

# TRANSPORT IN LIQUID SYSTEMS WITH DIFFUSION AND REACTION COUPLING

H. L. TOOR

*Carnegie Institute of Technology,  
Pittsburgh, Pennsylvania*

When chemical reactions take place in nonhomogeneous mixtures of many components, complicated behavior may be expected since any entity may pass through many different environments in its lifetime. Interaction with neighboring species may lead to chemical reaction or to a directed motion which we describe in terms of bulk motion and diffusion. Systems of this type are important in engineering as well as in biology.

In "homogeneous systems" in which there are concentration gradients present, but in which the concentration change is small over molecular dimensions, it is generally assumed that the laws of homogeneous chemical kinetics are valid locally and that the diffusion laws obtained in the absence of chemical reactions are also valid when chemical reactions are occurring.

It is necessary to distinguish here between the fine-scale diffusion effects that occur even in a mixture in which there are no large-scale concentration gradients [9] (rapid reactions) and the situation discussed above in which the effects are on a large scale. In the former case, the transport is from a local region to a nearby reaction site; in the latter, the diffusion results in a gross transport over distances much larger than molecular dimensions.

It is assumed that the homogeneous kinetic law to be used in the large-scale problem already contains in it any fine-scale diffusion effects. Reactions in which fine-scale diffusion effects are significant are rapid enough so that any large-scale transport process will be diffusion controlled, in which case a precise knowledge of the reaction rate is not required.

When reactions take place on solid surfaces, the chemical kinetics laws appear as boundary conditions on the diffusion equations; if the solid is of irregular shape, as with a catalyst particle, it is necessary, and conventional, to ignore the fine-scale effects by considering

a region large enough to contain many pores but small enough so that the concentration may be treated as uniform over the region. This leads to equations of a form similar to those used in systems with homogeneous reactions [14].

We assume here that even though biological systems are structured, it is possible to treat at least parts of the system in a manner similar to catalyst particles.

With assumptions of the above type it is possible to combine diffusion laws and kinetic laws to predict concentrations and rates of reaction as functions of time and position.

It is frequently possible to determine the kinetics of homogeneous reactions in the absence of diffusion by eliminating large-scale concentration gradients. It is much more difficult to determine experimentally the diffusion laws in a reacting system unless the reaction can be turned off, as might be the case in certain homogeneous catalytic systems.

In dilute gas mixtures a reasonably good kinetic theory description of the constitutive relation for diffusion exists so that one can proceed to combine these with experimental chemical kinetic and conservation laws and obtain sets of equations (with initial and boundary conditions) which describe the concentrations and reactions rates as functions of time and position in a given system [16, 17].

In liquid systems the best that can be done is to predict the form of the diffusion laws; in general there is a set of  $n^2$  coefficients to be determined experimentally where  $n + 1$  is the number of components present. Consequently, if diffusion effects are important in a nondilute system, even with a complete knowledge of the chemical kinetics, it is not possible to predict the behavior of the system completely. It is possible, however, to make some predictions as to the type of behavior, but it is necessary first to consider the constitutive equations of diffusion.

#### DIFFUSION IN MULTICOMPONENT SYSTEMS—CONSTANT TEMPERATURE AND PRESSURE, NO EXTERNAL FORCES

By assuming small deviations from equilibrium and linear relations between fluxes and thermodynamic forces one obtains for an  $n + 1$  component system [6, 8].

$$\mathbf{J}_i = - \sum_{k=1}^{n+1} L_{ij} \nabla \mu_j, \quad i = 1, \dots, n + 1 \quad (1)$$

where  $\mathbf{J}_i$  is the flux of species with respect to some reference velocity characteristic of the motion of the system as a whole and  $\mu_j$  is the chemical potential of species  $j$ . Microscopic reversibility leads to the Onsager Reciprocal Relationships (ORR) which allow one to choose  $L_{ij} = L_{ji}$  in Eq. (1) [10] but the  $L_{ij}$  can be predicted only in dilute gas mixtures. They are concentration dependent.

The  $L_{ij}$ 's are not unique since there are only  $n$ -independent  $\mathbf{J}_i$ 's by the choice of a reference frame and  $n$ -independent  $\nabla\mu_j$ 's by the Gibbs-Duhem equation, but the ORR allow choice of a positive definite  $L_{ij}$  matrix.

Since

$$\nabla\mu_j = \sum_{k=1}^n \frac{\partial\mu_j}{\partial C_k} \nabla C_k, \quad j = 1, \dots, n \quad (2)$$

then

$$\mathbf{J}_i = - \sum_{j=1}^n D_{ij} \nabla C_j, \quad i = 1, \dots, n \quad (3)$$

where

$$D_{ij} = \sum_{k=1}^{n+1} L_{ik} \frac{\partial\mu_k}{\partial C_j}, \quad i, j = 1, \dots, n \quad (4)$$

$C_j$  is the concentration of species  $j$  in mass or moles per volume and  $\mathbf{J}_i$  the flux in mass or moles per time area. The  $D_{ij}$ 's have dimensions of (length)<sup>2</sup> per time if mole or mass units are used alone but a change from mole to mass units changes the value of the cross-diffusion coefficients,  $D_{ij}$ ,  $i \neq j$ . However, the change in units is such that the two matrices of coefficients are related by a similarity transformation so that they have the same characteristic roots. If the convenient volume reference frame is chosen

$$\sum_{i=1}^{n+1} \mathbf{J}_i \bar{v}_i = 0 \quad (5)$$

where  $\bar{v}_i$  is the partial molal or mass volume of species  $j$ .

The  $D_{ij}$ 's in Eq. (3) are practical diffusion coefficients. They can be measured, and when these determinations have been made at various concentrations Eqs. (3) and (5) represent a complete description of

the constitutive equations of diffusion [2]. No activity information is required and none is required later on since activities do not appear in the additional relationships required to construct the full set of equations which define the system behavior.

If the ORR are valid there are relationships among the  $D_{ij}$ 's which leave only  $(n+1)n/2$  independent. Some restriction on the matrix is clearly necessary for if this were not the case negative roots could appear which would be quite disturbing. Kirkaldy *et al.* [11] have shown that the ORR and the thermodynamic stability condition make  $D_{ij}$  the product of two positive definite matrices; hence the  $D_{ij}$  matrix has real positive roots. This means, as will be seen, that divergent behavior or sustained oscillations cannot be obtained in purely diffusive processes.

Since

$$\sum_1^{n+1} \bar{v}_i \nabla C_i = 0 \quad (6)$$

it is clearly possible to construct from Eq. (3) an equation which contains all the fluxes and concentrations

$$\mathbf{J}_i = - \sum_{j=1}^{n+1} D_{ij}' \nabla C_j, \quad i = 1, \dots, n+1 \quad (7)$$

where the  $D_{ij}$ 's like the  $L_{ij}$ 's, have a certain arbitrariness. One can also use the linear relationships to write Eq. (1) in terms of independent fluxes and forces or, as DeGroot and Mazur [7] show, start with the independent form with symmetric coefficients and then construct Eq. (1).

If we start with Eq. (1) and expand  $\nabla \mu_j$  in terms of all the independent concentrations then

$$D_{ij} = \sum_{k=1}^{n+1} L_{ik} \frac{\partial \mu_k}{\partial C_j}, \quad i, j = 1, \dots, n+1 \quad (8)$$

The experimental information available to date in three component mixtures of solids, liquids, and gases indicates that the above equations represent a satisfactory description of multicomponent diffusion.

If ionized species are present and there is no electrical current

Eq. (3) may still be used for electrically neutral components and the symmetry relationships still hold [12]. In dilute ionic solutions some progress is being made in predicting the coefficients in terms of limiting equivalent conductivities [22].

If cross-terms are negligible considerable simplification results, i.e., if

$$\mathbf{J}_i = -D_i \nabla C_i, \quad i = 1, \dots, n + 1 \quad (9)$$

and we consider all  $n + 1$  equations, rather than just  $n$ , to be of this form because component  $n + 1$  is chosen arbitrarily. Combination of Eqs.(5), (6), and (8) gives

$$\sum_i^n (D_i - D_{n+1}) \bar{v}_i \nabla C_i = 0 \quad (10)$$

When none of the components is infinitely dilute the  $n \nabla C_i$  may be varied independently so the only solution to Eq. (9) is

$$D_i = D_{n+1}, \quad i = 1, \dots, n \quad (11)$$

Since a consistent definition of the flux expression in any other reference frame leads to the same diffusion coefficients, it is concluded that if none of the components is infinitely dilute the diffusivity matrix either has off-diagonal terms or is merely a scalar times the identity matrix—each component has the same Fickian diffusion coefficient. This is in accord with the intuitive idea that in concentrated systems the diffusion will be uncoupled only when the molecular species which make up the mixture are of a similar nature and when this is the case each component will not only diffuse independently, but will have the same diffusion coefficient as every other component; while in sufficiently dilute systems even dissimilar components will be uncoupled and hence may have dissimilar Fickian diffusion coefficients.

Under certain conditions a nondilute system with small but nonzero cross terms may be usefully approximated by neglecting the cross coefficients and using diagonal coefficients. However, since Eq. (10) will not be satisfied, the resulting diffusion equations will not be self-consistent.

In multicomponent systems in which the components are liquids in the pure state, limiting values of the  $D_{ij}$  at the binary borders of the multicomponent field are obtained in terms of binary diffusion

coefficients. For a three-component system [13, 15]

$$\lim_{C_j \rightarrow 0} D_{ii} = \mathfrak{D}_{i3} = \mathfrak{D}_{3i} \quad (12a)$$

$$\lim_{C_i \rightarrow 0} D_{ij} = 0 \quad (12b)$$

$$\lim_{C_i, C_3 \rightarrow 0} D_{ii} = \mathfrak{D}_{ij}^0 \quad \begin{matrix} i, j = 1, 2 \\ j \neq i \end{matrix} \quad (12c)$$

$$\lim_{C_i, C_3 \rightarrow 0} D_{ij} = (\mathfrak{D}_{3i}^0 - \mathfrak{D}_{ji}^0) \frac{\bar{v}_j}{\bar{v}_i} \quad (12d)$$

$$\lim_{C_i \rightarrow 0} \left( D_{ii} - D_{ij} \frac{\bar{v}_i}{\bar{v}_j} \right) = \mathfrak{D}_{ij} \quad (12e)$$

In the above equations  $D_{ij}$  is the binary diffusion coefficient for a mixture of  $i$  and  $j$ , and  $\mathfrak{D}_{ij}^0$  is the limiting value of the binary diffusion coefficient for dilute  $i$  in concentrated  $j$ . Equation (12d) gives some indication of the magnitude of the cross coefficient to be expected in a ternary mixture.

When a system is nearly ideal thermodynamically, binary diffusion coefficients tend to be linear functions of concentration, and Eq. (12) indicates the possibility of planar behavior of the multicomponent coefficients. Data in two relatively ideal ternary liquid mixtures are in accord with this [4, 15]. Since thermodynamically nonideal binary liquid mixtures generally show a nonlinear concentration dependence of the binary diffusion coefficients, one concludes from Eq. (12) that the multicomponent coefficients in nonideal multicomponent liquid mixtures must show a nonlinear concentration dependence also. In general, one expects that as the components of a multicomponent mixture become more dissimilar, the cross-diffusion coefficients will increase relative to the main coefficients and the concentration dependence will increase and become more nonlinear.

In binary systems, one defines the reference frame and concentration measure in such a way that there is only one diffusion coefficient and this diffusion coefficient is invariant to a change of reference frame [3]. For example, in three common reference frames:

$$\mathbf{J}_i^V = -\mathfrak{D}_{ij} \nabla C_i \text{ mass or moles} \quad (13a)$$

$$\mathbf{J}_i^m \text{ mass} = -\mathfrak{D}_{ij} \rho \nabla w_i \quad (13b)$$

$$\mathbf{J}_i^M \text{ moles} = -\mathfrak{D}_{ij} C \nabla f_i \quad (13c)$$

where  $w_i$  is mass fraction,  $f_i$  is mole fraction,  $\rho$  is total mass/volume,  $C$  total moles/volume, and  $m$ ,  $M$  and  $V$  refer to mass, molar and volume reference frames, respectively.

In a multicomponent system the elements of the diffusion matrix must change as the reference frame is changed, but if one retains the form of the binary equations in multicomponent systems then in matrix notation [5]

$$(\mathbf{J}^V) = -[D^V] \nabla(C) \text{ mass or moles} \quad (14a)$$

$$(\mathbf{J}^m)_{\text{mass}} = -[D^m] \rho \nabla(w) \quad (14b)$$

$$(\mathbf{J}^M)_{\text{moles}} = -[D^M] C \nabla(f) \quad (14c)$$

where ( ) represents column vectors and [ ] square matrices. The characteristic roots of all of the above matrices are the same [5]. Thus, the invariance of the characteristic roots of the diffusion coefficient matrix is analogous to the invariance of the binary diffusion coefficient.

Any one of these forms may be taken as a starting point in describing multicomponent systems.

### THE EQUATIONS OF CHANGE

The flux with respect to a fixed coordinate is given by [3]

$$\mathbf{N}_i = \mathbf{J}_i + \mathbf{V}C_i \quad (15)$$

$\mathbf{V}$  is the reference velocity. When this is combined with the continuity equation with a homogeneous chemical reaction

$$\frac{\partial C_i}{\partial \theta} + \nabla \cdot \mathbf{N}_i = r_i \quad (16)$$

one obtains

$$\frac{\partial C_i}{\partial \theta} + \nabla \cdot \mathbf{V}C_i = \nabla \cdot \mathbf{J}_i + r_i \quad (17)$$

and since one can choose any one of a number of reference velocities many forms of the above equation are possible.

In the volume reference frame

$$\frac{\partial C_i}{\partial \theta} + \nabla \cdot \mathbf{V}^V C_i = \nabla \cdot \sum_{j=1}^n D_{ij}^V \nabla C_j + r_i \quad (18)$$

while in the mass reference frame using mass units,

$$\frac{\partial C_i}{\partial \theta} + \nabla \cdot \mathbf{V}^m C_i = \nabla \cdot \rho \sum_{j=1}^n D_{ij}^m \nabla w_j + r_i \quad (19)$$

and since total mass is conserved we can rewrite this in the form

$$\rho \frac{\partial w_i}{\partial \theta} + \mathbf{V}^m \cdot \nabla w_i = \nabla \cdot \rho \sum_{j=1}^n D_{ij}^m \nabla w_j + r_i \quad (19a)$$

Equations (18) and (19) are identical term by term in a system of constant mass density if Eq. (19) is written in mass units. Also since mass is conserved the overall continuity equation becomes

$$\frac{\partial \rho}{\partial \theta} + \nabla \cdot \mathbf{V}^m \rho = 0 \quad (20)$$

It is usually permissible to assume that partial volumes are independent of concentration (no volume change on mixing). Then the continuity equations give

$$\nabla \cdot \mathbf{V}^v = \sum_{i=1}^{n+1} r_i \bar{v}_i \quad (21)$$

The two reference velocities are related by

$$\mathbf{V}^v - \mathbf{V}^m = \frac{1}{\rho} \sum_{i=1}^{n+1} \mathbf{J}_i^v = \frac{1}{\rho} \sum_{i=1}^n \left( 1 - \frac{\bar{v}_i}{\bar{v}_{n+1}} \right) \mathbf{J}_i^v \quad (22)$$

and  $\mathbf{V}^m$  is given by the equations of motion.

#### DIFFUSION WITHOUT REACTION

Equation (18) becomes in matrix notation

$$\frac{\partial(C)}{\partial \theta} + \nabla \cdot \mathbf{V}^v(C) = \nabla \cdot [D] \nabla(C) \quad (23)$$

For small gradients higher-order terms in concentration gradients may be neglected so

$$\frac{\partial(C)}{\partial \theta} + \nabla \cdot \mathbf{V}^v(C) = [D^v] \nabla^2(C) \quad (24)$$

Studies in ternary gas mixtures [1, 16, 17] indicate that  $[D]$  may be taken as constant at the average system composition even in systems with large concentration gradients and large variations in the  $D_{ij}$  so we assume that only small errors will arise in liquids when  $[D^v]$  is taken as constant.



$[D^V]$  may be diagonalized by a similarity transform [5, 18]

$$[t]^{-1}[D^V][t] = \begin{bmatrix} D_1 & & & \\ & \cdot & & \\ & & \cdot & \\ & & & D_n \end{bmatrix} \equiv \Gamma D \_ \quad (25)$$

where the  $D_i$ 's are the characteristic roots of  $[D]$  and hence are real positive numbers. Writing a new concentration vector

$$(\chi) = [t]^{-1}(C) \quad (26)$$

Equation (23) becomes

$$\frac{\partial(\chi)}{\partial\theta} + \nabla \cdot \mathbf{V}^V(\chi) = \Gamma D \_ \nabla^2(\chi) \quad (27)$$

which represents the set of  $n$  binary problems

$$\frac{\partial\chi_i}{\partial\theta} + \Delta \cdot \mathbf{V}^V\chi_i = D_i\nabla^2\chi_i, \quad i = 1, \dots, n \quad (28)$$

Solutions are obtained readily when the  $\chi_i$ 's at the boundaries are uncoupled and  $\mathbf{V}^V$  is independent of the  $\chi_i$  (small fluxes). Thus, if the initial and boundary concentrations and  $\mathbf{V}^V$  are specified and the solution to Eq. (28) is of the form

$$(\chi_i - \chi_{io}) = f(D_i, \theta, \mathbf{r})(\chi_{iI} - \chi_{io}) \quad (29)$$

where  $\mathbf{r}$  is the position vector, or

$$(\Delta\chi) = \begin{bmatrix} f(D_1, \theta, \mathbf{r}) \\ \cdot \\ \cdot \\ f(D_n, \theta, \mathbf{r}) \end{bmatrix} (\Delta\chi_o) \quad (30)$$

then converting back to real concentrations with Eq. (26)

$$(\Delta C) = [t] \begin{bmatrix} f(D_1, \theta, \mathbf{r}) \\ \cdot \\ \cdot \\ f(D_n, \theta, \mathbf{r}) \end{bmatrix} [t]^{-1}(\Delta C_o) \quad (31)$$

$$(\Delta C) = f([D], \theta, \mathbf{r})(\Delta C_o) \quad (32)$$

and we conclude that the multicomponent solution is the matrix generalization of the scalar binary problem, which says that the multicomponent solution is a linear combination of binary solutions. Since the characteristic roots are real positive numbers the binary solutions are stable.

The flux is given by

$$(\mathbf{N}) = k([D], \theta, \mathbf{r}, \theta)(\Delta C_o) \quad (33)$$

where  $k(D_i, r, \theta)$  is the binary mass transfer coefficient.

Since the  $n$  linear combinations diffuse independently there can be  $n - 1$  extreme values (not counting initial and final values) of the flux or concentration at any point in the system if none of the linear combinations have extreme values and more if the initial and boundary conditions lead to extreme values for the linear combinations.

Thus, in multicomponent systems initial and boundary conditions which in a binary system would not lead to oscillations can give a finite number of oscillations in a multicomponent system.

#### HOMOGENEOUS REACTIONS WITHOUT DIFFUSION

If we consider a system which is never far from equilibrium then all reactions may be considered to be first order and, to some extent, at least, reversible. Consider first the general reversible first-order scheme [21]. If  $r$  components react we can write

$$(r_r) = -[k_r](C_r) \quad (34)$$

where  $[k_r]$  is a constant  $r \times r$  matrix and

$$(r_r) = \begin{pmatrix} r_1 \\ r_2 \\ \cdot \\ \cdot \\ r_r \end{pmatrix}, (C_r) = \begin{pmatrix} C_1 \\ C_2 \\ \cdot \\ \cdot \\ C_r \end{pmatrix} \quad (35)$$

As in the diffusion problem, changing from molar to mass units changes the values of the  $k_{ij}$  but leaves the characteristics roots unchanged.

Wei and Prater [21] show from the principle of detailed balance of chemical reactions that  $[k_r]$  has one zero root and  $r - 1$  positive roots. If there are no concentration gradients present inerts do not couple with the reactants (it is assumed that there is no coupling in

the chemical mechanism itself); consequently Eq. (18) reduces to

$$\frac{d(C_r)}{d\theta} = (r_r) = -[k_r](C_r) \quad (36)$$

The equations can be uncoupled by diagonalizing  $[k_r]$  and are equivalent to a set of first-order irreversible reactions with rate constants equal to the characteristic roots of  $[k_r]$ . The solution is formally

$$(C_r) = e^{-[k_r]\theta}(C_{r0}) \quad (37)$$

where  $(C_{r0})$  is the initial value of  $(C_r)$ . This problem with no inerts has been thoroughly analyzed by Wei and Prater [21]. Since the roots are real and nonnegative the system decays smoothly to equilibrium. Since the inert concentrations are unaffected by the reaction under these conditions the inerts may be ignored. For  $n + 1$  reactants there are  $n - 1$  possible extreme values for each component.

Wei [20] has shown that in the general mass action system near equilibrium  $[k_r]$  has the same essential structure as in truly first-order systems. Hence the above results hold for mass action systems near equilibrium if we write

$$(r_r) = -[k_r](C_r - C_{re}) \quad (38)$$

where  $e$  indicates equilibrium value.

#### SIMULTANEOUS DIFFUSION AND REACTION

In systems in which there is simultaneous diffusion and reaction inerts can couple with the reacting species through the cross-diffusion coefficients  $D_{ij}$ . Hence it is desirable to modify the reaction matrix by adding a row and column of zeros for each inert [19]

$$(r') = - \begin{bmatrix} [k_r] & 0 \dots 0 \\ 0 \dots 0 & 0 \dots 0 \\ 0 \dots 0 & 0 \dots 0 \end{bmatrix} (C' - C_e') = -[k'](C' - C_e') \quad (39)$$

Here  $(r')$  and  $(C' - C_e')$  are column vectors of order  $n + 1$  and  $[k']$  is order  $(n + 1) (n + 1)$ .

For a constant density system (mass or molar)

$$\sum_1^{n+1} (C_i - C_{ie}) = 0 \quad (40)$$

so the order can be reduced by one without changing the form of the equation,

$$(r) = -[k](C - C_e) \quad (41)$$

where  $[k]$  is obtained from  $[k']$  by deleting the last row and column and subtracting the last column from the earlier columns.

The simplest meaningful class of problems is obtained when the mass or molar density can be taken as constant. The former is more useful in liquid systems and the latter is more useful in gaseous systems, but if we start with Eq. (18) both cases can be treated together.

Combining Eqs. (18) and (41)

$$\frac{\partial(C)}{\partial\theta} = \nabla \cdot \mathbf{V}^v(C) = \nabla \cdot [D^v] \nabla(C) - [k](C - C_e) \quad (42)$$

For constant density Eq. (21) gives

$$\nabla \cdot \mathbf{V}^v = 0 \quad (43)$$

and since  $(C_e)$  is a constant vector

$$\frac{\partial(C - C_e)}{\partial\theta} + \mathbf{V}^v \cdot \nabla(C - C_e) = \nabla \cdot [D^v] \nabla(C - C_e) - [k](C - C_e) \quad (44)$$

Dividing through by the density, defining  $y_i$  as mass or mole fraction and  $x_i$  as  $y_i - y_{ie}$ , and taking  $[D^v]$  as constant

$$\frac{\partial(x)}{\partial\theta} + \mathbf{V}^v \cdot \nabla(x) = [D^v] \nabla^2(x) - [k](x) \quad (45)$$

This is the starting equation that will be used for the analysis of the first-order diffusion-reaction problem. The same form is obtained if the equations are formulated in  $n + 1$  concentration space, but unless noted otherwise it is assumed below that the equations are written in  $n$  space.

### *Diagonal Problems*

It was seen earlier that when diffusion takes place alone or reaction takes place alone then the equations are diagonal and the systems are stable in the sense that only a finite number of extreme values of the concentration are allowable.

When diffusion takes place alone certain linear combinations of components diffuse independently of each other, and when reaction takes place alone other linear combinations react independently of

each other. Only when both linear combinations are the same are there linear combinations in the diffusion-reaction system which diffuse and react independently of each other. The linear combinations are the same only when  $[D]$  and  $[k]$  have the same characteristic vectors, which is equivalent to saying that they can be diagonalized by the same similarity transform.

$[D]$  and  $[k]$  may be diagonalized by the same similarity transform when they commute and if  $[t]$  is the modal matrix of both  $[D^v]$  and  $[k]$  Eq. (45) transforms to

$$\frac{\partial(\chi)}{\partial\theta} + \mathbf{V}^v \cdot \nabla(\chi) = \begin{bmatrix} D_1 & & & \\ & \cdot & & \\ & & \cdot & \\ & & & D_n \end{bmatrix} \nabla^2(\chi) - \begin{bmatrix} k_1 & & & \\ & \cdot & & \\ & & \cdot & \\ & & & k_n \end{bmatrix} (\chi) \quad (46)$$

This represents a set of uncoupled equations and each equation corresponds to a binary system with a single irreversible reaction or no reaction. This system is stable since the  $D_i$  and  $k_i$  are real non-negative numbers. The maximum number of extreme values is  $n - 2$  if each linear combination has no extreme values and possibly a few more if the initial and boundary conditions lead to extreme values in the  $\chi_i$ .

If neither  $[D]$  nor  $[k]$  is a scalar times the identity matrix the commuting of  $[D]$  and  $[k]$  represents an exceptional case which does not appear to have much physical significance. Also, since the case in which  $[k]$  is a scalar times the identity matrix has physical significance only in a binary system, the only unexceptional case of interest in which  $[D]$  and  $[k]$  commute is that system in which  $[D]$  is a scalar times the identity matrix. This represents the general system of like components with no diffusional coupling as shown before. The only uncoupled systems which do not fall in this class are those in which all but one of the components are infinitely dilute in ordinary diffusion or those in which Knudsen diffusion takes place. In these systems it was seen that  $[D]$  is diagonal, but the diagonal elements need not be equal. Then  $[D]$  and  $[k]$  do not in general commute and the more general solutions considered below are required.

#### *The Nondiagonalable Dual Problem*

Whenever we have mixtures of dissimilar components, dilute or not, diagonal forms are not usually possible and solutions of the diffusion-reaction problem are not linear combinations of scalar solutions.

They must be developed for the particular boundary value problem of interest. We consider a bounded system in which the diffusion is in one dimension, a slab, sphere, or cylinder. The mixture of  $n + 1$  components has some given initial concentration which may or not be a stationary state and we consider a step change in the concentrations at the boundary to some final concentration which may or may not be an equilibrium value.

The boundary is assumed to be fixed so  $\mathbf{V}^V = 0$  at the boundary. Since  $\nabla \cdot \mathbf{V}^V = 0$  by the assumption of constant density,  $\mathbf{V}^V = 0$  everywhere. Equation (45) then becomes

$$\frac{\partial(x)}{\partial\theta} = [D] \frac{1}{Z^s} \frac{\partial}{\partial Z} Z^s \frac{\partial(x)}{\partial Z} - [k](x) \tag{47}$$

where  $s = 1,2,3$  for slabs, cylinders, and spheres, respectively. The boundary conditions are

	$\theta = 0,$	$(x) = (y(Z,0) - y_e)$	(47a)
slabs	$Z = \pm a,$	$(x) = (y_{\pm a} - y_e)$	(47b)
cylinders	$Z = a,$	$(x) = (y_a - y_e)$	(47c)
and			
spheres	$Z = 0,$	$\frac{\partial(x)}{\partial Z} = 0$	(47d)

In the case of slabs we have allowed for different concentrations at the two surfaces.

The solution for the slab of thickness  $2a$  obtained by separation of variables is [19]

$$(y(Z,\theta) - y(Z)) = \sum_{p=0}^{\infty} \cos \{ \sqrt{A_p} Z \} e^{-[L_p]\theta} \frac{1}{a} \int_{-a}^a (y(Z',0) - y(Z')) \cos \{ \sqrt{A_p} Z' \} dZ' \tag{48}$$

where  $(y(Z))$  is the concentration in the final stationary state, which may be an equilibrium state,  $(y(Z,0))$  is the initial concentration,

$$A_p = \left( \frac{2p + 1}{2a} \pi \right)^2 \tag{48a}$$

$$[L_p] = A_p[D] + [k] \tag{48b}$$

Similar solutions are obtained for spheres and cylinders. The characteristic functions and characteristic values of the boundary value problem,  $\cos \{ \sqrt{A_p} Z \}$  and  $\sqrt{A_p}$ , respectively, are merely replaced

by the forms corresponding to the particular geometry. (The method of superposition may be used to construct solutions for time dependent boundary concentrations.)

It is seen that the behavior of Eq. (48) depends critically upon the nature of the roots of the matrix  $[L_p]$ . Before considering this behavior a few other points of interest will be considered.

First it is noted that the scalar solution analogous to Eq. (48), the solution of the binary diffusion problem with a single irreversible chemical reaction, merely replaces  $(y)$  by a single  $y_i$  and replaces  $\exp\{-[L_p]\theta\}$  by  $\exp\{-(A_p D_i + k_i)\theta\}$ . But the scalar exponential can be written in any one of three ways,

$$e^{-(A_p D_i + k_i)\theta} = e^{-A_p D_i \theta} e^{-k_i \theta} = e^{-k_i \theta} e^{-A_p D_i \theta}$$

Only when  $[D]$  and  $[k]$  commute are the matrix generalizations of these equalities valid. Otherwise of the three possible matrix generalizations only the first is the correct one!

When the boundaries of the system are held at equilibrium the stationary state is an equilibrium state and the concentration everywhere is equal to the boundary concentration. When the boundary concentration is not an equilibrium concentration then the concentration varies with  $Z$  in the stationary state. For example, the stationary state solution to Eq. (45) for the slab with

$$\begin{aligned} (y_{+a}) &= (y_{-a}) = (y_I) \text{ is} \\ (y(Z) - y_e) &= \cosh\{[B]Z\} [\cosh\{[B]a\}]^{-1} (y_I - y_e) \end{aligned} \quad (49)$$

where

$$[B] = [[D]^{-1}[k]]^{1/2} \quad (49a)$$

When no inerts are present  $(y_e)$  is the equilibrium composition vector, so that if the boundaries are at equilibrium  $(y_I) = (y_e)$  and  $(y(Z)) = (y_e)$ . When inerts are present  $(y_e)$  is not unique but expansion of the matrix functions in Eq. (49) and use of the condition  $[k](y_e) = 0$  again gives  $(y(Z)) = (y_e)$ .

If we write Eq. (49) as

$$(y(Z) - y_e) = [Q(Z)](y_I - y_e) \quad (50)$$

and consider the initial state of the system to be a stationary state with the boundary concentration  $(y_{I0})$  then the initial concentrations

are given by

$$(y(Z,0) - y_e = [Q(Z)](y_{I0} - y_e) \quad (51)$$

and subtracting Eq. (50) from (51)

$$(y(Z,0) - y(Z)) = [Q(Z)](y_{I0} - y_I) \quad (52)$$

If the normalized integral on the right of Eq. (48) is called ( $h_p$ ) then

$$\begin{aligned} (h_p) &= \frac{1}{a} \int_{-a}^a [Q(Z')] \cos \{ \sqrt{A_p} Z' \} dZ' (y_{I0} - y_I) \\ &= [\tilde{Q}_p](y_{I0} - y_I) \end{aligned} \quad (53)$$

and ( $y_{I0} - y_I$ ) represents the concentration change applied to the boundary. The mean concentration in the slab is given by

$$(\bar{y}(\theta)) = (\bar{y}_s) + \frac{2}{\pi} \sum_{p=0}^{\infty} \frac{(-1)^p}{2p+1} e^{-[L_p]\theta} [\tilde{Q}_p](y_{I0} - y_I) \quad (54)$$

where  $\bar{y}_s$  is the mean concentration in final stationary state. The mean rate of reaction is

$$\bar{r}(\theta) = \bar{r}_s - \frac{2d}{\pi} [k] \sum_{p=0}^{\infty} \frac{(-1)^p}{2p+1} e^{-[L_p]\theta} [\tilde{Q}_p](y_{I0} - y_I) \quad (55)$$

where  $d$  is the total mass or molar density and  $\bar{r}_s$  is the mean rate in the final stationary state.

The rate of transfer into the system per unit area is easily obtained as

$$(J)_{\pm a} = [D] \sum_{p=0}^{\infty} (-1)^p \sqrt{A_p} e^{-[L_p]\theta} [\tilde{Q}_p](y_{I0} - y_I) \quad (56)$$

Although the principle of microscopic reversibility and the second law of thermodynamics ensure that  $[D]$  and  $[k]$  have real positive roots, it has not been shown that the  $[L_p]$  also have real positive roots under all conditions, but it can be shown that under many conditions, the roots are indeed real and positive [19] and no counter examples have been found. If complex or imaginary roots do occur then oscillatory behavior is insured.

However, even if the  $[L_p]$  have only real positive roots oscillations may be obtained. Each of the terms

$$e^{-[L_p]\theta}$$



which appear in all the above transient solutions, can have  $n - 1$  extreme values. Thus, although the system must eventually reach its final stationary state without oscillating, the number of extreme values obtained may be considerably larger than the number of components present.

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