

## Interphase transfer with non-equilibrium chemical reaction

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**Abstract**—Steady, multicomponent diffusion through two phases, accompanied by an arbitrary number of reversible reactions between the diffusing species, is formulated as a boundary value problem. The results, achieved after linearization, indicate that non-equilibrium reaction in the neighborhood of the interface is possible even though equilibrium may exist in the bulk phases. The effect of the reaction(s) is to augment the transfer as in the case of single films. The extent of this augmentation effect for a pair of simultaneous, coupled reactions of the form



is shown. A reaction coupling effect increases the transfer above that due to each reaction occurring alone.

### INTRODUCTION

A GROWING body of data in both chemical engineering applications (see [4, 13], for example) and in biochemical areas [3, 9] exhibits the effect of chemical reaction on interphase transport, and emphasizes the need for a simple theory for predicting the effect on transfer of diffusion-reaction coupling in multicomponent, multi-reaction, two phase systems.

That chemical reaction may produce an appreciable effect upon transport in a single homogeneous film has been known at least since Hatta's explanation [8] of CO<sub>2</sub> absorption into caustic solution. Hatta's explanation was based upon the postulation of a single, essentially irreversible, pseudo first order chemical reaction as being rate controlling, and his analysis predicted enhanced transfer due to the chemical reaction. This result was in qualitative agreement (at least) with the experimental results.

The extension of the diffusive transport-with-chemical reaction-theory to systems involving more complicated reactions under non-equilibrium conditions has been limited because of the associated non-linearities. However, Olander [11] was able to obtain the maximum extent to which steady transfer is enhanced in a single film due to certain elementary reactions occurring singly, by

use of a model in which diffusion was considered controlling. That is, the reaction was considered to be in quasi-equilibrium.

A relaxation of the quasi-equilibrium condition was achieved by Friedlander and Keller [7] by use of the affinity function, again for steady diffusive transport through a single film. This linearized analysis showed that the extent to which the reaction is displaced from equilibrium by the diffusion flux is characterized by the ratio of the film thickness  $a$  to the diffusion-reaction length  $\lambda'$ . Olander's results based on quasi-equilibrium are obtained as an asymptotic limit of this theory as  $a/\lambda' \rightarrow \text{large}$ . The effect of the reaction-diffusion coupling was thus shown to always enhance, or augment, the diffusive transport; the maximum augmentation occurring under conditions such that the reaction proceeds essentially at equilibrium.

Further developments in the linearized, single phase transfer-with-reaction problem were provided by Brown [3], Toor [15], and Wei [17]. In brief, in these analyses the linearized theory was extended to multicomponent, multi-reaction systems by the use of the theory of matrices, and various properties of the linear systems were discussed. Brown's formulation was posed in the language of irreversible thermodynamics

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whereas Toor and Wei worked in terms of concentration.

With this background the extension of the linearized theory to the steady two phase multi-component, multi-reaction system is possible and it is the results of the analysis of this problem that are presented here. The approach taken is to linearize the conservation equations via a "small" flux, dilute solute restriction, and to proceed with the use of matrix algebra in the solution of the two phase boundary value problem.

The results are applicable, for example, insofar as the restrictions hold, to convection free liquid-films, and also to those biochemical problems dependent on transport through liquid-membrane interfaces.

#### APPROACH

The balance equations for species  $i$  in phase  $j$  may be written in terms of either the chemical potential  $\mu_{ij}$ , or the concentration  $c_{ij}$ . A formulation in terms of the latter quantity is normally more useful in two phase systems for which the phase distribution coefficients are either known, or can be measured. For certain systems such as those involving transport with reaction through liquid-membrane interfaces, especially in biochemical systems the phase distribution coefficients are not readily available, however. For such situations, a statement in terms of the species chemical potentials may be more useful. A formulation of the problem in terms of the chemical potential, however, requires knowledge of the Onsager transport coefficients  $\mathcal{L}_{ik}$ , mean values of which may be estimated from the ordinary diffusion coefficients, under conditions such that the activity coefficients can be taken as approximately constant.

The transport equations for a steady, isothermal pure diffusion two phase system with reaction may be written as

$$\sum_{k=1,n} (\mathcal{L}_{ik} \nabla^2 \mu_k + \nabla \mu_k \cdot \nabla \mathcal{L}_{ik}) = -R_i \quad i, k = 1, 2, \dots, n. \quad (1)$$

For the flux sufficiently small, and  $\mathcal{L}_{ik}$  a "weak" function of  $\mu_k$  the  $\mathcal{L}_{ik}$  may be taken essentially

constant. Hence, written in terms of the species chemical potential vector ( $\mu$ ) and the species reaction rate vector ( $R$ ), the restricted form of Eq. (1) becomes in each phase  $j$ :

$$[\mathcal{L}]_j \nabla^2 (\mu)_j = - (R)_j \quad j = 1, 2 \quad (2)$$

where  $[\mathcal{L}]$  is the matrix of Onsager (phenomenological) coefficients.  $[\mathcal{L}]$  is symmetric in form (by principle of microscopic reversibility) and the characteristic values of  $[\mathcal{L}]$  are real and positive.  $[\mathcal{L}]$  need not be strictly diagonal in the following development.

The  $n$ -dimensional species reaction vector ( $R$ ) is the resultant of  $r$  independent reactions among the  $n$  species. For any non-trivial situation there are at most  $n-1$  independent reactions between the  $n$  species [1]. The reaction rates of these  $r$ -reactions are defined as components of an  $r$ -dimensional column vector ( $\omega$ ) connected through the stoichiometry as follows:

$$(R)_j = [\nu](\omega)_j \quad (3)$$

where  $[\nu]$  is an  $n \times r$  matrix of the stoichiometric coefficients defined such that  $\nu_{ik}$  represents the coefficient of the  $i$ th species in the  $k$ th reaction.

For a system near equilibrium (consistent with the small flux restriction stated above) the reaction vector ( $\omega$ ) may be linearized in terms of the affinity function [12]:

$$(\omega)_j = [L]_j (a)_j. \quad (4)$$

$[L]$  is an  $r$ -dimensional matrix of the phenomenological reaction coefficients. In terms of the chemical potential, Eq. (4) becomes

$$(\omega)_j = -[L]_j [\nu]^T (\mu). \quad (5)$$

Substitution of Eqs. (3) and (5) into (2) yields

$$[\mathcal{L}]_j \nabla^2 (\mu) = [\nu][L]_j [\nu]^T (\mu). \quad (6)$$

Because of the solvent-fixed frame chosen at the outset, the matrix  $[\mathcal{L}]_j$  is non-singular and there-

fore has an inverse[14]. Multiplying by that inverse on the left gives

$$\nabla^2(\mu) = [W]_j(\mu) \quad (7)$$

where

$$[W]_j = [\mathcal{L}]_j^{-1}(\nu)(L)_j[\nu]^T.$$

Equation (7) may be considered the starting point of a (linearized) theory of interphase transport with multiple reactions among the  $n$  components.

A parallel development in terms of the (perturbed) concentration variables may be made for the restriction of small deviation from chemical equilibrium, yielding

$$\nabla^2(c') = [D]^{-1}[K](c') \quad (8)$$

where  $(c') = (c) - (c^e)$

$[D]$  = matrix of pseudo-binary diffusion coefficients

$[K]$  =  $r$ -dimensional matrix of pseudo first order reaction rate coefficients.

One may formulate the two phase boundary value problem in terms of Eq. (8). In terms of the perturbed concentration vector  $(c')$ , however, one interfacial boundary condition may be shown to be inhomogeneous. In view of this a more convenient approach, for the case of quasi-chemical equilibrium specified at the outer boundaries of the two phases, is to add

$$[D]\nabla^2(c^e) = [K](c^e) = 0$$

to Eq. (8), yielding

$$\nabla^2(c) = [D]^{-1}[K](c) \quad (8a)$$

where  $[K]$  is defined in Eq. (8). The linearized equations (7) and (8a) in terms of the chemical potential vector  $(\mu)$  and the concentration vector  $(c)$  are therefore of the same form. The properties of the solution in both  $\mu$ -space

and  $c$ -space are similar so the primary development in the following section shall be continued in  $\mu$ -space, with corresponding results in  $c$ -space provided where appropriate.

#### TRANSFORMATION AND NORMALIZATION

The matrix coefficient  $[W]$  in Eq. (7) although an  $n \times n$  matrix is of rank  $r$ ,  $r < n$ . Thus for example, for a system of five species and two independent reactions, the rank of the matrix will be two, hence singular. Furthermore,  $[W]$  need not be symmetric even though it is a product of the symmetric matrices  $[\mathcal{L}]^{-1}$  and  $[\nu][L][\nu]^T$ . The eigenvalues are always positive or zero[3, 6]. The chemical potential vector  $(\mu)$  given by Eq. (7) is related parametrically to diffusion, reaction rates, and stoichiometry through the matrix  $[W]$ . Thus while not assumed to be explicitly coupled in the Onsager sense, diffusion and reaction nevertheless affect one another through mass conservation. This interdependence may be thought of as diffusion-reaction coupling in the sense of Toor[15].

The approach toward obtaining a solution of such a linear, coupled set as Eq. (7) is to transform them to an equivalent uncoupled set. This consists of finding a matrix  $[S]$  such that

$$[S]^{-1}[\lambda^*]^2[S] = [W]. \quad (9)$$

$[\lambda^*]^2$  is a diagonal matrix whose diagonal entries are the eigenvalues of the matrix  $[W]$  arranged in descending order. As  $[W]$  is of rank  $r$ , a total of  $(n-r)$  of these eigenvalues will be zeroes. Also, there exists an infinite set of matrices  $[S]$  which will accomplish the desired uncoupling. Choosing one (convenient) matrix  $[S]$  from a subset of this infinite set (as described below), Eq. (7) becomes:

$$\nabla^2(\mu) = [S]^{-1}[\lambda^*]^2[S](\mu). \quad (10)$$

Multiplying on the left by  $[S]$  and recalling that for the small flux restriction the parameters are essentially independent of position, and also non-dimensionalizing the Laplacian operator by

use of the phase thickness  $l$ , results in

$$\nabla^2(u) = [\lambda]^2(u) \quad (11)$$

where

$$(u) \equiv [S](u)$$

$$[\lambda]^2 = l^2[\lambda^*]^2.$$

A property of the transformation matrix  $[S]$  in addition to uncoupling the Eqs. (7) is that the resulting modified state vector  $(\mu)$  created in the process contains components some of which describe only reaction effects, and the rest only diffusion effects. This separation is useful in that one may individually follow the course of the uncoupled reactions throughout the spatial domain of the problem. A demonstration of this diffusion reaction separation may be made[16] after introducing the useful normalization similar to that used by Wei[17, 10],

$$\frac{1}{l}[S]^{-T}[\mathcal{L}][S]^{-1} = [I]. \quad (12)$$

It can be shown[16] that a matrix  $[S]$  can be found satisfying both conditions (9) and (12). That Eq. (12) is a natural normalization to choose for the two phase problem becomes apparent in stating boundary condition (26) below.

#### THE PLANAR, TWO PHASE BOUNDARY VALUE PROBLEM

Our interest is in the mass flux through a two phase system and the influence of reaction interaction on the flux. We therefore formulate the boundary value problem in terms of a specification of the chemical potential vectors (or alternately, the concentration vectors) in each of the two phases, and seek a solution for the total mass flux, which is given by

$$T = (M)^T(J). \quad (13)$$

The region of many two phase systems in the neighborhood of the interface may be modeled as being essentially planar if the zones  $l_1, l_2$  in

which diffusive transfer takes place are small in extent compared with the radius of curvature of the interface, i.e. for the case of  $l_1, l_2 \ll R$ . Also, for equilibrium existing in the bulk phases the boundary conditions at the outer edge of each of the films may be taken as quasi-equilibrium to good approximation so long as the characteristic reaction-diffusion lengths  $1/\lambda_m$  are small compared with the phase thicknesses[7, 5]. Hence many physical situations of interest may be approximated by the model shown in Fig. 1, with the transition in properties from phase one to phase two taken as a step function at  $z = 0$ .

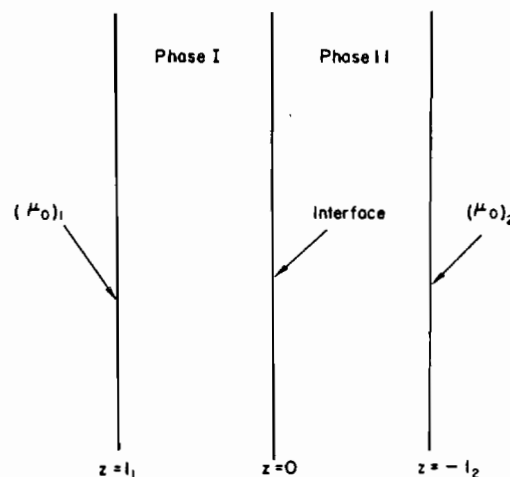


Fig. 1. Schematic model of a two phase system.

The linearized equations of change for the state vector  $(\mu)$  in each phase may now be written, in phase I

$$\frac{d^2}{d\eta_1^2}(\mu) = [W]_1(\mu) \quad (14)$$

and in phase II

$$\frac{d^2}{d\eta_2^2}(\mu) = [W]_2(\mu) \quad (15)$$

where

$$\eta_j = z/l_j, \quad j = 1, 2.$$

Equations (14) and (15) consist of  $2n$  second order coupled differential equations, requiring

4n boundary conditions to uniquely determine the solution. The required number of boundary conditions may be written as:

at

$$\eta_1 = 1 \quad \mu = (\mu_0)_1 \quad (16)$$

$$\eta_1 = \eta_2 = 0 \quad (\mu)^+ = (\mu)^- \quad (17)$$

$$\frac{1}{l_1} [\mathcal{L}]_1 \frac{d}{d\eta_1} (\mu) = \frac{1}{l_2} [\mathcal{L}]_2 \frac{d}{d\eta_2} (\mu) \quad (18)$$

at

$$\eta_2 = -1 \quad (\mu) = (\mu_0)_2. \quad (19)$$

That is, the chemical potential vector is specified at the outer boundaries via conditions (16) and (19), the fluxes of the components are matched at the interface, conditions (18), and the chemical potential vectors are also matched at the interface†, conditions (17). The statements (16) and (19) include the specification of quasi-chemical equilibrium at the outer boundaries. The results can be generalized to the case of non-equilibrium at the boundaries. The system of equations (14) and (15) subject to the constraints (16)–(19) now form a determinate set which may be solved for both the chemical potential distribution and also the flux.

The procedure is as described in the previous section. However, it is in general not possible to find a single transformation matrix which simultaneously uncouples the systems (14) and (15). Two separate transformations satisfying Eq. (9) are therefore chosen,  $[S]_1$  for phase I and  $[S]_2$  for phase II, resulting in modified state vectors for each phase,

$$(u)_1 = [S]_1(\mu) \quad (20)$$

$$(u)_2 = [S]_2(\mu) \quad (21)$$

such that Eqs. (14) and (15) can be written respectively as

†This latter condition is known to provide a good approximation to physical reality in a large number of transfer situations[4], although this may not be strictly valid in general[5].

$$\frac{d^2}{d\eta_1^2} (u)_1 = [\lambda]_1^2 (u)_1 \quad (22)$$

$$\frac{d^2}{d\eta_2^2} (u)_2 = [\lambda]_2^2 (u)_2. \quad (23)$$

Under the above transformations the boundary conditions (16)–(19) become:

$$\text{at } \eta_1 = 1 \quad (u)_1 = [S]_1(\mu_0)_1 \equiv (u_0)_1 \quad (24)$$

$$\eta_1 = \eta_2 = 0 \quad [S]_1^{-1}(u)_1 = [S]_2^{-1}(u)_2 \quad (25)$$

$$[S]_1^T \frac{d}{d\eta_1} (u)_1 = [S]_2^T \frac{d}{d\eta_2} (u)_2 \quad (26)$$

$$\eta_2 = -1 \quad (u)_2 = [S]_2(u_0)_2 \equiv (u_0)_2. \quad (27)$$

The equations (22)–(27) restate the problem in terms of the two modified state vectors  $(u)_1$ , and  $(u)_2$ .

Turning now to the system (22) one recognizes that the solution to the first  $r$  of the uncoupled equations has the form,

$$u_{1i} = A_{1i} \sinh \lambda_{1i} \eta_1 + B_{1i} \cosh \lambda_{1i} \eta_1 \quad i = 1, 2, \dots, r \quad (28)$$

whereas the last  $n-r$  equations have solutions of the form

$$u_{1i} = A_{1i} \eta_1 + B_{1i} \quad i = r+1, r+2, \dots, n. \quad (29)$$

Solutions (28) and (29) can be combined into a single matrix formula:

$$(u)_1 = [\sinh \lambda \eta]_1 (A)_1 + [\cosh \lambda \eta]_1 (B)_1. \quad (30)$$

The matrix  $[\sinh \lambda \eta]_1$  is diagonal, and its first  $r$  diagonal terms are the entries  $\sinh \lambda_{1i} \eta_1$  while the last  $n-r$  diagonal elements are simply  $\eta_1$ . Similarly, the diagonal matrix  $[\cosh \lambda \eta]_1$  has as its first  $r$  elements the functions  $\cosh \lambda_{1i} \eta_1$ , with the last  $n-r$  entries being unity.

The solution for the modified state vector in phase II is:

$$(u)_2 = [\sinh \lambda \eta]_2 (A)_2 + [\cosh \lambda \eta]_2 (B)_2. \quad (31)$$

Applying the boundary conditions (24)–(27) to Eqs. (30) and (31) yields the following values for the vectors of the integration constants:

$$(A)_1 = [\lambda]_1^{-1} [S]_1^{-T} \{ [R]_1^{-1} + [R]_1^{-1} \}^{-1} (\mu_0) \quad (32)$$

$$(B)_1 = (u_0)_1 - [\tanh \lambda]_1 [\lambda]_1^{-1} [S]_1^{-T} \{ [R]_1^{-1} + [R]_2^{-1} \}^{-1} (\mu_0) \quad (33)$$

$$(A)_2 = [\lambda]_2^{-1} [S]_2^{-T} \{ [R]_1^{-1} + [R]_2^{-1} \}^{-1} (\mu_0) \quad (34)$$

$$(B)_2 = (u_0)_2 + [\tanh \lambda]_2 [\lambda]_2^{-1} [S]_2^{-T} \{ [R]_1^{-1} + [R]_2^{-1} \}^{-1} (\mu_0). \quad (35)$$

See Eq. (38) for definitions of  $[R]_1$ ,  $[R]_2$ , and  $(\mu_0)$ .

The flux vectors  $(J)_j$  for the two phases in terms of the gradients of their respective modified state vectors  $(u)_j$  are

$$(J)_j = [S]_j^T \nabla (u)_j \quad j = 1, 2 \quad (36)$$

so that the total mass flux  $T$ , which is independent of position, for the one spatial dimensional case, becomes:

$$T = (M)^T [S]_1^T \nabla (u)_1. \quad (37)$$

Using the first of Eqs. (31) to form the gradient of  $(u)$  for use in Eq. (37) leads to the desired expression for the total flux:

$$T = (M)^T \{ [R]_1^{-1} + [R]_2^{-1} \} (\mu_0) \quad (38)$$

where

$$(\mu_0) = (\mu_0)_1 - (\mu_0)_2$$

$$[R]_1 \equiv [S]_1^T [\lambda]_1 [\tanh \lambda]_1^{-1} [S]_1$$

$$[R]_2 \equiv [S]_2^T [\lambda]_2 [\tanh \lambda]_2^{-1} [S]_2.$$

A similar development in terms of the concentration state vector leads to

$$T = (M)^T \{ [R']_1^{-1} + [m] [R']_2^{-1} \}^{-1} \{ (c^e)_1 - [m] (c^e)_2 \} \quad (39)$$

where  $[m]$  = matrix of phase distribution coefficients

$$[R']_1 = [c^e]_1 [S']_1^T [\lambda]_1 [\tanh \lambda]_1^{-1} [S']_1$$

$$[R']_2 = [c^e]_2 [S']_2^T [\lambda]_2 [\tanh \lambda]_2^{-1} [S']_2.$$

The results (38) and (39) are both reminiscent of a scalar equation relating a flux to a driving force linearly through a mass transfer coefficient. In this analogy the matrices  $[R]_1$  and  $[R]_2$ , as well as the "primed" ones, are identified with the mass transfer coefficients of their respective phases. The phases I and II being linked in tandem in this particular case causes the mass transfer coefficients to be combined in analogy with the law of additive resistances to yield an overall coefficient matrix for mass transfer. This interpretation is an extension to the case of interface transfer with near equilibrium reaction of that of Toor[14] for the case without reaction.

The matrix  $[R]_1^{-1} + [R]_2^{-1}$  is symmetric and unchanged by a transposition of the parameters of phases I and II. The linearized system in terms of chemical potential as driving force is therefore isotropic with respect to mass transfer.

An important property of a phase interface exhibited by results, Eqs. (38) or (39), is that a non-equilibrium solution for the flux exists for the two phase system even when quasi-chemical equilibrium is specified on both outer boundaries. This is in contrast to the behavior of the steady, single phase system without convection, for which only the trivial solution for the affinity exists if quasi-chemical equilibrium is specified on both boundaries of the system. This latter result is due to the homogeneous nature of the single phase boundary value problem.

Hence, the results of the linearized theory for the chemical potential vector, Eqs. (30) and (31),

show that for the two phase problem, transfer forces the reaction from equilibrium within the system even though quasi equilibrium is specified on the outer boundaries. A consequence of this is that a non-equilibrium distribution among the various chemical species may exist in the neighborhood of an interface during transfer even though equilibrium may exist within the bulk phases. This situation is illustrated in the following section.

#### PROPERTIES OF THE LINEARIZED THEORY

The results, Eqs. (38) and (39), contain the effect of the near-equilibrium chemical reactions upon the interfacial transport. Of particular interest is the way in which diffusion and reaction effects interact, and in the multi-reaction case, how reactions affect one another through diffusion. The following examples illustrate these phenomena. A comparison of both results, Eqs. (38) and (39), with experimental data for some simple reacting systems is provided by Wendt [18].

*Case 1—Transport of two species which may undergo the reaction*



For this two-dimensional problem the matrices may be taken as follows:

$$[\mathcal{L}]_j = \begin{bmatrix} \mathcal{L}_{Aj} & 0 \\ 0 & \mathcal{L}_{Bj} \end{bmatrix} \quad (41)$$

$$[\nu] = \begin{bmatrix} -\nu_A \\ \nu_B \end{bmatrix} \quad (42)$$

$$[L]_j = \begin{bmatrix} L_j & 0 \\ 0 & 0 \end{bmatrix} \quad (43)$$

$$(M) = M \begin{pmatrix} \nu_B \\ \nu_A \end{pmatrix} \quad (44)$$

$$(\mu_0) = \mu_0 \begin{pmatrix} \nu_B \\ \nu_A \end{pmatrix}. \quad (45)$$

Definitions (44) and (45) are convenient ways of expressing  $(M)$  and  $(\mu_0)$  because they introduce the least number of new parameters.

The resulting combined parameter matrix according to (7) is:

$$[W]_j = \begin{bmatrix} \frac{\nu_A^2}{\mathcal{L}_{Aj}} & \frac{-\nu_A \nu_B}{\mathcal{L}_{Aj}} \\ \frac{-\nu_A \nu_B}{\mathcal{L}_{Bj}} & \frac{\nu_B^2}{\mathcal{L}_{Bj}} \end{bmatrix} \quad (46)$$

for which the eigenvalues are

$$\lambda_{1j}^{*2} = L_j \left\{ \frac{\nu_A^2}{\mathcal{L}_{Aj}} + \frac{\nu_B^2}{\mathcal{L}_{Bj}} \right\} \\ \lambda_{2j}^{*2} = 0. \quad (47)$$

An acceptable  $[S]^{-1}$  is:

$$[S]^{-1} = \begin{bmatrix} \frac{-\nu_A}{\mathcal{L}_A} & \nu_B \\ \frac{\nu_B}{\mathcal{L}_B} & \nu_A \end{bmatrix} \quad (48)$$

which is to be normalized according to Eq. (12), the result after inversion being:

$$[S] = \left\{ \frac{\mathcal{L}_A \mathcal{L}_B}{l} \right\}^{1/2} \left\{ \frac{\nu_A^2}{\mathcal{L}_A} + \frac{\nu_B^2}{\mathcal{L}_B} \right\}^{-1/2} \\ \times \begin{bmatrix} \frac{-\nu_A}{\{\mathcal{L}_A \mathcal{L}_B\}^{1/2}} & \frac{\nu_B}{\{\mathcal{L}_A \mathcal{L}_B\}^{1/2}} \\ \frac{\nu_B}{\mathcal{L}_B} & \frac{\nu_A}{\mathcal{L}_A} \end{bmatrix}. \quad (49)$$

The employment of the foregoing matrix forms in the quadratic form (38) yields, after rearrangement:

$$T = \frac{l_1}{\nu_B^2 \mathcal{L}_{A1} + \nu_A^2 \mathcal{L}_{B1}} + \frac{l_2}{\nu_B^2 \mathcal{L}_{A2} + \nu_A^2 \mathcal{L}_{B2}} + \frac{M \mu_0}{\frac{\nu_A^2 \nu_B^2 \{\mathcal{L}_{A1} \mathcal{L}_{B2} - \mathcal{L}_{A2} \mathcal{L}_{B1}\}^2}{\{\nu_B^2 \mathcal{L}_{A1} + \nu_A^2 \mathcal{L}_{B1}\}^2 \{\nu_B^2 \mathcal{L}_{A2} + \nu_A^2 \mathcal{L}_{B2}\}^2} + \frac{\mathcal{L}_{A1} \mathcal{L}_{B1} \lambda_{11}^*}{\{\nu_B^2 \mathcal{L}_{A1} + \nu_A^2 \mathcal{L}_{B1}\} \tanh l_1 \lambda_{11}^*} + \frac{\mathcal{L}_{A2} \mathcal{L}_{B2} \lambda_{12}^*}{\{\nu_B^2 \mathcal{L}_{A2} + \nu_A^2 \mathcal{L}_{B2}\} \tanh l_2 \lambda_{12}^*}} \quad (50)$$

As can be seen in (50) the reaction parameters enter only in the third term of the denominator in the form of  $\lambda_{ij}^*/\tanh l_j \lambda_{ij}^*$ . As the eigenvalues become very large (50) simplifies to

$$T_c = \frac{M\mu_0}{\frac{l_1}{\nu_{B2}\mathcal{L}_{A1} + \nu_A^2\mathcal{L}_{B1}} + \frac{l_2}{\nu_{B2}\mathcal{L}_{A2} + \nu_A^2\mathcal{L}_{B2}}} \quad (51)$$

which is easily verified to be the total flux when the reaction (40) is everywhere at equilibrium. Inspection shows (51) to be an upper bound upon (50), hence maximum transfer is achieved with equilibrium reaction as in the case of transport with reaction through single films [3, 7].

As the eigenvalues become diminishingly small, (50) approaches as a limit:

$$T_d = \left[ \frac{\nu_A^2}{\frac{l_1}{\mathcal{L}_{B1}} + \frac{l_2}{\mathcal{L}_{B2}}} + \frac{\nu_B^2}{\frac{l_1}{\mathcal{L}_{A1}} + \frac{l_2}{\mathcal{L}_{A2}}} \right] M\mu_0 \quad (52)$$

which is the result one would obtain for inter-phase transport without reaction. Although the near-equilibrium assumption (4) breaks down after a point, (50) is seen to behave properly throughout the entire range of parameters.

Another feature exhibited by Eq. (50) is that the reaction effect on the transfer is essentially independent of the phase thicknesses for the special case of the transport coefficients related such that  $\mathcal{L}_{A1}\mathcal{L}_{B2} = \mathcal{L}_{A2}\mathcal{L}_{B1}$ . For this case it can be shown that Eqs. (50), (51), and (52) become identical, and the steady state is such that the diffusing components are in chemical equilibrium throughout each of the two films. However, in contrast with the equilibrium reaction effect pointed out above, the reaction does not enhance the transport. In other words, when the above special relationship occurs among the transport coefficients, there is no augmentation effect due to the reaction regardless of the film thickness. A similar situation exists in more complex systems also, but a number of parameter groupings are required to be null instead of the one grouping as in the two component system.

The form of the flux in (50), normalized to the flux without reaction, is shown in Fig. 2 for the case of the dimerization reaction,  $\nu_A = 1$ ,  $\nu_B = 2$ . The monomer form is dominant in phase II,  $\bar{c}_{B2}/\bar{c}_{A2} \gg 1$ , while different ratios of  $\bar{c}_{B1}/\bar{c}_{A1}$  are

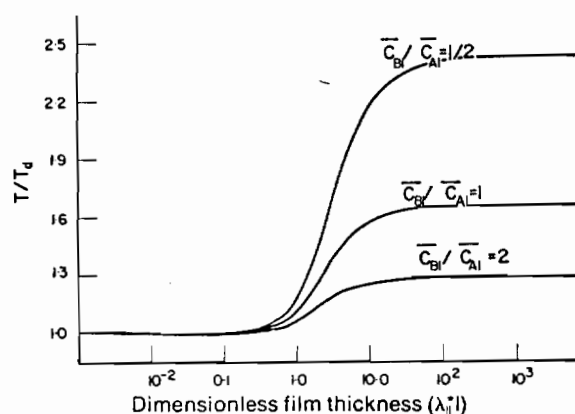


Fig. 2. The effect of diffusion-reaction coupling as a function of phase length (Case I).

shown in the three curves. This situation corresponds physically to the transfer of an alcohol from a hydrocarbon phase to an aqueous phase, for example. The Onsager transfer coefficients were approximated by

$$\mathcal{L}_i = \frac{\bar{c}_i \mathcal{D}_i}{RT} \quad (53)$$

where the concentrations were taken in the range of a few tenths of gmoles/l. and the ordinary pseudo binary diffusion coefficients were taken of the order of  $10^{-5}$  cm<sup>2</sup>/sec. Also the forward reaction rates were taken such that  $k_2 \gg k_1$ , with  $k_1$  in the range of  $10^2 - 10^4$ /sec. The phase thicknesses were set such that  $l_1 = l_2$ . Figure 2 shows that as the dimer-monomer ratio is increased in phase I, the augmentation effect of the reaction on the transport also increases. The chief effect of decreasing the reaction rate coefficients is to increase the film thickness at which non-equilibrium effects become important, although this is not seen on a dimensionless plot such as Fig. 2.



Finally, all the foregoing phenomena mentioned in this two dimensional example can be generalized to  $n$  species and  $r$  reactions.

*Case II—Transport of three species according to the reaction*



This three-dimensional situation is very similar to Case I. One new aspect has been introduced, however, in the form of an extra degree of freedom in the specification of the chemical potential vector at the outer boundaries. In Case I the chemical potentials at the outer boundaries were in the fixed ratio  $\nu_B/\nu_A$  because of the quasi-equilibrium specification. Now only one constraint between three chemical potentials gives one more latitude in specifying a vector which is at equilibrium.

Again Onsager coefficients were approximated by relation (53) where the  $\mathcal{D}_i$  were taken of the order of  $10^{-5}$  cm<sup>2</sup>/sec and the concentrations taken in the range of tenths of a gmole/l. or less. Species  $B$  was assumed to heavily predominate over  $C$  and  $D$  in phase I, whereas  $C$  and  $D$  assumed reasonable fractions of  $B$  in phase II. Here  $k_1 \ll k_2$  with the latter in the range of  $10^2$  l/sec.

A computer was used to evaluate the total flux directly from (38). Special procedures were devised to handle the highly singular matrices which occurred [16]. For a representative profile of total flux for this case as a function of film thickness see Case III.

*Case III—Transport of four species, A, B, C, and D with two concomitant reactions, (40) and (54).*

With the inclusion of two simultaneous reactions an extra degree of interaction is added to the model. Not only does each reaction couple with the diffusing species, but because some species in general are coupled to more than one reaction (species  $B$  in this case), these species serve to couple the two reactions. (In the case where direct diffusion-diffusion coupling is allowed through off diagonal Onsager coefficients the reactions need not even share species

in common). It has thus far been demonstrated how coupling serves to increase the mass transfer. It would only seem natural that this new degree of interaction would further enhance the mass transfer, as shown in Fig. 3.

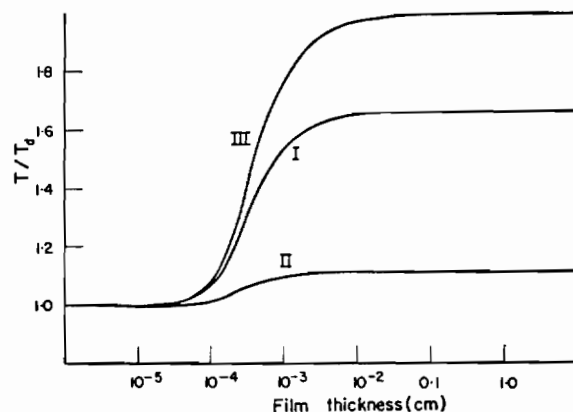


Fig. 3. A comparison of the effect of diffusion-reaction coupling in Cases I, II and III.

Figure 3 consists of three profiles of the total flux of the four species as a function of film thickness. Curve I shows the enhancement to mass transfer that would derive from reaction (40) alone. Curve II, likewise, shows the enhancement from reaction (54) alone. Curve III shows the effect of (40) and (54) occurring simultaneously. As anticipated, the increase in total flux with both reactions occurring is greater than the sum of the enhancements caused by the reactions individually (by some 22 per cent in this case). Parameters used in these trials are exactly those described in Cases I and II.

Finally, Fig. 4 shows the normalized chemical potential profiles across the length of the two phases. The norm for the chemical potential vector was chosen as

$$|\mu| = \{(\mu_0)^T(\mu_0)\}^{1/2}. \quad (55)$$

Of special interest is the profile of  $\mu_D$ . Fed by reaction (54) in a positive sense, species  $D$  appears to have "accumulated" at the interface, i.e. its potential is higher there than at either end of the two phases.

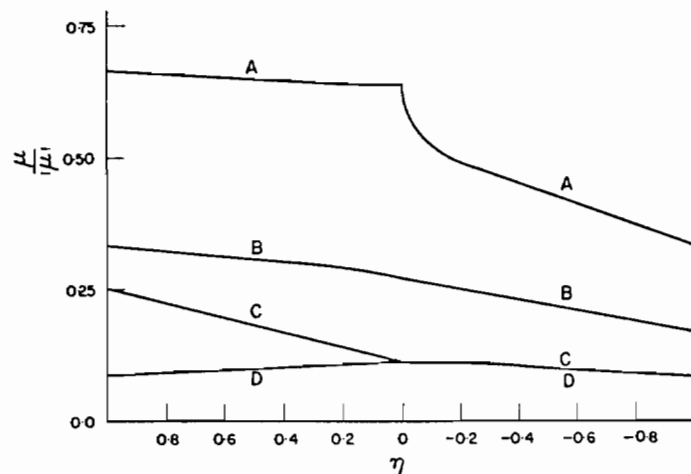


Fig. 4. Chemical potential profiles near the interface (Case III).

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## NOTATION

$A$	species in reaction (40)
$A_{ji}$	integration constant for transformed species $i$ in phase $j$ .
$(A)$	vector constant of integration
$(a)$	vector of affinities
$B$	species in reactions (40) and (54)
$B_{ji}$	integration constant for transformed species $i$ in phase $j$
$(B)$	vector constant of integration
$c_{ij}$	concentration of species $i$ in phase $j$
$\bar{c}_{ij}$	mean concentration of species $i$ in phase $j$
$C$	species in reaction (54)
$(c)$	vector of concentrations
$(c^e)$	vector of equilibrium concentrations
$(c')$	defined after Eq. (8)
$[\cosh \lambda \eta]$	matrix defined after Eq. (30)
$D$	species in reaction (54)
$\mathcal{D}_i$	pseudo-binary diffusion coefficient of species $i$
$[D]$	matrix of pseudo-binary diffusion coefficients
$[I]$	identity matrix
$(J)$	molar flux vector

$k_j$	a forward reaction rate in phase $j$
$[K]$	matrix of pseudo first order rate constants
$l_j$	the length of phase $j$
$\mathcal{L}_{ik}$	Onsager phenomenological coefficient of diffusion relating species $i$ and $k$
$\mathcal{L}_{Aj}$	Onsager diffusion coefficient of species $A$ in phase $j$
$\mathcal{L}_{Bj}$	Onsager diffusion coefficient of species $B$ in phase $j$
$[\mathcal{L}]$	matrix of Onsager coefficients of diffusion
$[L]$	matrix of Onsager coefficients of reaction
$M$	defined by Eq. (44)
$(M)$	vector of molecular weights
$[m]$	matrix of phase distribution coefficients
$n$	number of species present
$r$	number of independent reactions
$R$	gas constant
$R_i$	molar reaction rate of species $i$
$[R]$	matrix defined after Eq. (38)
$[R']$	matrix defined after Eq. (39)
$[S]$	transformation diagonalizing $[W]$
$[S']$	transformation diagonalizing $[D]^{-1}$
$[K]$	
$[\sinh \lambda \eta]$	matrix defined following equation (30)

$T$	total mass flux, absolute temperature	$\nu_B$	stoichiometric coefficient of $B$ in Eq. (40)
$T_e$	defined by Eq. (51)	$\nu_{im}$	stoichiometric coefficient of species $i$ in reaction $m$
$T_d$	defined by Eq. (52)	$[\nu]$	$n \times r$ matrix of stoichiometric coefficients
$[\tanh \lambda]$	matrix defined similarly as $[\cosh \lambda \eta]$	$(\omega)$	reaction velocity vector
$(u)$	the vector $(\mu)$ transformed by $[S]$		
$(u_0)_j$	the vector $(\mu_0)_j$ transformed by $[S]_j$		
$[W]$	matrix defined following Eq. (7)		
$z$	distance from the interface		
<b>Greek letters</b>		<b>Subscripts</b>	
$\eta_j$	dimensionless distance in phase $j$	$i$	species index
$\lambda'$	reaction-diffusion length	$j$	phase index
$\lambda_{mj}^*$	root of eigenvalue $m$ in phase $j$	$k$	species index
$[\lambda^*]^2$	matrix $[W]$ in normal form	$m$	reaction index
$[\lambda]^2$	matrix $[\lambda^*]^2$ in dimensionless form		
$[\lambda]$	matrix defined similarly to $[\cosh \lambda \eta]$	<b>Superscript operators</b>	
$\mu_0$	defined by Eq. (45)	$-1$	matrix inversion
$\mu_{ij}$	chemical potential of species $i$ in phase $j$	$T$	matrix transposition
$(\pi)$	vector of chemical potentials	$-T$	commutative inversion and transposition
$(\mu_0)_j$	chemical potential vector at outer boundary of phase $j$	<b>Operators</b>	
$(\mu_0)$	vector defined after Eq. (38)	$\nabla$	gradient operator
$\nu_A$	stoichiometric coefficient of $A$ in Eq. (40)	$\bar{\nabla}$	dimensionless gradient operator
		$\nabla \cdot$	divergence operator
		$\nabla^2$	Laplacian operator
		$\bar{\nabla}^2$	dimensionless Laplacian operator

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