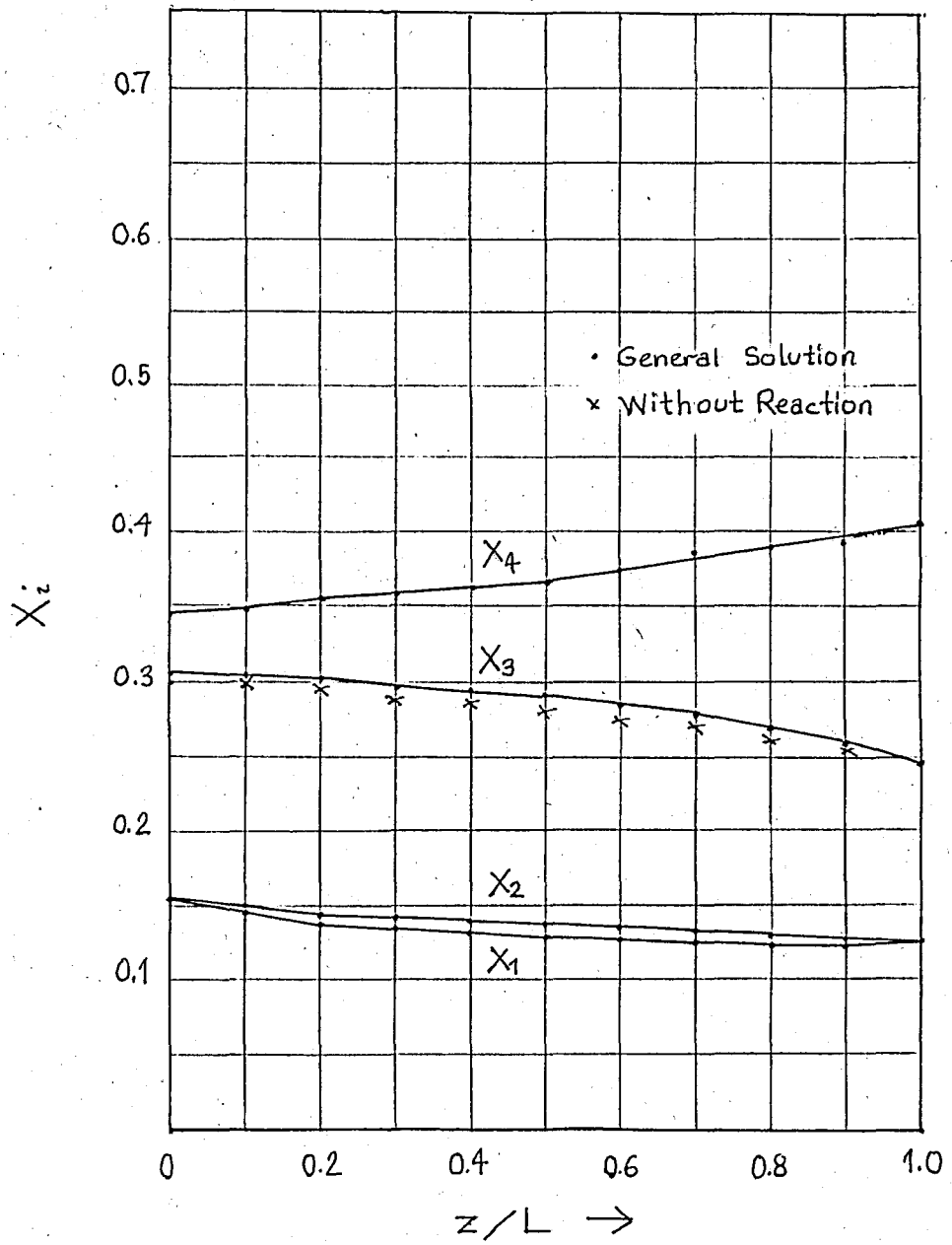


Fig. 3. Comparison of concentration profiles

1 = I_2, 2 = H_2, 3 = HI, 4 = A_r

$X_1(o)$ = .1525 $X_1(L)$ = .1242

$X_2(o)$ = .1525 $X_2(L)$ = .1242

$X_3(o)$ = .3050 $X_3(L)$ = .2484

Conditions given in Table 6.

are only small deviations between the reacting and nonreacting cases. For some other systems at different conditions that can be studied, these deviations may be greater. But it could be mentioned here that Smith and Taylor concluded that the solution of the linearized equations are satisfactory to find out the finite fluxes for design purposes rather to determine concentration profiles.

For liquid mixtures, existing theoretical computation procedures for calculating multicomponent diffusivities require complete information about the components properties, i.e. the activity coefficient γ_i. Most of these data are not available. So, in this thesis, calculations for reacting multicomponent liquid mixture could not be carried out.

In this thesis, in order to find out the fluxes in 3 cases; the general solution, Case 1 and Case 2, the same solution of the reduced second order differential eqtn was used. In literature the solution of Case 1 which covers the without reaction case (Amundson, 1964; and Taylor 1982) is quite similar to this, but in our solution the derivatives are taken simultaneously as the solution is obtained. For Case 2, where convective term is zero, the solution is given by Toor (1965). In this thesis, through the same reduction method the result is obtained much easier, since in Toor's method of solution the square root of the [D] matrix has to be taken, which is a difficult procedure.

So, the method of solution obtained for the multicomponent mass transfer with chemical reaction developed in this work can also be given as alternative solutions to the available solutions in literature for the two subcases, as in Case 1 giving $[k] = 0$, or Case 2 inserting $N_t = 0$ and without iteration.

V. CONCLUSIONS AND RECOMMENDATIONS

The conclusions that can be drawn for this thesis are listed as follows

1. As diffusive fluxes get smaller or reaction rate fluxes get higher, the enhancement factor deviates from unity in a greater extent. The relative values of the diffusive fluxes and the reaction rates are affected by the following :

   a. The higher the temperature, the greater the rate constant and the greater the reaction rate.

   b. As pressure increases, the concentration of the materials in the system increases whereas the diffusion coefficients decrease which leads to increases in rate fluxes and decreases in diffusive fluxes.

   c. The greater the ratio of the reactant, the greater the reaction rate.

   d. Higher average concentrations in between the boundaries results in higher diffusion coefficients and consequently greater diffusive fluxes.

e. Higher concentration gradient creates higher diffusive flux.

f. Higher moleculer weight differences between the molecules increases the diffusion coefficients and consequently the diffusive fluxes.

2. The constituent fluxes calculated for the case in which the convective term is zero are less than the constituent fluxes computed by the general solution and also the solution with no reaction. This seems to indicate that the convective mechanism is just as important as the diffusive and reactive mechanisms in the system.

3. Nonlinear reactions can also be dealt with by the method of solution developed in this work by linearizing the nonlinear terms as shown by Delancey (1974).

4. The advantage of the uncoupling method is that the tiresome computation of the eigenvalues of multicomponent diffusion matrix is avoided. In addition, the uncoupling method must be utilized if [D] can not be diagonalized or the modal matrix can not be found.

5. The method of solution obtained in this thesis for the multicomponent mass transfer with chemical reaction can also be given as alternative solutions to the available solutions in literature for the two subcases; one without reaction, and the other without convective term.

The recommendations for future work can be summarized as follows;

1. The method of solution developed in this work can be applied to other systems with different reaction mechanisms and at different conditions.
2. The diffusion coefficients and constituent flux calculations should be carried out for multicomponent liquid mixtures.
3. The method of solution of this work can be applied to the reactive mixture where total molar flux is not constant by rewriting the variables in mass units since the total mass flux remains a constant.
4. The linearized equations with the reference velocities changing with distance can be tried to be solved.
5. The calculations done by the general solution for the film model can also be developed for the penetration model.

NOTATION

b_{ij}	order of reverse rate in reaction j associated with species i.
(C)	concentration vector
D_{ij}	binary diffusion coefficients.
$Đ_{ik}$	Maxwell-Stefan diffusion coefficients
[D]	multicomponent diffusion coefficient matrix
D_i	eigenvalues of [D] matrix
E	activation energy
f_{ij}	order of forward rate for reaction j associated-with species i.
[I]	identity matrix
(J)	diffusion flux vector with element j_i
[k]	matrix of reaction rate constants, k_{ij}; reaction i, species j.
k_{if}	forward reaction rate constant
k_{ib}	backward reaction rate constant
(N)	constituent flux vector with elements N_i
N_t	total constituent flux
P_c	critical pressure
(r)	reaction rate vector with element r_i
T	temperature of the system
T_c	criticial temperature
[t]	modal matrix
$\underline{V}$	reference velocity
(x_2)	mole fraction vector with elements x_i
$(\hat{x})$	pseudo composition vector with elenets $\hat{x}_i$
Z	position coordinate

Greek Letters

Γ_{ij} thermodynamic factors

δ_{ij} Kronecker delta

(η) pseudo constituent flux vector

ϕ_{ij} correction factor associated with species j in the i^{th} reaction arising from linearization procedure

M_i chemical potential of species i.

γ_i coefficient of species i.

REFERENCES

1. Amundson, N.R., "Mathematical Methods in Chemical Engineering", Prentice-Hall,Inc., London, 1966.

2. Bamford, C.H., and C.F.H. Tipper, ed., "Comprehensive Chemical Kinetics", Vol.5, Elsevier Publishing Company, Amsterdam, 1972.

3. Beker, H., Private Communication, Boğaziçi University,1984

4. Benson, S.W., "The Foundations of Chemical Kinetics", Mc Graw-Hill Book Campany, Inc., New York,1960.

5. Bird, R.B., W.E. Stewart, and E.N. Lightfoot, "Transport Phenomena," John Wiley and Sons, Inc., New York, 1960.

6. Bronson, R. "Matrix Methods-An Introduction", Academic Press, New York, 1970.

7. Chambers, T.S., and G.B. Kistiakowsky, J.Am.Chem.Soc., Vol.56, p. 399, 1934.

8. Cussler, E.L., "Multicomponent Diffusion", Elsevier Scientific Publishing Company, Amsterdam, 1976.

9. Delancey, G.B., Chem. Eng'g Sci., Vol.29, P. 2315, 1974.

10. Kondratev, V.N., "Chemical Kinetics of Gas Reactions", Addison Wesley Publishing Company Inc., 1964.

11. Krishna, R., and G.L. Standart, Chem. Eng. Commun., Vol.3, p.201, 1979.

12. Lee, S.T., and G.B. Delancey, Chem. Eng'g Sci., Vol. 29, p. 2325,1974.

13. Reid, R.B., and T.K. Sherwood," The properties of Gases and Liquids", Mc Graw-Hill Book Company, Inc., New York, 1958.

14. Robinson, P.J. and K.A. Holbrook, "Unimolecular Reactions", John Wiley and Sons Ltd., London, 1972.

15. Smith, L.W., and R. Taylor, Ind. Eng. Chem. Fundam., Vol. 22, P. 97, 1983.

16. Taylor, R., Computers and Chem. Eng., Vol. 6, No 1, p. 69., 1982 a.

17. Taylor, R., Ind. Eng. Chem. Fundam., Vol. 21, p. 407, 1982 b.

18. Torr, H.L., AIChE Journal , Vol. 10, No.4, P. 448, 1964 a.

19. Toor, H.L., AIChE Journal , Vol. 10., No.4, p. 460, 1964 b.

20. Toor, H.L., Chem. Eng'g Sci., Vol. 20, p. 941, 1965.

21. Wilke, C.R., Chem. Eng'g Progress, Vol. 46, No.2, P. 95, 1950.

APPENDICES

APPENDIX A

TABLE 4.a - CONCENTATION PROFILE CALCULATIONS FOR CYCLOPROPANE(C)-PROPENE(P)-ARGON(A)-NEON QUATERNARY SYSTEM*

Z/L	0.0†	0.1	.0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0††
C	.1555	.1545	.1535	.1527	.1520	.1514	.1509	.1505	.1503	.1501	.1501
P	.0095	.0092	.0088	.0083	.0077	.0069	.0061	.0051	.0040	.0028	.0015
A	.0033	.0033	.0034	.0034	.0034	.0035	.0035	.0035	.0035	.0036	.0036
C	.2112	.2088	.2067	.2049	.2033	.2020	.2010	.2002	.1997	.1995	.1995
P	.1823	.1832	.1838	.1841	.1842	.1840	.1835	.1828	.1818	.1805	.1789
A	.2645	.2651	.2657	.2663	.2668	.2674	.2680	.2687	.2693	.2699	.2705
C	.1112	.1095	.1079	.1065	.1052	.1039	.1028	.1018	.1009	.1002	.0995
P	.1725	.1727	.1727	.1727	.1725	.1722	.1718	.1712	.1706	.1698	.1689
A	.2645	.2651	.2657	.2663	.2669	.2675	.2681	.2687	.2693	.2699	.2705
C	.2700	.2683	.2670	.2660	.2654	.2651	.2652.	.2656	.2663	.2574	.2688
P	.1815	.1829	.1839	.1846	.1849	.1849	.1846	.1839	.1829	.1815	.1798
A	.0200	.0201	.0202	.0203	.0204	.0205	.0206	.0207	.0208	.0209	.0210

* For General solution and at the conditions given in Table 4

† Mole fractions at point 1.

†† Mole fractions at point 2.

TABLE 4.b - CONCENTRATION PROFILE CALCULATIONS FOR CYCLOPROPHANE(C)-PROPENE(P)-ARGON(A)-NEON QUATERNARY SYSTEM*

Z/L	0.0†	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0††
C	.1555	.1550	.1544	.1539	.1533	.1528	.1523	.1517	.1512	.1506	.1501
P	.0095	.0087	.0079	.0071	.0063	.0055	.0047	.0039	.0031	.0023	.0015
A	.0033	.0033	.0034	.0034	.0034	.0035	.0035	.0035	.0035	.0036	.0036
C	.2112	.2101	.2089	.2078	.2066	.2054	.2043	.2031	.2019	.2007	.1995
P	.1823	.1820	.1816	.1813	.1809	.1806	.1803	.1799	.1796	.1792	.1789
A	.2645	.2651	.2657	.2662	.2668	.2674	.2680	.2686	.2693	.2699	.2705
C	.1112	.1101	.1089	.1077	.1066	.1054	.1042	.1031	.1019	.1007	.0995
P	.1725	.1721	.1718	.1714	.1711	.1707	.1703	.1700	.1696	.1693	.1689
A	.2645	.2651	.2657	.2663	.2669	.2675	.2681	.2687	.2693	.2699	.2705
C	.2700	.2699	.2698	.2696	.2695	.2694	.2693	.2692	.2690	.2689	.2688
P	.1815	.1813	.1812	.1810	.1808	.1807	.1805	.1803	.1801	.1800	.1798
A	.0200	.0201	.0202	.0203	.0204	.0205	.0206	.0207	.0208	.0209	.0210

* For unreacting case and at the conditions given in Table 4.

† Mole fractions at point 1.

†† Mole fractions at point 2.

TABLE 4.c - CONCENTRATION PROFILE CALCULATIONS FOR CYCLOPROPANE(C)-PROPENE(P)-ARGON(A)-NEON QUATERNARY

	†SYSTEM*										‡‡
Z/L	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
C	.1555	.1545	.1535	.1527	.1520	.1514	.1509	.1505	.1503	.1501	.1501
P	.0095	.0092	.0088	.0083	.0077	.0069	.0061	.0051	.0040	.0028	.0015
A	.0033	.0033	.0034	.0034	.0034	.0035	.0035	.0035	.0035	.0036	.0036
C	.2112	.2088	.2067	.2048	.2032	.2019	.2009	.2002	.1997	.1995	.1995
P	.1823	.1832	.1838	.1841	.1842	.1840	.1835	.1828	.1817	.1805	.1789
A	.2645	.2651	.2657	.2663	.2669	.2675	.2681	.2687	.2693	.2699	.2705
C	.1112	.1095	.1079	.1064	.1051	.1039	.1028	.1018	.1009	.1001	.0995
P	.1725	.1727	.1727	.1727	.1725	.1722	.1718	.1712	.1706	.1698	.1689
A	.2645	.2651	.2657	.2663	.2669	.2675	.2681	.2687	.2693	.2699	.2705
C	.2700	.2683	.2670	.2660	.2654	.2651	.2652	.2656	.2663	.2674	.2688
P	.1815	.1829	.1839	.1846	.1849	.1849	.1846	.1839	.1829	.1815	.1798
A	.0200	.0201	.0202	.0203	.0204	.0205	.0206	.0207	.0208	.0209	.0210

* For the case where convective term is zero and at the condictions given in Table 4.

† Mole fractions at point 1.

‡‡ Mole fractions at point 2.

TABLE 5.a - CONCENTRATION PROFILE CALCULATIONS FOR CYCLOPROPANE(C)-PROPENE(P)-ARGON(A)-NEON QUATERNARY SYSTEM *

Z/L	0.0 †	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0 ††
C	.1000	.0990	.0980	.0972	.0965	.0959	.0955	.0951	.0949	.0949	.0950
P	.1000	.0919	.0834	.0747	.0657	.0564	.0468	.0368	.0266	.0160	.0050
A	.1000	.0994	.0988	.0982	.0977	.0972	.0967	.0962	.0958	.0954	.0950
C	.3700	.3675	.3655	.3640	.3631	.3627	.3628	.3635	.3647	.3665	.3688
P	.1815	.1837	.1854	.1866	.1872	.1873	.1869	.1859	.1844	.1824	.1798
A	.0200	.0201	.0202	.0203	.0204	.0205	.0206	.0207	.0208	.0209	.0210
C	.5000	.4964	.4934	.4912	.4896	.4887	.4885	.4890	.4902	.4922	.4950
P	.0050	.0076	.0096	.0109	.0115	.0114	.0106	.0090	.0068	.0038	.0000
A	.0950	.0940	.0931	.0921	.0911	.0901	.0891	.0881	.0871	.0860	.0850
C	.7000	.6944	.6899	.6865	.6843	.6833.	.6834	.6848	.6874	.6913	.6965
P	.0050	.0098	.0134	.0160	.0173	.0175	.0165	.0143	.0108	.0061	.0000
A	.0050	.0054	.0040	.0035	.0031	.0026	.0021	.0016	.0010	.0005	.0000

* For general solution and at the conditions given in Table 5.

† Mole fractions at point 1.

†† Mole fractions at point 2.

TABLE 5.b - CONCENTRATION PROFILE CALCULATIONS FOR CYCLOPROPANE(C)-PROPENE(P)-ARGON(A)-NEON QUATERNARY SYSTEM*

Z/L	0.0†	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0††
C	.1000	.0993	.0986	.0980	.0974	.0969	.0964	.0959	.0956	.0953	.0950
P	.1000	.0195	.0828	.0739	.0648	.0554	.0459	.0360	.0259	.0156	.0050
A	.1000	.0994	.0988	.0982	.0977	.0972	.0967	.0962	.0958	.0954	.0950
C	.3700	.3699	.3698	.3696	.3695	.3694	.3693	.3692	.3690	.3689	.3688
P	.1815	.1813	.1812	.1810	.1808	.1807	.1805	.1803	.1801	.1800	.1798
A	.0200	.0201	.0202	.0203	.0204	.0205	.0206	.0207	.0208	.0209	.0210
C	.5000	.4995	.4989	.4984	.4979	.4974	.4969	.4964	.4959	.4955	.4950
P	.0050	.0045	.0041	.0036	.0031	.0026	.0021	.0016	.0011	.0005	.0000
A	.0950	.0940	.0931	.0921	.0911	.0901	.0891	.0881	.0871	.0860	.0850
C	.7000	.6996	.6992	.6989	.6985	.6982	.6978	.6975	.6971	.6968	.6965
P	.0050	.0045	.0041	.0036	.0031	.0026	.0021	.0016	.0011	.0005	.0000
A	.0050	.0045	.0040	.0035	.0031	.0026	.0021	.0016	.0010	.0005	.0000

*For unreacting case and at the conditions given in Table 5.

†Mole fractions at point 1.

††Mole fractions at point 2.

TABLE 5.c - CONCENTRATION PROFILE CALCULATIONS FOR CYCLOPROPANE(C)-PROPENE(P)-ARGON(A)-NEON QUATERNARY SYSTEM *

Z/L	0.0†	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0††
C	.1000	.0992	.0984	.0977	.0971	.0965	.0961	.0957	.0954	.0952	.0950
C	.1000	.0909	.0816	.0723	.0629	.0535	.0439	.0343	.0246	.0148	.0050
A	.1000	.0995	.0990	.0985	.0980	.0975	.0970	.0965	.0960	.0955	.0950
C	.3700	.3675	.3655	.3640	.3631	.3627	.3628	.3635	.3647	.3665	.3688
P	.1815	.1837	.1855	.1866	.1872	.1873	.1869	.1859	.1844	.1824	.1798
A	.0200	.0201	.0202	.0203	.0204	.0205	.0206	.0207	.0208	.0209	.0210
C	.5000	.4963	.4934	.4911	.4896	.4887	.4886	.4891	.4904	.4923	.4950
P	.0050	.0077	.0096	.0109	.0114	.0113	.0104	.0089	.0066	.0037	.0000
A	.0950	.0940	.0930	.0920	.0910	.0900	.0890	.0880	.0870	.0860	.0850
C	.7000	.6943	.6897	.6864	.6843	.6833	.6836	.6850	.6877	.6915	.6965
P	.0050	.0099	.0136	.0160	.0173	.0174	.0163	.0140	.0105	.0059	.0000
A	.0050	.0045	.0040	.0035	.0030	.0025	.0020	.0015	.0010	.0005	.0000

* For the case where convective term is zero and at the conditions given in Table 5

† Mole fractions at point 1.

†† Mole fractions at point 2.

TABLE 6.a - CONCENTRATION PROFILE CALCULATIONS FOR IODINE(I)-HYDROGEN(H)-HYDROGEN IODIDE(HI)-ARGON QUATERNARY SYSTEM*

Z/L	0.0†	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0††
I	.1525	.1475	.1428	.1386	.1348	.1315	.1287	.1265	.1250	.1242	.1242
H	.1525	.1496	.1466	.1438	.1409	.1381	.1352	.1324	.1297	.1269	.1242
HI	.3050	.3039	.3020	.2992	.2954	.2905	.2846	.2775	.2692	.2595	.2484
I	.0500	.0473	.0444	.0413	.0378	.0338	.0295	.0245	.0189	.0214	.0050
H	.1000	.0951	.0902	.0853	.0804	.0754	.0704	.0653	.0602	.0551	.0500
HI	.3000	.2871	.2730	.2574	.2403	.2216	.2012	.1789	.1547	.1284	.1000
I	.1055	.1021	.0986	.0950	.0913	.0875	.0835	.0795	.0755	.0714	.0674
H	.1124	.1068	.1011	.0955	.0897	.0839	.0781	.0723	.0664	.0605	.0545
HI	.3137	.3034	.2916	.2782	.2629	.2456	.2260	.2040	.1791	.1512	.1199
I	.1455	.1414	.1377	.1343	.1314	.1290	.1269	.1254	.1244	.1240	.1242
H	.1137	.1122	.1108	.1094	.1080	.1066	.1053	.1039	.1026	.1014	.1001
HI	.3050	.3028	.2999	.2963	.2921	.2871	.2813	.2747	.2673	.2590	.2498
I	.1057	.1018	.0977	.0934	.0888	.0839	.0788	.0733	.0675	.0612	.0545
H	.1057	.1005	.0953	.0900	.0847	.0794	.0740	.0686	.0632	.0578	.0523
HI	.3132	.3021	.2896	.2756	.2598	.2421	.2223	.2003	.1759	.1488	.1188

* For general solution and at the conditions given Table 6.

† Mole fractions at point 1.

†† Mole fractions at point 2

TABLE 6.b - CONCENTRATION PROFILE CALCULATIONS FOR IODINE(I)-HYDROGEN(H)-HYDROGEN IODIDE(HI)-ARGON QUATERNARY SYSTEM*

Z/L	0.0†	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0††
I	.1525	.1505	.1483	.1460	.1435	.1409	.1380	.1349	.1316	.1280	.1242
H	.1525	.1497	.1469	.1442	.1413	.1385	.1357	.1328	.1300	.1271	.1242
HI	.3050	.3005	.2958	.2908	.2856	.2801	.2743	.2683	.2619	.2553	.2484
I	.0500	.0478	.0453	.0424	.0391	.0352.	.0308	.0257	.0918	.0130	.0050
H	.1000	.0952	.0903	.0854	.0804	.0755	.0704	.0654	.0603	.0552	.0500
HI	.3000	.2865	.2719	.2560	.2387	.2199	.1995	.1775	.1536	.1278	.1000
I	.1055	.1031	.1004	.0975	.0943	.0907	.0868	.0825	.0779	.0729	.0674
H	.1124	.1069	.1013	.0956	.0899	.0841	.0783	.0724	.0665	.0605	.0545
HI	.3137	.3022	.2894	.2752	.2594	.2418	.	.2006	.1764	.1497	.1199
I	.1455	.1437	.1418	.1399	.1379	.1358	.1336	.1314	.1291	.1267	.1242
H	.1137	.1124	.1110	.1097	.1083	.1069	.1056	.1042	.1028	.1015	.1001
HI	.3050	.3002.	.2952	.2901	.2849	.2795	.2739	.2681	.2622	.2561	.2498
I	.1057	.1027	.0995	.0958	.0917	.0871	.0819	.0762	.0697	.0626	.0545
H	.1057	.1006	.0954	.0902	.0849	.0796	.0742	.0688	.0633	.0578	.0523
HI	.3132	.3010	.2875	.2727	.2564	.2384	.2187	.1971	.1734	.1473	.1188

*For uncreacting case and at the condidions given in Table 6.

† Mole fractions at point 1.

†† Mole fractions at point 2.

TABLE 6.c - CONCENTRATION PROFILE CALCULATIONS FOR IODINE(I)-HYDROGEN(H)-HYDROGEN IODIDE(HI)-ARGON QUATERNARY SYSTEM*

Z/L	0.0†	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0††
I	.1525	.1461	.1406	.1359	.1320	.1288	.1265	.1248	.1239	.1237	.1242
H	.1525	.1495	.1465	.1436	.1407	.1379	.1351	.1323	.1296	.1269	.1242
HI	.3050	.3033	.3006	.2970	.2926	.2873	.2811	.2741	.2664	.2578	.2484
I	.0500	.0450	.0401	.0354	.0308	.0263	.0219	.0176	.0134	.0092	.0050
H	.1000	.0950	.0900	.0849	.0799	.0749	.0699	.0650	.0600	.0550	.0500
HI	.3000	.2806	.2610	.2413	.2214	.2014	.1813	.1611	.1408	.1204	.1000
I	.1055	.1004	.0956	.0911	.0869	.0831	.0795	.0761	.0730	.0701	.0674
H	.1124	.1065	.1007	.0949	.0891	.0833	.0775	.0717	.0660	.0602	.0545
HI	.3137	.2958	.2776	.2589	.2400	.2207	.2011	.1812	.1610	.1406	.1199
I	.1455	.1408	.1368	.1333	.13003	.1280	.1261	.1249	.1241	.1239	.1242
H	.1137	.1122	.1108	.1093	.1079	.1066	.1052	.1039	.1026	.1013	.1001
HI	.3050	.3023	.2989	.2949	.2903	.2850	.2792	.2727	.2627	.2580	.2498
I	.1057	.0993	.0933	.0876	.0821	.0769	.0720	.0673	.0629	.0586	.0545
H	.1057	.1003	.0949	.0895	.0842	.0788	.0735	.0682	.0629	.0576	.0523
HI	.3132	.2952	.2768	.2581	.2390	.2196	.2000	.1800	.1599	.1394	.1188

* For the case where convective term is zero and at the conditions given in Table 6.

† Mole fractions at point 1.

†† Mole fractions at point 2.

APPENDIX B - CALCULATION OF THE BINARY DIFFUSION COEFFICIENTS AND LIST OF CALCULATED BINARY DIFFUSION COEFFICIENTS.

The following equation for the estimation of the binary diffusion coefficients D_{AB} at low concentrations has been devoloped (Bird, 1960) from a combination of kinetic theory and corresponding states arguments:

$$\frac{P\, D_{AB}}{(P_{CA}\, P_{CB})^{1/3}\, (T_{CA}\, T_{CB})^{5/12} \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2}} = a \left(\frac{T}{\sqrt{T_{CA}\, T_{CB}}} \right)^{b}$$

D_{AB} : $cm^2 . sec^{-1}$

P : atm

T : ^{o}K

For nonpolar gas pairs :

$a = 2.475 \times 10^{-4}$

$b = 1.823$

For H_2O with a nonpolar gas :

$a = 3.640 \times 10^{-4}$

$b = 2.334$

Calculated Binary Diffusion Coefficients

a. For $CO_2(1)$-$H_2O(2)$-$H_2(3)$ ternary system

T = 313 °K , P = 150. mm Hg.

D_{12} = 0.0922 cm^2/sec.

D_{13} = 0.27064 cm^2/sec.

$D_{2,3}$ = 0.34576 cm^2/sec.

b. For cyclopropane(1)-propene(2)-argon(3)-neon(4) quaternary system

T = 865 °K , P = 70 atm

D_{12} = .0147 cm^2/sec.

D_{13} = .0294 cm^2/sec

D_{14} = .0746 cm^2/sec

D_{23} = .0296 cm^2/sec

$D_{2,4}$ = .0752 cm^2/sec

$D_{3,4}$ = .1498 cm^2/sec

c. For $I_2(I)$-$H_2(2)$-HI(3)-Ar(4) quaternary system.

T = 781 °K , P = 60 atm

D_{12} = .0943 cm^2/sec

D_{13} = .0057 cm^2/sec

D_{14} = .0161 cm^2/sec

D_{23} = .1341 cm^2/sec

D_{24} = .2475 cm^2/sec

D_{35} = .0243 cm^2/sec

APPENDIX C - LIST OF COMPONENT PROPERTIES

C.1 - Critical Properties

Comp.	Tc(^{o}K)	Pc(atm)
Argon	150.07	48.0
Cyclopropane	397.8	54.2
Hydrogen	53.1	12.8
Hydrogen iodine	423.0	81.9
Iodine	785.0	116.0
Neon	44.4	27.2
Propene	365.0	45.6

C.2 - Activation Energies and Arrrhenius Constants of the Reactions

Reaction	log A*	E (k cal/mole)
Cyclopropane→Propene	15.5	65.6
$H_2+I_2 \rightarrow 2HI$	14.1	39.0
$2HI \rightarrow H_2 + I_2$	13.9	44.0

*A is sec^{-1} for 1^{st} order reaction and

$cm^3\ mole^{-1}\ sec^{-1}$ for 2^{nd} order reaction.

APPENDIX D - LINEARIZATION OF THE NONLINEAR REACTIONS

For a film model, the reaction velocities can be evaluated such that the isothermal reaction rate eqtn.

$$(r) = [k]\,(c)$$

represents the true kinetics of the nonlinear reaction rate expressions in the sense of the least square error between the concentration limits defined by the interfacial and bulk values (Delancey, 1974). For example, the nonlinear rate expression for a single reaction can be considered which depends upon the concentration of species i only and is given by $k_f C_i^m$ Delancey (1974) showed that the nonlinear expression can be replaced by $k_i C_i$ where k_i is to be evaluated from the condition

$$\underset{k_i}{\text{Min}} \int_{C_{io}}^{C_{iL}} \left[k_f C_i^m - k_i C_i \right]^2 d C_i$$

The rate expression is given by the eqtn

$$r_i = \sum_{j=1}^{N} k_{ij} C_j$$

which includes a wide class of reaction schemes, and the reaction rate constants of a multicomponent system is obtained as

$$k_{ij} = k_{if}\, \phi_{ij,f} \prod_{\substack{\ell=1 \\ \ell \neq j}}^{N} C_{\ell o}^{f_{\ell i}}\, C_{jo}^{f_{ij-1}} - k_{ib}\, \phi_{ij,b} \prod_{\substack{\ell=1 \\ \ell \neq j}} C_{\ell o}^{b_{\ell i}}\, C_{jo}^{b_{ji-1}}$$

$$i = 1,2,\ldots,R$$

$$j = 1,2,\ldots,N$$

for R independent reactions and N no of species where

$$\phi_{ij,f}\,(f_{1i},f_{2i},\ldots,f_{Ni}) = \frac{12\,(1+\gamma_j)}{(1-\gamma_j)} \left| \frac{1}{f_{ij}+2} \frac{1-\gamma_j^{f_{ij}+2}}{(1+\gamma_j)(1-\gamma_j^{f_{ij}+1})} \right.$$

$$\left. - \frac{1}{f_{ij}+1} \frac{\sum_{\substack{\alpha=1 \\ f_{i\alpha}\neq 0}}^{N} \frac{f_{i\alpha}+1}{f_{i\alpha}+2} \frac{(1-\gamma_\alpha^{f_{i\alpha}+2})(1+\gamma_\alpha)}{(1-\gamma_\alpha^{f_{i\alpha}+1})(1-\gamma_\alpha)^2}}{\frac{1}{3} + \sum_{\substack{\alpha=1 \\ f_{i\alpha}\neq 0}}^{N} \left(\frac{1+\gamma_\alpha}{1-\gamma_\alpha}\right)^2} \right|$$

$$\times \prod_{\substack{\ell=1 \\ \ell\neq j}}^{N} \frac{1}{m_\ell+1} \frac{(1-\gamma_\ell^{m_\ell+1})}{(1-\gamma_\ell)}$$

For $j = 1,2,\ldots,N$ and if $f_{ij} = 0$.

where $\gamma_j = \dfrac{C_j\,L}{C_j\,0}$ $\qquad \alpha = 1,2,\ldots N$

[k] = matrix of reaction rate constants, k_{ij}; reaction i, species,

k_{if} = forward reaction rate constant of reaction i.

k_{ib} = backward reaction rate constant of reaction i.

f_{ij} = order of forward rate for reaction j associated with species i.

b_{ij} = order of reverse rate in reaction j associated with species i.

ϕ_{ij} = correction factor associated with species j in the i^{th} reaction arising from linearization procedure

$C_{\alpha L}$ = concentration of species j at Z = L

$C_{\alpha 0}$ = concentration of species j at Z = 0

For the second order reaction

$$\underset{(1)}{H_2} + \underset{(2)}{I_2} \rightleftarrows \underset{(3)}{2HI}$$

$$k_{11} = k_{1f}\, \phi_{11,f}\, C_{20}$$

$$k_{12} = k_{1f}\, \phi_{12,f}\, C_{10}$$

$$k_{13} = -k_{1b}\, \phi_{13,b}\, C_{30}^{2}$$

$$\phi_{11,f} = \frac{2\,(1+\gamma_1)\,(1+\gamma_2)}{(1-\gamma_1)^2}\left[\frac{(1-\gamma_1)^3}{(1+\gamma_1)(1-\gamma_1)^2} - \frac{\dfrac{(1-\gamma_1)^3}{(1-\gamma_1)^3}\,\dfrac{(1-\gamma_2)^3}{(1-\gamma_2)^3}}{\dfrac{1}{3}+\left(\dfrac{1+\gamma_1}{1-\gamma_1}\right)^2\left(\dfrac{1+\gamma_2}{1-\gamma_2}\right)^2}\right]$$

Similarity $\phi_{12,f}$ is found. Also,

$$\phi_{13,b} = \frac{3\,(1+\gamma_3)}{(1-\gamma_3)^2}\left[\frac{(1-\gamma_3)^4}{(1+\gamma_3)\,(1-\gamma_3^3)} - \frac{\dfrac{(1-\gamma_3^4)\,(1+\gamma_3)}{(1-\gamma_3^3)\,(1-\gamma_3)^2}}{\dfrac{1}{3}\left(\dfrac{1+\gamma_3}{1-\gamma_3}\right)^2}\right]$$

Finally, the reaction rate matrix is written as

$$[k] = \begin{bmatrix} -k_1 & -k_2 & -k_3 \\ -k_1 & -k_2 & -k_3 \\ 2k_1 & 2k_2 & 2k_3 \end{bmatrix}$$

APPENDIX E- EVALUATION OF THE EIGENVALUES AND THE MODAL MATRIX OF SQUARE MATRICES.

A nonzero vector X is an eigenvector (or characteristic vector) of a square matrix A if there exists a scalar λ such that

$$A X = \lambda X \qquad \text{E.1}$$

then λ is an eigenvalue (or characteristic value) of A. Equivalently,

$$AX - \lambda X = 0 \qquad \text{E.2}$$

or

$$(A-\lambda I) X = 0 \qquad \text{E.3}$$

I being the indentity matrix. X will be an eigenvector of A if and only if

$$\det (A-\lambda I) = 0 \qquad \text{E.4}$$

Eqtn. E.4 is called the characteristic equation of matrix A. After the roots of eqtn E.4 are found as $\lambda_1, \lambda_2, \ldots, \lambda_n$ being the eigenvalues, the eqtn.

$$(A-\lambda_i I) X_i = 0 \qquad \text{E.5}$$

is utilized for each λ_i to find each eigenvector X_i.

i.e. for $\lambda_i = \lambda_1$

$$(A-\lambda_1 I) X_1 = 0 \qquad \text{E.6}$$

$$X_1 = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix}$$

Or,

$$\left\{ \begin{vmatrix} a_{11} & a_{12} \cdots q_{12} \\ a_{21} & \cdots \\ \vdots & \\ a_{n1} & \cdots q_{nn} \end{vmatrix} - \begin{vmatrix} \lambda_1 & & 0 \\ & \lambda_2 & \\ & \ddots & \\ 0 & & \lambda_n \end{vmatrix} \right\} \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \qquad \text{E.8}$$

From eqtn. E.8., knowing the numerical values of λ_n, n eqtns which are the linear combinations of the n unknowns $x_1, x_2, \ldots, x_n$ are obtained.

$$\begin{aligned} C_{11}\ x_1 + C_{12}\ x_2 + \ldots\ldots + C_{12}\ x_n &= 0 \\ C_{21}\ x_1 + C_{22}\ x_2 + \ldots\ldots + C_{2n}\ x_n &= 0 \\ \vdots \qquad\qquad \vdots \qquad\qquad \vdots & \\ C_{n1}\ x_1 + C_{n2}\ x_2 + \ldots\ldots\ C_{nn}\ x_n &= 0 \end{aligned}$$

C_{ij} are numerical values. Solving these n equations simultaneously, eigenvector X_1 for eigenvalue λ_1 is found

$$X_1 = x_i \begin{pmatrix} d_1 \\ d_2 \\ \vdots \\ d_n \end{pmatrix}$$

where $d_1, d_2, \ldots, dn$ are numeriracl values and x_n an arbitary value. The x_n can be chosen in such a manner that the resulting eigenvector becomes a unit vector.

Then one by one the n eigenvectors are found separately in the same way. Finally, by writing n columns of eigenvectors side by side, the modal matrix [t] as mentioned in Chapter II. A is found.

For a ternary systems, the eigenvalues found are

$$\bar{D}_{1,2} = \frac{(D_{11}+D_{22}) \pm (D_{11}-D_{22})\sqrt{1 + 4D_{12}D_{21} / (D_{11}-D_{22})^2}}{2}$$

and the modal matrix is;

$$t = \begin{vmatrix} 1 & \dfrac{D_{12}}{\bar{D}_2-D_{11}} \\ \dfrac{\bar{D}_1-D_{11}}{D_{12}} & 1 \end{vmatrix}$$

which are used in the subroutine DIAG.

APPENDIX F

```
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
C       MAIN PROGRAM
C
C       PURPOSE: CALCULATES THE CONSTITUENT MOLAR FLUXES AND CON-
C                CENTRATION PROFILES OF MULTICOMPONENT SYSTEMS
C                FOR A FILM MODEL.
C
C       PARAMETERS
C
C          CONTROL VARIABLES
C
C          NN      _ NUMBER OF COMPONENTS
C          KEY     _ EXECUTION CODE WHICH IS EQUAL TO
C                    1 _ FOR GENERAL SOLUTION
C                    2 _ FOR UNREACTING CASE
C                    3 _ FOR THE CASE WHERE CONVECTIVE TERM IS ZERO
C          KO        EXECUTION CODE WHICH DEFINES THE ORDER OF THE
C                    REACTION
C                    1 _ FIRST ORDER IRREVERSIBLE REACTION
C                    2 _ SECOND ORDER REVERSIBLE REACTION
C
C       PROGRAM VARIABLES TO BE SUPPLIED
C
C          YO      _ MOLE FRACTION AT POINT 1
C          YL      _ MOLE FRACTION AT POINT 2
C          CT      _ MOLAR CONCENTRATION OF THE MIXTURE
C          L       _ FILM THICKNESS
C          KF1     _ FORWARD REACTION VELOCITY
C          KB1     _ BACKWARD REACTION VELOCITY
C          P       _ PRESSURE OF THE SYSTEM
C          T       _ TEMPERATURE OF THE SYSTEM
C          PC      _ CRITIAL PRESSURE
C          TC      _ CRITICAL TEMPERATURE
C          MW      _ MOLECULAR WEIGHT
C
C       CALCULATED VARIABLES
C
C          DB      _ BINARY DIFFUSION COEFFICIENT
C          DM      _ MULTICOMPONENT DIFFUSION COEFFICIENT
C          JD      _ DIFFUSIVE FLUX
C          PHIF    _ FORWARD RATE CORRECTION FACTOR ARISING FROM NON-
C                    LINEARITY
C          PHIB    _ BACKWARD RATE CORRECTION FACTOR ARISING FROM
C                    NONLINEARITY
C          KRL     _ RATE CONSTANT OF THE LINEARIZED RATE EXPRESSION
C          R       _ REACTION RATE
C          N       _ CONSTITUENT MOLAR FLUX
C          NT      _ TOTAL MOLAR FLUX
C
C       SUBROUTINES USED
C          DBIN    : CALCULATES THE BINARY DIFFUSION COEFFICINTS
C          BSTEF   : CALCULATES THE MULTICOMPONENT DIFFUSION COEFFI-
C                    CIENTS
C          RATELIN : LINEARIZES THE NONLINEAR REACTION
C          INVER   : TAKES THE INVERSE OF THE MATRICES
C          MATMUL  : MULTIPLIES MATRICES
C          COLMUL  : MULTIPLIES A MATRIX AND A COLUMN
C          TT      : THE MATRIX OF WHICH EXP. IS TAKEN
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
```

```
      PROGRAM CHETA(INV,OUT,TAPE5=INV,TAPE6=OUT)
      DIMENSION NAM(9),Y(9),DM(9,9),YO(9),YL(9),DI(9,9),A(9,9),B(9
      DIMENSION DS(9,9),DEVP2(9),EXL(9,9),T5(9,9),EXLZ(9,9),CON(9)
      DIMENSION E1(9,9),E12I(9,9),EXL12(9,9),T6(9,9)
      DIMENSION T(9,9),T2(9,9),T3(9,9),C1(9),C2(9),YMA(9),YM(9),R(
      DIMENSION PC(9),TC(9),DB(9,9),BB(9,9),BBB(9),T4(9,9),T7(9,9)
      DIMENSION T8(9,9),T9(9,9),GG(9,9),AA(9,9)
      REAL N(9),NT,NTU,L,KR(9,9),ID(9,9),JD(9),MW(9)
      REAL KF1,KB1,KRL(9,9)
      CHARACTER*20 NAM
      READ(5,2,END=227) NN,L,P,T,CT
    2 FORMAT(I2,F10.5,F10.4,2E10.4)
      WRITE(6,3) L,P,T,CT
    3 FORMAT(/,10X,'L=',F10.4,2X,'P=',F10.4,2X,'T=',F10.4,2X,'CT='
     +E10.4)
      NL=NN-1
      DO 11 I=1,NN
      READ(5,5181) NAM(I),PC(I),TC(I),MW(I)
 5181 FORMAT(A7,3F10.4)
      WRITE(6,1815) I,NAM(I),PC(I),TC(I),MW(I)
 1815 FORMAT(/,10X,'NAM(',I1,')=',A7,'PC=',F10.4,'TC=',F10.4,'MW='
     +F10.4)
   11 CONTINJE
      READ(5,4) KF1,KB1,KO
    4 FORMAT(2E10.4,I1)
      WRITE(6,5) KO,KF1,KB1
    5 FORMAT(/,10X,'ORDER OF THE REACTION =',I1,/,10X,'KF1=',E10.4
     +3X,'KB1=',E10.4)
      DO 15 I=1,NN
      READ(5,8,END=227) YO(I),YL(I)
    8 FORMAT(2F10.7)
      WRITE(6,9)I,YO(I),I,YL(I)
    9 FORMAT(/,10X,'YO(',I1,')=',F10.7,2X,'YL(',I1,')=',F10.7)
   15 CONTINJE
      DO 3928 I=1,NN
      Y(I)=(YO(I)+YL(I))/2.
 3928 CONTINJE
      NG=2*NL
      DO 6666 I=1,NG
      DO 5555 J=1,NG
      IF(I.EQ.J) GO TO 4444
      ID(I,J)=0.0
      GO TO 5555
 4444 ID(I,J)=1.0
 5555 CONTINJE
 6666 CONTINJE
      CALL DBIN(NN,PC,TC,MW,T,P,DB)
      CALL BSTEF(NL,DB,Y,BB)
      CALL INVER(BB,ID,DM)
      DO 5801 I=1,NL
      DO 4790 J=1,NL
      WRITE(6,2735) I,J,DM(I,J)
 2735 FORMAT(/,10X,'DM(',I1,',',I1,')=',E10.4)
 4790 CONTINJE
 5801 CONTINJE
      CALL INVER(DM,ID,DI)
      KEY=1
      IF(KO.EQ.1) GO TO 5532
      CALL RATELIN(YL,YO,CT, KF1,KB1,KRL)
      DO 5910 I=1,NL
```

```
0129)        DO 1095 J=1,NL
0130)        IF(I.EQ.3) GO TO 9105
0131)        KR(I,J)=-KRL(1,J)
0132)        GO TO 1095
0133) 9105   KR(I,J)=2.*KRL(1,J)
0134) 1095   CONTINUE
0135) 5910   CONTINUE
0136)        GO TO 1181
0137) 5532   DO 5197 I=1,NL
0138)        KR(I,J)=0.0
0139) 5197   CONTINUE
0140)        KR(1,1)=-KF1
0141)        KR(2,1)=KF1
0142) 1181   CALL MATMUL(NL,DI,KR,B)
0143)C INITIALIZE THE TOTAL FLUX.
0144) 5192   SUM=0.0
0145)        DO 1215 I=1,NL
0146)        DO 1512 J=1,NL
0147)        SUM=SUM+DM(I,J)*(YO(I)-YL(I))/L
0148) 1512   CONTINUE
0149) 1215   CONTINUE
0150)        NT=SUM
0151)        WRITE(6,43) NT
0152) 43     FORMAT(/,10X,'NTIN=',E10.4)
0153) 70     CALL TT(NL,NT,B,DI,CT,T)
0154)        CALL MATMUL(NG,T,T,T2)
0155)        CALL MATMUL(NG,T2,T,T3)
0156)        CALL MATMUL(NG,T3,T,T4)
0157)        CALL MATMUL(NG,T4,T,T5)
0158)        CALL MATMUL(NG,T5,T,T6)
0159)        CALL MATMUL(NG,T6,T,T7)
0160)        CALL MATMUL(NG,T7,T,T8)
0161)        CALL MATMUL(NG,T8,T,T9)
0164)        DO 718 I=1,NG
0165)        DO 817 J=1,NG
0166)        EXL(I,J)=ID(I,J)+T(I,J)*L+T2(I,J)*L**2./2.+T3(I,J)*L**3./6.
0167)+       +T4(I,J)*L**4./24.+T5(I,J)*L**5./120.+T6(I,J)*L**6./720.
0168)+       +T7(I,J)*L**7./5040.+T8(I,J)*L**8./40320.+T9(I,J)*L**9./3627
0169) 817    CONTINUE
0170) 718    CONTINUE
0171)        DO 673 I=1,NL
0172)        DO 674 J=1,NL
0173)        E1(I,J)=EXL(I,J)
0174) 674    CONTINUE
0175) 673    CONTINUE
0176)        CALL COLMUL(NL,E1,YO,YMA)
0177)        DO 161 I=1,NL
0178)        YM(I)=YL(I)-YMA(I)
0179) 161    CONTINUE
0180)        DO 1111 I=1,NL
0181)        DO 2222 J=1,NL
0182)        KL=J+3
0183)        EXL12(I,J)=EXL(I,KL)
0184) 2222   CONTINUE
0185) 1111   CONTINUE
0186)        CALL INVER(EXL12,ID,E12I)
0187)        CALL COLMUL(NL,E12I,YM,C2)
0188)        DO 1199 I=1,NL
0189)        WRITE(6,9191) I,C2(I)
```

```
0190)  9191  FORMAT(/,10X,'C2(',I1,')=',E10.4)
0191)  1199  CONTINUE
0192)        CALL COLMUL(NL,DM,C2,JO)
0193)        CALL COLMUL(NL,KR,YO,JO)
0194)        DO 7519 I=1,NL
0195)        JO(I)=-CT*JO(I)
0196)        R(I)=CT*R(I)
0197)        N(I)=JO(I)+YO(I)*NT+R(I)
0198)        WRITE(6,7193) I,JO(I),I,R(I),I,N(I)
0199)  7193  FORMAT(/,10X,'JO(',I1,')=',E10.4,2X,'R(',I1,')=',E10.4,2X,
0200)+       'N(',I1,')=',E10.4)
0201)  7519  CONTINUE
0211         IF(KEY.EQ.3) GO TO 101
0202)        NTU=NT
0203)        NT=N(1)+N(2)+N(3)
0204)        WRITE(6,63) NT
0205)  63    FORMAT(/,10X,'NT=',E10.4)
0207)        DEV=NTU-NT
0208)        DEVP=ABS(DEV/NTU)*100.
0209)        WRITE(6,9582) DEVP
0210)  9582  FORMAT(/,10X,'DEVP=',E10.5)
0211)        IF(DEVP.LE.0.01) GO TO 101
0212)        GO TO 70
0213)  101   WRITE(6,150)
0214)  150   FORMAT(1H1,//,10X,'CALCULATED CONSTITUENT FLUXES',/,10X,
0215)+       29('-'),/)
0216)        DO 103 I=1,NL
0217)        WRITE(6,199) I,N(I)
0218)  199   FORMAT(/,10X,'N(',I1,')=',E11.4)
0219)  103   CONTINUE
0220)        WRITE(6,104) NT
0221)  104   FORMAT(/,10X,'NT=',E10.4)
0222)        Z=0.0
0223)        DO 5928 KA=1,10
0224)        Z=Z+0.02
0225)        DO 5925 I=1,NG
0226)        DO 3951 J=1,NG
0227)        EXLZ(I,J)=ID(I,J)+T(I,J)*Z+T2(I,J)*Z**2./2.+T3(I,J)*Z**3./6.
0228)+       +T4(I,J)*Z**4./24.+T5(I,J)*Z**5./120.+T6(I,J)*Z**6./720.
0229)+       +T7(I,J)*Z**7./5040.+T8(I,J)*Z**8./40320.+T9(I,J)*Z**9./3627
0230)  3951  CONTINUE
0231)  5925  CONTINUE
0232)        DO 5678 I=1,NL
0233)        KS=I+3
0234)        C1(I)=YO(I)
0235)        C1(KS)=C2(I)
0236)  5678  CONTINUE
0237)        CALL COLMUL(NL,EXLZ,C1,CON)
0238)        WRITE(6,7513) Z
0239)  7513  FORMAT(/,10X,'Z=',F10.4)
0240)        DO 5917 II=1,NL
0241)        WRITE(6,9121) II,CON(II)
0242)  9121  FORMAT(/,10X,'Y(',I1,')=',F10.4)
0243)  5917  CONTINUE
0244)  5928  CONTINUE
0245)        IF(KEY.EQ.2) GO TO 7189
0246)        IF(KEY.EQ.3) GO TO 227
0247)        DO 2118 IK=1,NL
0248)        DO 8112 J=1,NL
0249)        KR(IK,J)=0.0
```

```
 8112  CONTINUE
 2118  CONTINUE
       KEY=2
       GO TO 1181
 7189  WT=0.0
       KEY=3
       GO TO 1181
 227   STOP
       END
       SUBROUTINE DBIN(NN,PC,TC,MW,T,P,DB)
       DIMENSION PC(9),TC(9),DB(9,9)
       REAL MW(9)
       DO 5 I=1,NN
       DO 6 J=1,NN
       IF(I.GE.J) GO TO 7
       A1=(PC(I)*PC(J))**(1./3.)
       A2=(TC(I)*TC(J))**(5./12.)
       A3=(1./MW(I)+1./MW(J))**(1./2.)
       A4=(T/SQRT(TC(I)*TC(J)))**2.334
       DB(I,J)=.0003640*A4*A1*A2*A3/P
       WRITE(6,9470) I,J,DB(I,J)
 9470  FORMAT(/,10X,'DB(',I1,',',I1,')=',E10.4)
       GO TO 6
 7     DB(I,J)=DB(J,I)
 6     CONTINUE
 5     CONTINUE
       RETURN
       END
       SUBROUTINE BSTEF(NL,DB,Y,BB)
       DIMENSION DB(9,9),Y(9),BB(9,9)
       DO 1 I=1,NL
       E1=Y(I)/DB(I,4)
       SUM=0.0
       NN=NL+1
       DO 2 K=1,NN
       IF(I.EQ.K) GO TO 2
       SUM=SUM+Y(K)/DB(I,K)
 2     CONTINUE
       BB(I,I)=E1+SUM
       WRITE(6,3095) I,I,BB(I,I)
 3095  FORMAT(/,10X,'BB(',I1,',',I1,')=',E10.4)
 1     CONTINUE
       DO 3 I=1,NL
       DO 4 J=1,NL
       IF(I.EQ.J) GO TO 4
       BB(I,J)=-Y(I)*(1./DB(I,J)-1./DB(I,4))
 4     CONTINUE
 3     CONTINUE
       RETURN
       END
       SUBROUTINE RATELIN(YL,YO,CT,KF1,KB1,KRL)
       DIMENSION YL(9),YO(9),Y(9),PHIF(9,9),PHIB(9,9)
       REAL KRL(9,9),KF1,KB1
       DO 111 I=1,3
111    Y(I)=YL(I)/YO(I)
       A1=(1.-Y(1)**3.)/(1.-Y(1))**3.+(1.-Y(2)**3.)/(1.-Y(2))**3.
       A2=1./3.+((1.+Y(1))/(1.-Y(1)))**2.+((1.+Y(2))/(1.-Y(2)))**2.
       A=A1/A2
       E1=2.*(1.+Y(1))*(1.+Y(2))/(1.-Y(1))**2.
```

```
0309)         E2=(1.-Y(1)**3.)/((1.+Y(1))*(1.-Y(1)**2.))
0310)         PHIF(1,1)=E1*(E2-A)
0311)         F1=2.*(1.+Y(1))*(1.+Y(2))/(1.-Y(2))**2.
0312)         F2=(1.-Y(2)**3.)/((1.+Y(2))*(1.-Y(2)**2.))
0313)         PHIF(1,2)=F1*(F2-A)
0314)         G1=3.*(1.+Y(3))/(1.-Y(3))**2.
0315)         G2=(1.-Y(3)**4.)/((1.+Y(3))*(1.-Y(3)**3.))
0316)         G3=(1.-Y(3)**4.)*(1.+Y(3))/((1.-Y(3)**3.)*(1.-Y(3))**2.)
0317)         G4=1./3.+((1.+Y(3))/(1.-Y(3)))**2.
0318)         PHIB(1,3)=G1*(G2-G3/G4)
0319)         KRL(1,1)=KF1*PHIF(1,1)*YD(2)*CT
0320)         KRL(1,2)=KF1*PHIF(1,2)*YD(1)*CT
0321)         KRL(1,3)=-KB1*PHIB(1,3)*(YD(3)*CT)**2.
0322)         DO 5692 J=1,3
0323)         WRITE(6,2073) J,KRL(1,J)
0324) 2073    FORMAT(/,10X,'KRL(1,',I1,')=',E10.4)
0325) 5692    CONTINUE
0326)         RETURN
0327)         END
0328)         SUBROUTINE INVER(DM,ID,DI)
0329)         DIMENSION DM(9,9),DI(9,9),DS(9,9)
0330)         REAL ID(9,9)
0331)         DET1=DM(1,1)*DM(2,2)*DM(3,3)-DM(1,1)*DM(2,3)*DM(3,2)
0332)         DET2=-DM(1,2)*DM(2,1)*DM(3,3)+DM(1,2)*DM(2,3)*DM(3,1)
0333)         DET3=DM(1,3)*DM(2,1)*DM(3,2)-DM(1,3)*DM(2,2)*DM(3,1)
0334)         DET=DET1+DET2+DET3
0335)         D11=-DM(3,3)*DM(1,1)-DM(3,3)*DM(2,2)-DM(1,1)*DM(2,2)
0336)         D111=DM(2,3)*DM(3,2)+DM(1,2)*DM(2,1)+DM(1,3)*DM(3,1)
0337)         D1=D11+D111
0338)         D2=+DM(1,1)+DM(2,2)+DM(3,3)
0339)         DO 91 I=1,3
0340)         DO 81 J=1,3
0341)         SUM=0.0
0342)         DO 71 K=1,3
0343)         SUM=SUM+DM(I,K)*DM(K,J)
0344) 71      CONTINUE
0345)         DS(I,J)=SUM
0346) 81      CONTINUE
0347) 91      CONTINUE
0348)         DO 123 I=1,3
0349)         DO 234 J=1,3
0350)         DI(I,J)=(-D1*ID(I,J)-D2*DM(I,J)+DS(I,J))/DET
0351) 234     CONTINUE
0352) 123     CONTINUE
0353)         RETURN
0354)         END
0355)         SUBROUTINE MATMUL(NF,G1,G2,G)
0356)         DIMENSION G1(9,9),G2(9,9),G(9,9)
0357)         DO 551 I=1,NF
0358)         DO 661 J=1,NF
0359)         SUM=0.0
0360)         DO 771 K=1,NF
0361)         SUM=SUM+G1(I,K)*G2(K,J)
0362) 771     CONTINUE
0363)         G(I,J)=SUM
0364) 661     CONTINUE
0365) 551     CONTINUE
0366)         RETURN
0367)         END
0368)         SUBROUTINE COLMUL(NI,ABB,BBB,CC)
```

```
0369)        DIMENSION ABB(9,9),BBB(9),CC(9)
0370)        DO 191 I=1,NI
0371)        SUM=0.0
0372)        DO 181 J=1,NI
0373)        SUM=SUM+ABB(I,J)*BBB(J)
0374) 181    CONTINUE
0375)        CC(I)=SUM
0376) 191    CONTINUE
0377)        RETURN
0378)        END
0379)        SUBROUTINE TT(NL,NT,B,DI,CT,T)
0380)        DIMENSION T(9,9),B(9,9),DI(9,9),A(9,9)
0381)        REAL NT
0382)        DO 112 I=1,NL
0383)        DO 223 J=1,NL
0384)        A(I,J)=NT*DI(I,J)/CT
0385) 223    CONTINUE
0386) 112    CONTINUE
0387)C FIND T MATRIX
0388)        DO 5 I=1,NL
0389)        DO 6 J=1,NL
0390)        T(I,J)=0.0
0391)        KP=J+3
0392)        KDIF=KP-J
0393)        IF(KDIF.EQ.3) GO TO 5209
0394)        T(I,KP)=0.0
0395)        GO TO 6
0396) 5209   T(I,KP)=1.0
0397) 6      CONTINUE
0398) 5      CONTINUE
0399)        NG=2*NL
0400)        NN=NL+1
0401)        DO 7 I=NN,NG
0402)        DO 8 J=1,NL
0403)        K=I-3
0404)        T(I,J)=-B(K,J)
0405) 8      CONTINUE
0406) 7      CONTINUE
0407)        DO 9 I=NN,NG
0408)        DO 10 J=NN,NG
0409)        K=I-3
0410)        L=J-3
0411)        T(I,J)=+A(K,L)
0412) 10     CONTINUE
0413) 9      CONTINUE
0414)        RETURN
0415)        END
16.03.44.UCLP, AA, P04     ,       0.449KLNS.
```

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C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
C       THE PURPOSE OF THIS PROGRAM IS TO CALCULATE THE CONSTITUENT
C       MOLAR FLUXES OF MULTICOMPONENT SYSTEMS.
C
C       THE SOLUTION OBTAINED FROM THE LINEARIZED CONTINUITY EQUA-
C       TIONS BY THE UNCOUPLING METHOD IS USED.
C
C       PARAMETERS
C
C          CONTROL VARIABLES
C
C          NN    _ NUMBER OF COMPONENTS
C          NDD   _ NUMBER OF DATA SETS
C
C          PROGRAM VARIABLES TO BE SUPPLIED
C
C          YO    _ MOLE FRACTION AT POINT 1
C          YL    _ MOLE FRACTION AT POINT 2
C          DB    _ BINARY DIFFUSIN COEFFICIENT
C          CT    _ MOLAR CONCENTRATION OF THE MIXTURE
C          L     _ FILM THICKNESS
C          NCD   _ CONSTITUENT FLUX OBTAINED BY THE MAXWELL-SEFAN
C                  EQUATIONS
C          ND    _ TOTAL MOLAR FLUX OBTAINED BY THE MAXWELL-STEFAN
C                  EQUATIONS
C
C          CALCULATED VARIABLES
C
C          DM    _ MULTICOMPONENT DIFFUSION COEFFICIENTS
C          D     _ EIGENVALUE OF THE SDO MATRIX
C          STO   _ MODAL MATRIX
C          YOP   _ PSEUDO MOLE FRACTION AT POINT 1
C          YLP   _ PSEUDO MOLE FRACTION AT POINT 2
C          NP    _ PSEUDO CONSTITUENT MOLAR FLUX
C          J     _ DIFFUSIVE FLUX
C          N     _ CONSTITUENT MOLAR FLUX
C          NT    _ TOTAL MOLAR FLUX
C
C          SUBROUTINES USED
C          DIAG: CALCULATES THE EIGENVALUES AND THE MODAL MATRIX
C                OF SDO MATRIX.
C          NERA: APPLIES NEWTON RAPHSON PROCEDURE
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
C
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```

```
      PROGRAM TOOR
      DIMENSION NAM(9),Y(9),DB(9,9),DM(9,9),D(9),YO(9),YL(9),T(9,9)
      DIMENSION TI(9,9),YOP(9),YLP(9),DEVP2(9)
      REAL ND,NP(9),N(9),NT,NTU,L,NCD(9)
      COMMON/TR/NL
      CHARACTER*20 NAM
      OPEN(UNIT=5,FILE='DATA')
      OPEN(UNIT=6,FILE='RESULT')
      READ(5,1) NDD
      WRITE(6,1) NDD
    1 FORMAT(15X,I2)
      DO 14 K=1,NDD
      READ(5,2,END=227) NN,L,ND,CT
    2 FORMAT(I2,F10.5,E11.4,2X,E10.4)
      WRITE(6,3) ND,CT,L
    3 FORMAT(/,10X,'ND=',E11.4,2X,'CT=',E10.4,'L=',F10.5)
      DO 11 I=1,NN
      READ(5,4) NAM(I),NCD(I)
    4 FORMAT(A7,E11.4)
      WRITE(6,5) I,NAM(I),I,NCD(I)
    5 FORMAT(/,10X,'NAM(',I1,')=',2X,A7,3X,'NCD(',I1,')=',E11.4)
   11 CONTINUE
      DO 12 I=1,NN
      DO 13 J=1,NN
      IF(J.LE.I) GO TO 13
      READ(5,6) DB(I,J)
    6 FORMAT(F10.5)
      WRITE(6,7) I,J,DB(I,J)
    7 FORMAT(/,10X,'DB(',I1,',',I1,')=',2X,F10.5)
   13 CONTINUE
   12 CONTINUE
      DO 115 I=1,NN
      READ(5,8,END=14) YO(I),YL(I)
    8 FORMAT(2F10.7)
      WRITE(6,9) I,YO(I),I,YL(I)
    9 FORMAT(/,10X,'YO(',I1,')=',F10.7,2X,'YL(',I1,')=',F10.7)
  115 CONTINUE
      DO 20 I=1,NN
   20 Y(I)=(YO(I)+YL(I))/2.
      NL=NN-1.
      DB(2,1)=DB(1,2)
      S=Y(1)*DB(2,3)+Y(2)*DB(1,3)+Y(3)*DB(1,2)
      DO 21 I=1,NL
      DO 22 J=1,NL
      IF(I.EQ.J) GO TO 22
      DM(I,I)=DB(I,3)*((1.-Y(I))*DB(I,J)+Y(I)*DB(J,3))/S
      DM(I,J)=Y(I)*DB(J,3)*(DB(I,3)-DB(I,J))/S
      WRITE(6,23) I,I,DM(I,I),I,J,DM(I,J)
   23 FORMAT(/,10X,2(2X,'DM(',I1,',',I1,')=',F10.5))
   22 CONTINUE
   21 CONTINUE
      CALL DIAG(D,DM,T,TI)
      YOP(1)=TI(1,1)*YO(1)+TI(1,2)*YO(2)
      YOP(2)=TI(2,1)*YO(1)+TI(2,2)*YO(2)
      YLP(1)=TI(1,1)*YL(1)+TI(1,2)*Y_(2)
      YLP(2)=TI(2,1)*YL(1)+TI(2,2)*YL(2)
      WRITE(6,32) YOP(1),YOP(2),YLP(1),YLP(2)
   32 FORMAT(/,10X,'YOP(1)=',F10.7,'YOP(2)=',F10.7,2X,2F10.7)
   30 CONTINUE
```

```
      NT=ND
      WRITE(6,43) NT
   43 FORMAT(/,10X,'NT=',E10.4)
   70 DO 50 I=1,NL
      A1=YLP(I)-YOP(I)
      A2=EXP(NT/(CT*D(I)))-1.
      NP(I)=-A1*NT/(L*A2)+NT*YOP(I)
      WRITE(6,51) I,NP(I)
   51 FORMAT(/,10X,'NP(',I1,')=',E10.4)
   50 CONTINUE
      NTU=NT
      SUMT=0.0
      DO 60 I=1,NL
      SUMN=0.0
      DO 61 J=1,NL
      SUMN=SUMN+T(I,J)*NP(J)
   61 CONTINUE
      N(I)=SUMN
      WRITE(6,62) I,N(I)
   62 FORMAT(/,10X,'N(',I1,')=',E10.4)
      SUMT=SUMT+N(I)
   60 CONTINUE
      NT=SUMT
      WRITE(6,63) NT
   63 FORMAT(/,10X,'NT=',E10.4)
      DEV=NTJ-NT
      DEVP=ABS(DEV/NTU)*100.
      IF(DEVP.LE.0.01) GO TO 101
      CALL NERA(NT,T,D,YLP,YOP,CT,_,NP)
      GO TO 70
  101 DEV1=(ND-NT)
      DEVP1=ABS(DEV1/ND)*100.
      DO 700 I=1,NL
      DEVP2(I)=ABS((NCD(I)-N(I))/NCD(I))*100.
  700 CONTINUE
      WRITE(6,150)
  150 FORMAT(1H1,//,10X,'CALCULATED RESULTS ARE:',/,10X,28('-'),/
      DO 103 I=1,NL
      WRITE(6,102) I,N(I),I,DEVP2(I)
  102 FORMAT(/,10X,'N(',I1,')=',E11.4,2X,'%ERRN(',I1,')=',F10.4)
  103 CONTINUE
      WRITE(6,104) NT,DEVP1
  104 FORMAT(//,10X,'NT=',E10.4,5X,'%ERRNT=',F10.5,//)
   14 CONTINUE
  227 STOP
      END
      SUBROUTINE DIAG(D,DM,T,TI)
      DIMENSION D(9),DM(9,9),T(9,9),TI(9,9)
      COMMON/TR/NL
      C=DM(1,1)*DM(2,2)-DM(1,2)*DM(2,1)
      B=DM(1,1)+DM(2,2)
      E=SQRT(B**2.-4.*C)
      D(1)=(B+E)/2.
      D(2)=(B-E)/2.
      G=(DM(1,2)**2.+(DM(2,2)-D(1))**2.)**0.5
      H=(DM(1,2)**2.+(DM(2,2)-D(2))**2.)**0.5
      T(1,1)=1.0
      T(2,2)=1.0
      T(1,2)=DM(1,2)/(D(2)-DM(1,1))
      T(2,1)=(D(1)-DM(1,1))/DM(1,2)
```

```
0175)         R=T(1,1)*T(2,2)-T(1,2)*T(2,1)
0176)         TI(1,1)=1.0*T(2,2)/R
0177)         TI(2,2)=T(1,1)/R
0178)         TI(1,2)=-T(1,2)/R
0179)         TI(2,1)=-1.0*T(2,1)/R
0180)         DO 15 I=1,NL
0181)         WRITE(6,25) I,D(I)
0182)      25 FORMAT(/,10X,'D(',I1,')=',F10.5)
0183)         DO 35 J=1,NL
0184)         WRITE(6,45) I,J,T(I,J),I,J,TI(I,J)
0185)      45 FORMAT(/,10X,2(2X,'T(',I1,',',I1,')=',F10.5))
0186)      35 CONTINUE
0187)      15 CONTINUE
0188)         RETURN
0189)         END
0190)         SUBROUTINE NERA(NT,T,D,YLP,YOP,CT,L,NP)
0191)         DIMENSION T(9,9),D(9),YLP(9),YOP(9),A(9),B(9),E(9)
0192)         REAL NP(9),NT,NTU,L
0193)         COMMON/TR/NL
0194)         F=-NT+(T(1,1)+T(2,1))*NP(1)+(T(1,2)+T(2,2))*NP(2)
0195)         SUM=0.0
0196)         DO 55 I=1,NL
0197)         A(I)=EXP(NT/(CT*D(I)))
0198)         B(I)=YLP(I)-YOP(I)
0199)         E(I)=T(1,I)+T(2,I)
0200)         FP1=B(I)*(A(I)-1.)/L
0201)         FP2=NT*B(I)*A(I)/(L*CT*D(I))
0202)         FP3=E(I)*((FP1-FP2)/(A(I)-1.)**2.-YOP(I))
0203)         SUM=SUM-FP3
0204)      55 CONTINUE
0205)         NTU=NT
0206)         FP=SUM
0207)         NT=NTU+F/(FP-1.)
0208)         WRITE(6,105) NT
0209)     105 FORMAT(/,10X,'FROM SUBR. NERA: NT=',E10.5)
0210)         RETURN
0211)         END
17.28.05.UCLP, A4, P04     ,       0.236KLNS.
```

```
00100C
00110C
00120C
00130C
00140C
00150C
00160C
00170C
00180C
00190C
00200C
00210C
00220C
00230C
00240C
00250C
00260C* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
00270C
00280C      THE PURPOSE OF THIS PROGRAM IS TO CALCULATE THE CONSTI-
00290C      TUENT MOLAR FLUXES OF MULTICOMPONENT SYSTEMS.
00300C
00310C      THE SOLUTION OBTAINED FROM THE LINEARIZED CONTINUITY
00320C      EQUATIONS WITHOUT THE UNCOUPLING METHOD IS USED
00330C
00340C      PARAMETERS
00350C
00360C        CONTROL VARIABLES
00370C
00380C          NN      - NUMBER OF COMPONENTS
00390C          NDD     - NUMBER OF DATA SETS
00400C
00410C          PROGRAM VARIABLES TO BE SUPPLIED
00420C
00430C          YO      - MOLE FRACTION AT POINT 1
00440C          YL      - MOLE FRACTION AT POINT 2
00450C          DD      - BINARY DIFFUSION COEFFICIENT
00460C          CT      - MOLAR CONCENTRATION OF THE MIXTURE
00470C          L       - FILM THICKNESS
00480C          ND      - TOTAL FLUX FOUND BY THE MAXWELL STEFAN EQTNS.
00490C          NCD     - INDIVIDUAL CONSTITUENT FLUXES FOUND BY THE
00500C                    MAXWELL-STEFAN EQUATIONS.
00510C
00520C      CALCULATED VARIABLES
00530C
00540C          DM      - MULTICOMPONENT DIFFUSION COEFFICIENT
00550C          J       - DIFFUSION FLUX
00560C          N       - CONSTITUENT MOLAR FLUX
00570C          NT      - TOTAL MOLAR FLUX
00580C
00590C      SUBROUTINE USED
00600C          ALFA: USED FOR THE CALCULATION OF EXP. MATRIX.
00610C
00620C* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
00630C
00640C
00650C
00660C
00670C
00680C
00690C
00700C
00710C
00720C
00730C
00740C
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```
      PROGRAM TAYLOR
      DIMENSION NAM(9),Y(9),DB(9,9),DM(9,9),YO(9),YL(9)
      DIMENSION PHI(9,9),EPHI(9,9),S(9,9),T(9,9),P(9,9),DEVP2(9)
      REAL ND,N(9),NT,NTO,L,NCD(9),JO(9)
      CHARACTER*20 NAM
      OPEN(UNIT=5,FILE='DATA')
      OPEN(UNIT=6,FILE='RESULT')
      READ(5,1) NDD
      WRITE(6,1) NDD
    1 FORMAT(15X,I2)
      DO 14 K=1,NDD
      READ(5,2,END=227) NN,L,ND,CT
    2 FORMAT(I2,F10.5,E11.4,2X,E10.4)
      WRITE(6,3) ND,CT,L
    3 FORMAT(/,10X,'ND=',E11.4,2X,'CT=',E10.4,'L=',F10.5)
      DO 11 I=1,NN
      READ(5,4) NAM(I),NCD(I)
    4 FORMAT(A7,E11.4)
      WRITE(6,5) I,NAM(I),I,NCD(I)
    5 FORMAT(/,10X,'NAM(',I1,')=',2X,A7,3X,'NCD(',I1,')=',E11.4)
   11 CONTINUE
      DO 12 I=1,NN
      DO 13 J=1,NN
      IF(J.LE.I) GO TO 13
      READ(5,6) DB(I,J)
    6 FORMAT(F10.5)
      WRITE(6,7) I,J,DB(I,J)
    7 FORMAT(/,10X,'DB(',I1,',',I1,')=',2X,F10.5)
   13 CONTINUE
   12 CONTINUE
      DO 15 I=1,NN
      READ(5,8,END=14) YO(I),YL(I)
    8 FORMAT(2F10.7)
      WRITE(6,9) I,YO(I),I,YL(I)
    9 FORMAT(/,10X,'YO(',I1,')=',F10.7,2X,'YL(',I1,')=',F10.7)
   15 CONTINUE
      DO 20 I=1,NN
   20 Y(I)=(YO(I)+YL(I))/2.
      NL=NN-1.
      DB(2,1)=DB(1,2)
      G=Y(1)*DB(2,3)+Y(2)*DB(1,3)+Y(3)*DB(1,2)
      DO 21 I=1,NL
      DO 22 J=1,NL
      IF(I.EQ.J) GO TO 22
      DM(I,I)=DB(I,3)*((1.-Y(I))*DB(I,J)+Y(I)*DB(J,3))/G
      DM(I,J)=Y(I)*DB(J,3)*(DB(I,3)-DB(I,J))/G
      WRITE(6,23) I,I,DM(I,I),I,J,DM(I,J)
   23 FORMAT(/,10X,2(2X,'DM(',I1,',',I1,')=',F10.5))
   22 CONTINUE
   21 CONTINUE
      A33=(DM(1,1)+DM(2,1))*(YO(1)-YL(1))
      A44=(DM(1,2)+DM(2,2))*(YO(2)-YL(2))
      NT=CT*(A33+A44)/L
      WRITE(6,43) NT
   43 FORMAT(/,10X,'NTIN=',E10.4)
      V=L/(CT*(DM(1,1)*DM(2,2)-DM(1,2)*DM(2,1)))
   70 PHI(1,1)=NT*V*DM(2,2)
      PHI(2,2)=NT*V*DM(1,1)
      PHI(1,2)=-NT*V*DM(1,2)
      PHI(2,1)=-NT*V*DM(2,1)
```

```
      DO 608 I=1,2
      DO 609 J=1,2
      WRITE(6,707) I,J,PHI(I,J)
  707 FORMAT(/,10X,'PHI(',I1,',',I1,')=',E10.4)
  609 CONTINJE
  608 CONTINUE
      CALL A_FA(PHI,AL1,AL2)
      EPHI(1,1)=AL1*PHI(1,1)+AL2
      EPHI(1,2)=AL1*PHI(1,2)
      EPHI(2,1)=AL1*PHI(2,1)
      EPHI(2,2)=AL1*PHI(2,2)+AL2
      G=((EPHI(1,1)-1.)*(EPHI(2,2)-1.))-(EPHI(1,2)*EPHI(2,1))
      S(1,1)=(EPHI(2,2)-1.)/G
      S(1,2)=-EPHI(1,2)/G
      S(2,1)=-EPHI(2,1)/G
      S(2,2)=(EPHI(1,1)-1.)/G
      T(1,1)=CT*((DM(1,1)*PHI(1,1))+(DM(1,2)*PHI(2,1)))/L
      T(1,2)=CT*((DM(1,1)*PHI(1,2))+(DM(1,2)*PHI(2,2)))/L
      T(2,1)=CT*((DM(2,1)*PHI(1,1))+(DM(2,2)*PHI(2,1)))/L
      T(2,2)=CT*((DM(2,1)*PHI(1,2))+(DM(2,2)*PHI(2,2)))/L
      P(1,1)=(T(1,1)*S(1,1))+(T(1,2)*S(2,1))
      P(1,2)=(T(1,1)*S(1,2))+(T(1,2)*S(2,2))
      P(2,1)=(T(2,1)*S(1,1))+(T(2,2)*S(2,1))
      P(2,2)=(T(2,1)*S(1,2))+(T(2,2)*S(2,2))
      JO(1)=(P(1,1)*(YO(1)-YL(1)))+(P(1,2)*(YO(2)-YL(2)))
      JO(2)=(P(2,1)*(YO(1)-YL(1)))+(P(2,2)*(YO(2)-YL(2)))
      WRITE(6,5981) JO(1),JO(2)
 5981 FORMAT(/,10X,'JO(1)=',E10.4,'JO(2)=',E10.4)
      Y1=(S(1,1)*(YO(1)-YL(1)))+(S(1,2)*(YO(2)-YL(2)))+YO(1)
      Y2=(S(2,1)*(YO(1)-YL(1)))+(S(2,2)*(YO(2)-YL(2)))+YO(2)
      N(1)=JO(1)+NT*YO(1)
      N(2)=JO(2)+NT*YO(2)
      NTU=NT
      NT=N(1)+N(2)
      WRITE(6,63) NT
   63 FORMAT(/,10X,'NT=',E10.4)
      DEV=NTJ-NT
      DEVP=ABS(DEV/NTU)*100.
      IF(DEVP.LE.0.01) GO TO 101
      GO TO 70
  101 DEV1=(ND-NT)
      DEVP1=DEV1/ND*100
      IF(DEVP1.GT.0.) GO TO 5921
      DEVP1=-DEVP1
 5921 DO 700 I=1,NL
      DEVP2(I)=(NCD(I)-N(I))/NCD(I)*100
      IF(DEVP2(I).GT.0.) GO TO 700
      DEVP2(I)=-DEVP2(I)
  700 CONTINJE
      WRITE(6,150)
  150 FORMAT(1H1,//,10X,'CALCULATED RESULTS ARE:',/,10X,28('-'),/)
      DO 103 I=1,NL
      WRITE(6,102) I,N(I),I,DEVP2(I)
  102 FORMAT(/,10X,'N(',I1,')=',E11.4,2X,'%ERRN(',I1,')=',F10.4)
  103 CONTINJE
      WRITE(6,104) NT,DEVP1
```

```
0167)   104 FORMAT(//,10X,'NT=',E10.4,5X,'%ERRNT=',F10.5,//)
0168)    14 CONTINJE
0169)   227 STOP
0170)       END
0171)       SUBROUTINE ALFA(PHI,AL1,AL2)
0172)       DIMENSION PHI(9,9)
0173)       REAL LA1,LA2
0174)       C=PHI(1,1)*PHI(2,2)-PHI(1,2)*PHI(2,1)
0175)       B=PHI(1,1)+PHI(2,2)
0176)       E=SQRT(B**2.-4.*C)
0177)       LA2=(B+E)/2.
0178)       LA1=(B-E)/2.
0179)       WRITE(6,25) LA1,LA2
0180)    25 FORMAT(/,10X,'LA1=',E12.5,2X,'LA2=',E12.5)
0181)       AL1=(EXP(LA1)-EXP(LA2))/(LA1-LA2)
0182)       AL2=(LA1*EXP(LA2)-LA2*EXP(LA1))/(LA1-LA2)
0183)       WRITE(6,35) AL1,AL2
0184)    35 FORMAT(/,10X,'AL1=',E10.4,2X,'AL2=',E10.4)
0185)       RETURN
0186)       END
16.50.53.UCLP, AA, P04     ,       0.211KLNS.
```