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Film transfer with non-equilibrium chemical reaction

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Abstract – The asymmetric property of the nonlinear chemical affinity equation is shown to result in a diffusive flux augmentation effect, due to nonlinear chemical reaction rate, that is dependent on the direction in which the reaction is displaced from equilibrium. Because of this, a film when coupled with an external driving force can act as a "chemical pump". A simple model is suggested for a quasi steady pump of this type which provides maximum pumping effect when the film thickness is in the range of eight to ten times the mean characteristic diffusion reaction length.

INTRODUCTION

FILM TRANSFER with chemical reaction is in general a nonlinear problem, special cases of which have been treated by, for example, Olander[1], Friedlander and Keller[2], and Toor [3, 4]. By use of a model in which the reaction was considered sufficiently rapid as to be in quasi-equilibrium, Olander was able to show that the effect of a single reaction is to enhance, or augment, the transport. Friedlander and Keller extended the analysis to slightly removed from equilibrium situations. In addition to showing that equilibrium reaction provides an upper limit of the enhancement effect, they also provided a criterion in the form of a characteristic reaction–diffusion length for estimating when local equilibrium exists. Toor considered the problem of dual diffusion–reaction coupling in systems in which the components participate in any number of first order reactions.

Although each of the above mentioned analyses is based upon a linear or linearized model, they have provided considerable insight into the film transport phenomenon. However, one may lose certain qualitative aspects of the behavior of systems which are basically nonlinear, strictly speaking, in a linear or linearized treatment, as is well known. In the case of film transfer with arbitrary order chemical reaction, the asymmetry of the problem with respect to the direction in which the reaction is displaced from equilibrium is lost in a linearized treatment, and it is the purpose of this communication to explore the nature of the effect of reaction asymmetry on film transfer at a "zeroth order" level for the case of pure, steady diffusion of species that participate in a single reaction in the domain of interest.

To retain at least part of the asymmetric character of the general problem of reaction diffusion coupling (in the sense of Toor[3]), it is necessary to include some or all of the nonlinear terms in the appropriate transport equations. Two approaches come to mind. One may formulate the problem in concentration (or mole fraction) space in terms of ordinary Fickian diffusion. This approach has the advantage that properties like ordinary diffusion coefficients and boundary concentrations are readily available, or measureable. A major disadvantage of this approach is that the mathematical analysis of the resulting set of nonlinear second order differential equations is a formidable task. Also, a given set of results, in the event the analysis is successful, is limited to a single, net reaction rate form.

A second approach is to formulate the problem in chemical potential space. This approach has

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the advantage that the analysis is more tractable and the results are not limited to a specific reaction form. A disadvantage is that the results may be applicable over a more limited range in concentration variation if properties such as Onsager diffusion coefficients are stronger functions of chemical potential than Fickian coefficients are of concentration.

It is this second approach that is taken here, and an approximate solution is developed for a restricted form of the nonlinear chemical affinity equation. We write the conservation statement for species i in the steady, convection free one-dimensional system as:

$$\frac{\mathrm{d}}{\mathrm{d}z}\left(L_i\frac{\mathrm{d}\mu_i}{\mathrm{d}z}\right)=-R_i, i=1,\ldots,s$$
$$=-\nu_i v_f(1-\mathrm{e}^{-\phi}). \tag{1}$$

For the transport coefficient L_i a function of μ_i we may write this equation in the form:

$$\frac{\mathrm{d}^2}{\mathrm{d}z^2}\mu_i+\frac{L_i'(\mu_i)}{L_i}\left(\frac{\mathrm{d}\mu_i}{\mathrm{d}z}\right)^2=-\frac{\nu_i v_f}{L_i}(1-\mathrm{e}^{-\phi}). \tag{2}$$

If L_i were a function of more than one chemical potential, additional terms of the form of the second term on the left would be present. For sufficiently small chemical potential gradients, and for chemical potential ranges such that the ratios L'_i/L_i are small, we may neglect the second term on the left of Eq. (2) and form the normalized chemical affinity equation by multiplying by $-\nu_i/RT$ and summing over all the s species participating in the chemical reaction[2, 5]:

$$\frac{\mathrm{d}^2}{\mathrm{d}z^2}\phi=\lambda^2(1-\mathrm{e}^{-\phi}). \tag{3}$$

The quantity λ is a reciprocal characteristic reaction-diffusion length which depends on the (local) forward chemical reaction rate and the s transport coefficients L_i. As such it is therefore a function of the μ_i. One additional restriction is made here, and that is the approximation of λ as the first term of a Taylor series expansion about the mean chemical potentials $\bar{\mu}_i$ of the system. For this to be a useful zeroth approximation it is required both that the variation in the chemical potentials about their mean values be small, which is consistent with the small gradient approximation used above, and also that λ be a moderately weak function of the μ_i.

What this zeroth approximation means in terms of concentration and ordinary diffusion coefficients may be seen by considering a particular example, say the reaction $A+B=D$ where the forward rate is of the form $k_fC_AC_B$. We can identify the Onsager coefficients L_i in terms of the ordinary diffusion coefficients for ideal systems simply as $L_i=C_iD_i/RT$, and λ^2 becomes for this case:

$$\lambda^2=k_f\left(\frac{C_B}{D_B}\right)\left[\nu_A{}^2\cdot\frac{D_B}{D_A}+\nu_B{}^2\cdot\frac{C_A}{C_B}+\nu_D{}^2\cdot\frac{C_A}{C_D}\cdot\frac{D_B}{D_D}\right]. \tag{4}$$

Thus λ^2 is a "moderately" weak function of species concentration for those classes of systems for which D_B is an increasing function of concentration, D_B/D_A and C_A/C_B are essentially constant, and $C_AD_B/(C_DD_D)$ is either essentially constant or small relative to the other terms in the brackets. This last condition is normally fulfilled if deviations from equilibrium are moderately small and the value of the equilibrium constant is such that $C_A{}^e \ll C_D{}^e$.

The zeroth approximation to Eq. (3) is therefore written as:

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}\xi^2}=1-\mathrm{e}^{-\phi}, \tag{5}$$

where $\bar{\lambda}$ has been used as a scale factor on z such that $\xi=\bar{\lambda}z$. One may develop a solution of this nonlinear equation to any level of approximation desired by the procedure shown in the next section, but the restrictions specified above are such that the solution is applicable to the physical situation only for moderately small values of ϕ.

The asymmetric character of the film transfer with reaction problem is apparent in Eq. (5), for if the sign of the affinity is changed, say $\phi'=-\phi$, it is evident that the mathematical form of the equation is changed. The fundamental asymmetric character of the film transfer with reaction problem is preserved in this zeroth order approximation, and is reflected in the transfer flux computed from Eqs. (1) with the use of an approximate solution for ϕ from Eq. (5).

APPROXIMATE SOLUTION OF THE AFFINITY EQUATION

Approximations to the solution of Eq. (5) may be obtained by use of a power series expansion in ξ of the form:

$$\phi = a_0 + a_1\xi + a_2\xi^2 + a_3\xi^3 + \cdots. \tag{6}$$

Substitution of Eq. (6) into Eq. (5) and setting the coefficients of like powers in ξ equal to zero yields the following relations for the coefficients of the series (6):

$$a_0 = \text{arbitrary}$$
$$a_1 = \text{arbitrary}$$
$$a_2 = \tfrac{1}{2}(1 - e^{-a_0})$$
$$a_3 = \tfrac{1}{6}a_1 e^{-a_0}$$
$$a_4 = \tfrac{1}{12}e^{-a_0}(a_2 - \tfrac{1}{2}a_1^2)$$
$$a_5 = \tfrac{1}{20}e^{-a_0}(a_3 - a_1a_2 + \tfrac{1}{6}a_1^3)$$
$$a_6 = \tfrac{1}{30}e^{-a_0}(a_4 - a_1a_3 - \tfrac{1}{2}a_2^2 + \tfrac{1}{2}a_1^2a_2 - \tfrac{1}{24}a_1^4)$$
$$\vdots$$
$$a_{k+2} = \frac{-e^{-a_0}}{(k+2)(k+1)}\sum\left(\prod_{j=1}^{k}\frac{(-a_j)^{d_j}}{d_j!}\right). \tag{7}$$

The summation in the recursion relations (7) is taken over all non trivial non negative integer solution sets d_i of the equation:

$$\sum_{i=1}^{k} i d_i = k. \tag{8}$$

Each of the coefficients a_i in Eq. (6) is therefore a polynomial whose terms consist of certain products of the preceding coefficients. The affinity Eq. (5) is second order, and as such the solution contains two arbitrary constants of integration, which appear as a_0 and a_1. The other coefficients can be expressed in terms of these first two constants through the recurrsion relation, Eq. (7). However, the arbitrary constants of integration do not enter into the solution in a linear way as is the case in the general solutions of linear differential equations.

The form of the recursion relation, Eq. (7), is such that the series solution is not conveniently useful in general. However, for the physically interesting case of the affinity specified as zero on one boundary of a film, say $\phi = 0$ at $\xi = 0$, which corresponds to a quasi-equilibrium on that boundary, the coefficients a_0 and a_2 are zero, and the series, Eq. (6), becomes:

$$\phi = a_1 \sinh\xi - \sum_{i=1}^{\infty} a_1^{2i}U_i(\xi) + \sum_{i=1}^{\infty} a_1^{2i+1}F_i(\xi). \tag{9}$$

The functions $U_i(\xi)$ are even power series in ξ and the functions $F_i(\xi)$ are odd power series. Equation (9) is an infinite series of infinite series. The first function in each of the summations above is defined as follows:

$$U_1(\xi) = \sum_{n=1}^{\infty} b_n \frac{\xi^{2n}}{(2n)!} \tag{10}$$

where

$$b_1 = 0$$
$$b_n = 4b_{n-1} + 1 \tag{11}$$
$$F_1(\xi) = \sum_{k=1}^{\infty} c_k \frac{\xi^{2k+1}}{(2k+1)!} \tag{12}$$

where

$$c_1 = 0$$
$$c_k = c_{k-1} + \sum_{j=1}^{k-1}\frac{(2k-1)!\,b_j}{(2k-2j-1)!\,(2j)!} + \sum_{j=1}^{m_k}\frac{(2k-1)!}{n![(2j-1)!]^2(2k-4j+1)!} + \sum_{p_i}\frac{(2k-1)!}{p_1!\,p_2!\,p_3!} \tag{13}$$

where:

$$m_k = \begin{cases} k-1, & \text{if } k \text{ even} \\ k-2, & \text{if } k \text{ odd} \end{cases}$$

$$n = \begin{cases} 2, & \text{if } j \neq (k+1)/3 \\ 3, & \text{if } j = (k+1)/3. \end{cases}$$

The final summation in Eq. (13) is made over all the distinct, positive integer solutions of the equation

$$p_1+p_2+p_3=2k-1$$

for which all the p_i are odd. Numerical values of the first twenty five of the c_k are provided in the Appendix, as well as values of the functions $U_1(\xi)$ and $F_1(\xi)$ for a number of values of the argument ξ.

The zeroth, first, and second approximations to the solution of Eq. (5) for the boundary condition of vanishing ϕ at $\xi=0$ may therefore be written:

$$\phi \doteq a_1\sinh\xi - a_1{}^2U_1(\xi)+a_1{}^3F_1(\xi). \qquad (14)$$

The first term on the right corresponds to the solution of the linearized affinity equation whose characteristics are discussed in Ref.[2]. The terms $U_1(\xi)$ and $F_1(\xi)$ provide the higher order approximations, and are even and odd functions, respectively, as may be seen on referring to their definitions, Eqs. (10) and (12). Therefore, when the sign of the argument is changed in the terms on the right hand side of Eq. (14), the signs of terms one and three are changed, but the sign of the second term remains the same. Eq. (14) thus exhibits the asymmetric character of the nonlinear differential Eq. (5). Connected with this is the form in which the integration constant a_1 occurs in Eq. (14). A result of this form is that the shape of the affinity distribution is changed with the sign of the affinity specification on the boundary at $\xi=\xi_1$, say. This is a qualitative feature of the phenomenon of diffusion-reaction coupling that is lost in a linearized treatment of the problem. The effect of this characteristic on the flux is discussed below, for the case of the affinity distribution given by the approximate solution, Eq. (14). Higher order corrections to Eq. (14) can be developed from Eq. (9) if warranted in a particular application. The approximate solution, Eq. (14), is compared with the numerical integration of Eq. (5) in the Appendix, for representative values of $\phi(\xi_1)$ of interest here.

EFFECT OF REACTION ASYMMETRY ON THE FLUX

Consider the film shown in Fig. 1 where the diffusion species participate in a single reaction whose rate is given by the righthand side of Eq. (1). The net reaction rate R_i may be of arbitrary order. In this case the film is considered

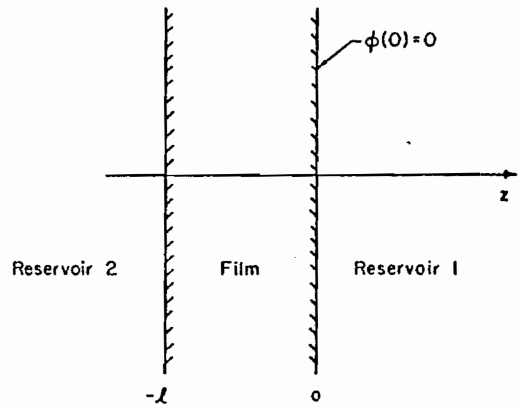

Fig. 1. Schematic representation of a film system.

semi-permeable in that only certain of the species are free to pass through the film boundary. This boundary value problem is similar to that treated in Ref.[2], the difference being that the affinity is specified on the one boundary at $\xi=0$ in this case. The results below can be extended to more general cases. The total flux through the film is given by:

$$N_T=\sum_{i=1}^{n} M_iJ_i = -\sum_{i=1}^{n} M_iL_i\frac{d\mu_i}{dz}. \qquad (15)$$

The chemical potential gradients $\mu'_i(z)$ for use in Eq. (15) are computed from the solution of the set of Eqs. (1), (2) and (5), subject to the boundary conditions:

at

$$\left.\begin{aligned} \xi=0,\quad \mu_i&=\mu_i(0)\\ \phi(0)&=0\\ \xi=-\xi_1,\quad \mu_i&=\mu_i(-\xi_1)\end{aligned}\right\}. \qquad (16)$$

Elimination of the function $(1-e^{-\phi})$ between the Eqs. (1) and (5), and writing the variables in normalized form yields:

$$\frac{d^2}{d\xi^2}[\theta_i + \alpha\phi] = 0 \tag{17}$$

at

$$\left.\begin{aligned} \xi = 0, \quad \theta_i &= 0 \\ \phi(0) &= 0 \\ \xi = -\xi_1, \quad \theta_i &= 1 \end{aligned}\right\}. \tag{18}$$

The solution of Eq. (17) subject to the conditions (18) is:

$$\theta_i = -\alpha\phi(\xi; a_1) - [1 + \alpha\phi(-\xi_1; a_1)]\frac{\xi}{\xi_1}. \tag{19}$$

The affinity distribution $\phi(\xi; a_1)$ for use in Eq. (19) is given by Eq. (14). The constant a_1 is not an independent constant under the conditions (18) as ϕ is defined in terms of a linear combination of the chemical potentials. The constant a_1 may be readily eliminated for the (special) case of only one species free to transfer through the boundary, say at $\xi = -\xi_1$, by forming the expression for the flux of species "i" from Eq. (19) and by use of:

$$\sum_{i=1}^{s} \frac{\nu_i J_i(-\xi_1)}{\bar{\lambda} R T L_i} = \phi'(-\xi_1; a_1). \tag{20}$$

For the case of only one species transferring through the boundary at $-\xi_1$, Eq. (20) reduces to:

$$\frac{\nu_1 J_1(-\xi_1)}{\bar{\lambda} R T L_1} = \phi'(-\xi_1; a_1). \tag{21}$$

Forming $J_1(-\xi_1)$ from Eq. (19), and putting the derivative of Eq. (14) into the result as well as into Eq. (21) yields the following two equations which can be solved for a_1;

$$W(-\xi_1) = [a_1 \cosh(-\xi_1) - a_1{}^2 U_1'(-\xi_1) + a_1{}^3 F_1'(-\xi_1)](\xi_1/\epsilon) \tag{22}$$

$$W(-\xi_1) = [1 + (\gamma^2/\epsilon)(a_1 \sinh(-\xi_1) - a_1{}^2 U_1(-\xi_1) + a_1{}^3 F_1(-\xi_1))]/(1 - \gamma^2). \tag{23}$$

$W(-\xi_1)$ is the flux of species "1" through the boundary at $-\xi_1$ normalized to the flux that would occur without reaction in the film. After elimination of a_1 between Eqs. (22) and (23) one notes that the flux W depends only on the two parameters, γ and ϵ for a given film thickness. The first of these parameters is a ratio of reciprocal reaction–diffusion lengths and depends only on the stoichiometry, the kinetics, and the phenomenological coefficients. γ is always less than unity as $\bar{\lambda}$ contains $\bar{\lambda}_1$. The second parameter ϵ is defined as:

$$\epsilon \equiv \nu_1 \Delta\mu_1/(RT) \tag{24}$$

and is a nondimensional driving force for the transfer. Hence, in contrast with the linearized treatment of this problem, the "flux per unit force" is not independent of the force. The flux (per unit force) based on the linearized analysis becomes:

$$W_l(-\xi_1) = [1 - \gamma^2(1 - \tanh \xi_1/\xi_1)]^{-1}, \tag{25}$$

and depends only on the parameter γ. This linearized result provides a sigmoidal shape in ξ_1 similar to that given earlier by Friedlander and Keller[2].

The asymmetric nature of the transfer due to the form of the Eqs. (22) and (23) is illustrated by the curves of Fig. 2, where the ratio $R_f \equiv$

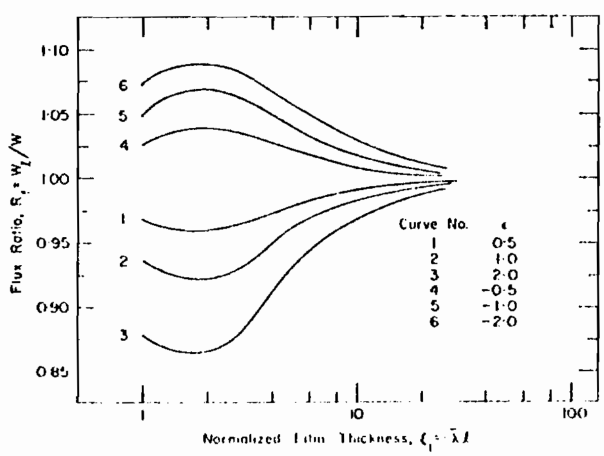

Fig. 2. Effect of asymmetry due to chemical reaction on the transfer.

$W_t(-\xi_1)/W(-\xi_1)$ is graphed for several values of the parameter ϵ for the case of $\gamma = 0{\cdot}9$. The deviation of the linearized result from the values shown increases with increasing $|\epsilon|$. It may be shown also that the deviation decreases as γ decreases. The extent of the deviations is not symmetric with change of sign (direction of transfer) of the normalized driving force ϵ. The extent of the agreement of the linearized result with the higher approximation result increases as the reduced film thickness ξ_1 increases for a given ϵ and γ; that is, as the system becomes diffusion controlling so that the reaction tends to proceed at equilibrium.

A QUASI STEADY CHEMICAL PUMP

The asymmetric character of a species flux that is augmented by a nonlinear chemical reaction suggests the phenomenon of "chemical pumping". Such a situation may exist in a primary system where a driving force in a contiguous reservoir, or secondary system, causes the reaction in the neighborhood of one boundary in the primary system to alternate first in one direction from equilibrium and then in the other. Schematically, the primary system may be represented as the region to the right of $\xi = -\xi_1$ in Fig. 1, and the secondary system the reservoir to the left of $-\xi_1$. The cycling of the chemical affinity at $-\xi_1^+$ may be brought about, for example, by external, forced, cycling in the composition of certain species in Reservoir 2 that are free to pass through the left film boundary and which also participate in the reaction taking place in the film. We seek the flux of species "1" through the semi-permeable boundary at $\xi = 0$.

A simple model of this situation may be developed in terms of the above results for the case of the system operating at quasi steady state. This requires that the forced cycling of the chemical affinity at $\xi = \xi_1$ occur with a period $\tau = 2\pi/\omega$ which is long compared with the characteristic transport time through the system $t_d = l^2/D_i$:

$$2\pi/\omega \gg l^2/D_i. \qquad (26)$$

For the case of only a single species passing through the boundary at $\xi = 0$, the flux may be expressed in terms of the gradient in chemical affinity:

$$\frac{\nu_1 J_1(0,t)}{\lambda RTL_1} = \phi'(0,t; a_1). \qquad (27)$$

The left hand side of Eq. (27) is a normalized flux which we call W'. In this notation and under quasi steady conditions such that ϕ' may be formed to good approximation from Eq. (14), Eq. (27) becomes:

$$W' \doteq a_1[\phi(-\xi_1, t)]. \qquad (28)$$

The net, normalized transfer per cycle of species "1" through the boundary at $\xi = 0$ under quasi steady conditions is therefore:

$$T_n \equiv \int_0^{2\pi/\omega} W'\,\mathrm{d}t \doteq \int_0^{2\pi/\omega} a_1[-\xi_1, t)]\,\mathrm{d}t. \qquad (29)$$

The integration "constant" $a_1[\phi(-\xi_1, t)]$ may be determined under quasi steady conditions by use of Eq. (14) with the specification of $\phi = \phi(-\xi_1, t)$ at $\xi = -\xi_1$, where $\phi(-\xi_1, t)$ is forced (externally) through a slow oscillation of the form, say:

$$\phi(-\xi_1, t) = \phi_0 \sin \omega t. \qquad (30)$$

The above procedure has been used to evaluate T_n and the results are provided in Fig. 3, where the ratio,

$$R_n = T_n / \int_0^{\pi/\omega} a_1[\phi(-\xi_1, t)]\,\mathrm{d}t,$$

is shown for the case of ϕ_0, the amplitude of the variation of the normalized affinity at $\xi = -\xi_1$, equal to one-half and to unity. R_n is the fraction to the molecules passing through the boundary at $\xi = 0$ during the first half of the cycle that fail to return during the second half. The negative sign of the ordinate of Fig. 3 indicates the net transfer is from Reservoir 1 to Reservoir 2 of Fig. 1. The results of Fig. 3 illustrate the fact that the extent of the pumping passes through a maximum as

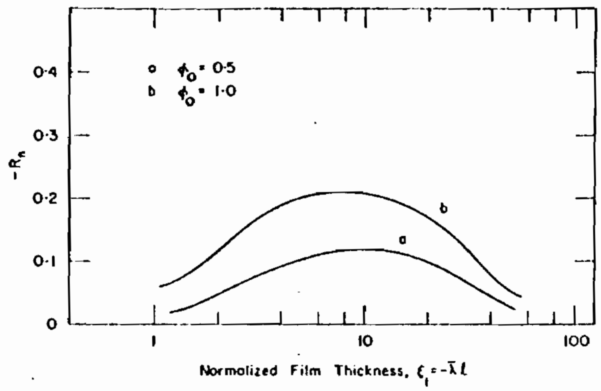

Fig. 3. Net transfer per cycle due to a sinusoidal variation of chemical affinity on one boundary of the film.

the normalized film thickness is increased, that the maximum lies in the range of $\xi_1(\equiv -\bar{\lambda}l)$ between eight and ten, and that the "pumping" vanishes as the normalized film thickness is increased.

In summary, an approximate solution to the nonlinear affinity equation has been developed which contains the asymmetric character of the equation itself. The result is that the extent of flux augmentation by nonlinear chemical reaction rate depends on the direction of displacement from equilibrium. Because of this a film has the property of acting as a chemical pump when coupled with an external driving force. It may be this property, in part, that is responsible for phenomena such as biological pumping that has been observed in certain living systems [6, 7].

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NOTATION

- A chemical affinity, $\equiv -\sum_{i=1}^{s} \nu_i\mu_i$
- a_i coefficients in the series, Eq. (6)
- b_n coefficients in the series, Eq. (10)
- c_n coefficients in the series, Eq. (12)
- C_i concentration of species i
- d_i roots of Eq. (8)
- D_i pseudo binary diffusion coefficients of species i
- F_1 function defined by Eq. (12)
- G_i diffusive flux without chemical reaction, $\equiv L_i\Delta\mu_i/l$
- J_i molar diffusion flux of species i in z-direction
- k_f reaction rate coefficient in the forward direction
- l film thickness
- L_i phenomenological transport coefficient of species i
- L_i' derivative of L_i with respect to μ_i
- M_i molecular weight of species i
- N_T total mass flux
- R gas constant
- R_i net molar reaction rate of species i
- R_f ratio of the flux based on linearized model to the flux computed by the higher approximations
- R_n fractional, molar transfer per cycle
- s number of components participating in the chemical reaction
- T absolute temperature
- T_n net, normalized transfer of species "1" per cycle
- t_d a characteristic, diffusive transport time
- U_1 function defined by Eq. (10)
- v reaction velocity
- v_f forward reaction velocity
- W normalized molar flux of species "1", $\equiv J_1/G_1$
- W_l normalized molar flux of species "1" based on linear model, $\equiv J_1^l/G_1$
- z coordinate variable

Greek symbols

- α parameter in Eq. (17), $\equiv \gamma^2/\epsilon$
- γ ratio of λ_1 to λ
- ϵ a characteristic, nondimensional driving force, defined by Eq. (24)
- θ_i normalized chemical potential of species i, $\equiv [\mu_i - \mu_i(0)]/\Delta\mu_i$
- $\bar{\lambda}_1$ $[v_f\nu_1^2/(RTL_1)]^{1/2}$
- λ reciprocal reaction–diffusion length $\equiv \left(\frac{v_f}{RT}\sum\frac{\nu_i^2}{L_i}\right)^{1/2}$
- $\bar{\lambda}$ λ evaluated under mean conditions
- μ_i chemical potential of species i
- ν_i stoichiometric coefficient of species i

ξ normalized coordinate variable, $= \lambda z$

τ period of normalized chemical affinity oscillation

ϕ normalized chemical affinity, $A/(RT)$

ω frequency of normalized chemical affinity oscillation

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APPENDIX

The coefficients in the function $F_1(\xi)$ are given by Eq. (13), the first seven of which may be written as follows:

$$c_1 = 0$$

$$c_2 = 1{\cdot}0$$

$$c_3 = c_2 + 5b_2 + 10$$

$$c_4 = c_3 + 7!\left[\frac{b_2}{4!3!} + \frac{b_3}{6!1!}\right] + 21$$

$$c_5 = c_4 + 9!\left[\frac{b_2}{4!5!} + \frac{b_3}{6!3!} + \frac{b_4}{8!1!}\right] + 9!\left[\frac{1}{2!7!} + \frac{1}{3!(3!)^2 3!}\right] + \frac{9!}{3!5!}$$

$$c_6 = c_5 + 11!\left[\frac{b_2}{4!7!} + \frac{b_3}{6!5!} + \frac{b_4}{8!3!} + \frac{b_5}{10!1!}\right] + \frac{11!}{2!}\left[\frac{1}{(1!)^2 9!} + \frac{1}{(3!)^2 5!} + \frac{1}{(5!)^2 1!}\right] + \frac{11!}{(3!7!)}$$

$$c_7 = c_6 + 13!\left[\frac{b_2}{4!9!} + \frac{b_3}{6!7!} + \frac{b_4}{8!5!} + \frac{b_5}{10!3!} + \frac{b_6}{12!1!}\right] + \frac{13!}{2!}\left[\frac{1}{(1!)^2 11!} + \frac{1}{(3!)^2 7!} + \frac{1}{(5!)^2 3!}\right] + \frac{13!}{1!}\left[\frac{1}{3!9!} + \frac{1}{5!7!}\right].$$

The numerical values of the first twenty-five c_k are given in Table 1 to ten significant figures.

The series defining the functions $U_1(\xi)$ and $F_1(\xi)$, Eqs. (10) and (12), converge relatively slowly for moderately large values of the argument. Values of these functions and of their derivatives are given in Table 2.

In order to provide an estimate of the upper limit of ϕ over which Eq. (14) may be considered an adequate solution of Eq. (5), Eq. (14) is compared in Table 3 with a numerical integration of Eq. (5) for a boundary value problem of the form:

$$\frac{d^2\phi}{d\xi^2} = 1 - e^{-\phi},$$

$$\text{B.C. } \phi(0) = 0; \text{ at } \xi = \xi_1, \phi = \phi(\xi_1)$$

for representative values of ξ_1 and of $\phi(\xi_1)$.

Table 1. Coefficients in the function $F_1(\xi)$

k	c_k	c_{k+1}/c_k
1	0·0	∞
2	$0{\cdot}1000000000 \times 10^{1}$	16·0
3	$0{\cdot}1600000000 \times 10^{2}$	11·06250000
4	$0{\cdot}1770000000 \times 10^{3}$	9·78531073
5	$0{\cdot}1732000000 \times 10^{4}$	9·32621247
6	$0{\cdot}1615300000 \times 10^{5}$	9·14059308
7	$0{\cdot}1476480000 \times 10^{6}$	9·06161275
8	$0{\cdot}1337929000 \times 10^{7}$	9·02720847
9	$0{\cdot}1207776400 \times 10^{8}$	9·01205720
10	$0{\cdot}1088455000 \times 10^{9}$	9·00535236
11	$0{\cdot}9801920800 \times 10^{9}$	9·00237727
12	$0{\cdot}8824058900 \times 10^{10}$	9·00105630
13	$0{\cdot}7942585100 \times 10^{11}$	9·00046936
14	$0{\cdot}7148699381 \times 10^{12}$	9·00020861
15	$0{\cdot}6433978573 \times 10^{13}$	9·00009272
16	$0{\cdot}5790640368 \times 10^{14}$	9·00004120
17	$0{\cdot}5211600192 \times 10^{15}$	9·00001832
18	$0{\cdot}4696449718 \times 10^{16}$	9·00000813
19	$0{\cdot}4221408564 \times 10^{17}$	9·00000362
20	$0{\cdot}3799269234 \times 10^{18}$	9·00000161
21	$0{\cdot}3419342922 \times 10^{19}$	9·00000071
22	$0{\cdot}3077408874 \times 10^{20}$	9·00000032
23	$0{\cdot}2769668084 \times 10^{21}$	9·00000014
24	$0{\cdot}2492701315 \times 10^{22}$	9·00000008
25	$0{\cdot}2243431199 \times 10^{23}$	

Table 2. Values of $U_1(\xi)$, $F_1(\xi)$, and of their derivatives

ξ	$U_1(\xi)$	$U_1'(\xi)$	$F_1(\xi)$	$F_1'(\xi)$
0	0·0	0·0	0·0	0·0
1	$0·4916 \times 10^{-1}$	0·2127	$0·1204 \times 10^{-1}$	$0·6879 \times 10^{-1}$
2	$0·1272 \times 10^{1}$	$0·3339 \times 10^{1}$	$0·1037 \times 10^{1}$	$0·3872 \times 10^{1}$
3	$0·1370 \times 10^{2}$	$0·3028 \times 10^{2}$	$0·3264 \times 10^{2}$	$0·1063 \times 10^{3}$
4	$0·1154 \times 10^{3}$	$0·2393 \times 10^{3}$	$0·7705 \times 10^{3}$	$0·2384 \times 10^{4}$
5	$0·8933 \times 10^{3}$	$0·1811 \times 10^{4}$	$0·1643 \times 10^{5}$	$0·4988 \times 10^{5}$
6	$0·6714 \times 10^{4}$	$0·1350 \times 10^{5}$	$0·3375 \times 10^{6}$	$0·1017 \times 10^{7}$
7	$0·4993 \times 10^{5}$	$0·1000 \times 10^{6}$	$0·6836 \times 10^{7}$	$0·2054 \times 10^{8}$
8	$0·3698 \times 10^{6}$	$0·7400 \times 10^{6}$	$0·1377 \times 10^{9}$	$0·4134 \times 10^{9}$
9	$0·2734 \times 10^{7}$	$0·5470 \times 10^{7}$	$0·2769 \times 10^{10}$	$0·8310 \times 10^{10}$
10	$0·2021 \times 10^{8}$	$0·4043 \times 10^{8}$	$0·5565 \times 10^{11}$	$0·1669 \times 10^{12}$
12	$0·1104 \times 10^{10}$	$0·2207 \times 10^{10}$	$0·2245 \times 10^{14}$	$0·6736 \times 10^{14}$
14	$0·6026 \times 10^{11}$	$0·1205 \times 10^{12}$	$0·9059 \times 10^{16}$	$0·2718 \times 10^{17}$
16	$0·3290 \times 10^{13}$	$0·6580 \times 10^{13}$	$0·3655 \times 10^{19}$	$0·1096 \times 10^{20}$
18	$0·1796 \times 10^{15}$	$0·3593 \times 10^{15}$	$0·1474 \times 10^{22}$	$0·4422 \times 10^{22}$
20	$0·9808 \times 10^{16}$	$0·1962 \times 10^{17}$	$0·5928 \times 10^{24}$	$0·1776 \times 10^{25}$

Table 3. Comparison of exact and approximate solutions of the affinity equation

ξ	$\phi(10) = 0·1$			$\phi(10) = 1·0$		
	Numerical sol'n of Eq. (5)	Eq. (14)	% Error	Numerical sol'n of Eq. (5)	Eq. (14)	% Error
0	0·0	0·0	0·0	0·0	0·0	0·0
1	$1·086 \times 10^{-5}$	$1·085 \times 10^{-5}$	−0·092	$1·261 \times 10^{-4}$	$1·237 \times 10^{-4}$	−1·9
2	$3·351 \times 10^{-5}$	$3·348 \times 10^{-5}$	−0·089	$3·891 \times 10^{-4}$	$3·817 \times 10^{-4}$	−1·9
3	$9·255 \times 10^{-5}$	$9·249 \times 10^{-5}$	−0·065	$1·075 \times 10^{-3}$	$1·054 \times 10^{-3}$	−1·95
4	$2·521 \times 10^{-4}$	$2·519 \times 10^{-4}$	−0·079	$2·927 \times 10^{-3}$	$2·871 \times 10^{-3}$	−1·91
5	$6·854 \times 10^{-4}$	$6·850 \times 10^{-4}$	−0·058	$7·950 \times 10^{-3}$	$7·799 \times 10^{-3}$	−1·9
6	$1·863 \times 10^{-3}$	$1·862 \times 10^{-3}$	−0·054	$2·156 \times 10^{-2}$	$2·115 \times 10^{-2}$	−1·9
7	$5·061 \times 10^{-3}$	$5·058 \times 10^{-3}$	−0·059	$5·826 \times 10^{-2}$	$5·716 \times 10^{-2}$	−1·89
8	$1·374 \times 10^{-2}$	$1·373 \times 10^{-2}$	−0·073	$1·558 \times 10^{-1}$	$1·529 \times 10^{-1}$	−1·86
9	$3·719 \times 10^{-2}$	$3·717 \times 10^{-2}$	−0·054	$4·062 \times 10^{-1}$	$3·993 \times 10^{-1}$	−1·7
10	0·100	0·100	0·0	1·000	1·000	0·0

Résumé—On montre que la propriété asymétrique de l'équation non linéaire d'affinité chimique se traduit en un effet d'augmentation du flux de diffusivité, dû au taux de réaction chimique non linéaire, qui dépend de la direction dans laquelle l'équation est déplacée par rapport à l'équilibre. C'est ainsi qu'un film, lié à une force d'entraînement externe, peut agir en tant que "pompe chimique". On suggère un modèle simple pour une pompe quasi stable de ce genre qui fournit un pompage maximum quand l'épaisseur du film est de huit à dix fois la longueur caractéristique moyenne de la réaction de diffusion.

Zusammenfassung—Es wird gezeigt, dass die asymmetrische Eigenschaft der nichtlinearen, chemischen Affinitätsgleichung zu einer diffusiven Strömungserhöhungswirkung führt, und zwar infolge der nichtlinearen chemischen Reaktionsgeschwindigkeit, die von der Richtung, in welcher die Reaktion aus dem Gleichgewicht verschoben, wird abhängig ist. Infolgedessen kann ein Film in Verbindung mit einer äusseren Triebkraft als "chemische Pumpe" wirken. Es wird ein einfaches Modell vorgeschlagen für eine quasi-stetige Pumpe dieser Art, die maximale Pumpwirkung liefert wenn die Filmdicke im Bereich der acht-bis zehnfachen durch-schnittlichen charakteristischen Diffusionsreaktionslänge liegt.