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Transient Multicomponent Diffusion with Heterogeneous Reaction

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The problem of transient multicomponent diffusion of an arbitrary number of components in one-dimension with heterogeneous reaction has been solved exactly by means of the Laplace transform. Linearized expressions for the diffusion and reaction were used. Numerical evaluations of the solution are given and a comparison made with results derived by use of an effective diffusivity.

The momentum and continuity equations for multicomponent mass transfer with chemical reaction in an isothermal system are coupled and nonlinear. These equations can be simplified considerably if the concentration variations throughout the system are small, if the concentrations are not too far from chemical equilibrium, and if there is no volume change with reaction or mixing. Under these conditions the flux of any component can be expressed as a linear combination of the concentration gradients of each species (*2*, *5* to *9*), the reaction rate expressions can be linearized (*10*), and the momentum equation can be solved independently of the continuity equations for each species (*6*). The problem thus reduces to solving a set of coupled, linear differential equations representing continuity of each component. The approximations involved in a linearization of the transport equations (*6* to *8*) and of the reaction rate expressions (*10*) have been clearly discussed in detail elsewhere.

When no chemical reaction is taking place, and when the concentration or flux of each component is known on the boundaries, the problem may be resolved by a rotation of the coordinate axes, which uncouples the continuity equations (*6* to *8*). If the equations are doubly coupled, this rotation will not in general uncouple the set. This double coupling may occur in the volume, as by diffusion and homogeneous reaction, or in the volume and on the boundaries, as by diffusion and either heterogeneous reaction or transport between two phases. It would be fortuitous if one rotation would uncouple such a system, and this occurs only in very special circumstances as pointed out by Toor (*9*).

In general, systems which exhibit dual coupling will have to be treated numerically or approximately. However, in some special geometries transient coupled problems can be solved exactly, and these solutions will lead to an understanding of the characteristics of more complicated problems. Toor has obtained an exact solution to the problem of transient multicomponent diffusion with homogeneous chemical reaction in a finite one-dimensional region (*9*). In this work, transient multicomponent diffusion with heterogeneous reaction will be reported. The geometry chosen was the simplest possible, namely, a stagnant film.

ANALYSIS

Consider multicomponent diffusion of $N + 1$ components through a film with heterogeneous reaction taking place. The system is initially at steady state with a mole fraction distribution (f), where the components of (f) are the N independent mole fractions and each is a function of position y. At time zero the mole fractions at the edge of the film are changed to new values, and the system is allowed to approach a new steady state. It is assumed that the system is not too far removed from equilibrium and that the concentration gradients are small so that the linearized equations may be used. Furthermore there is no volume change on reaction or mixing.

The equation governing this system is (9)

$$\frac{\partial(w)}{\partial\tau} = [\Lambda]\frac{\partial^2(w)}{\partial y^2} \tag{1}$$

where $[\Lambda] = [A]^{-1}[D][A]$, $[D]$ is the matrix of dimensionless diffusivities, and $[A]$ is the matrix of eigenvectors of $[D]$. The vector (w) is given by

$$(w) = [A]^{-1}(z) \tag{2}$$

where (z) is the mole fraction deviation from the initial steady state; that is

$$(z) = (x) - (f) \tag{3}$$

The matrix $[\Lambda]$ is diagonal. The initial and boundary conditions are

$$(w) = (0) \qquad \tau = 0 \tag{4a}$$

$$(w) = [A]^{-1}(z^o) = (w^o) \qquad y = 0 \tag{4b}$$

$$\frac{\partial(w)}{\partial y} + [B](w) = (0) \qquad y = 1 \tag{4c}$$

where $[B] = [A]^{-1}[K][A]$, $[K] = [D]^{-1}[K^*]$, and $[K^*]$ is the matrix of dimensionless reaction rate coefficients. The matrix $[B]$ is not diagonal. The Laplace transform of (1) yields

$$s(\overline{w}) = [\Lambda]\frac{d^2(\overline{w})}{dy^2} \tag{5}$$

with boundary conditions

$$(\overline{w}) = \frac{(w^o)}{s} \qquad y = 0 \tag{6a}$$

$$\frac{d(\overline{w})}{dy} + [B](\overline{w}) = 0 \qquad y = 1 \tag{6b}$$

The solution to (5) is

$$(\overline{w}) = \left[\sinh\sqrt{\frac{s}{\lambda}}\,y\right](a) + \left[\cosh\sqrt{\frac{s}{\lambda}}\,y\right](b) \tag{7}$$

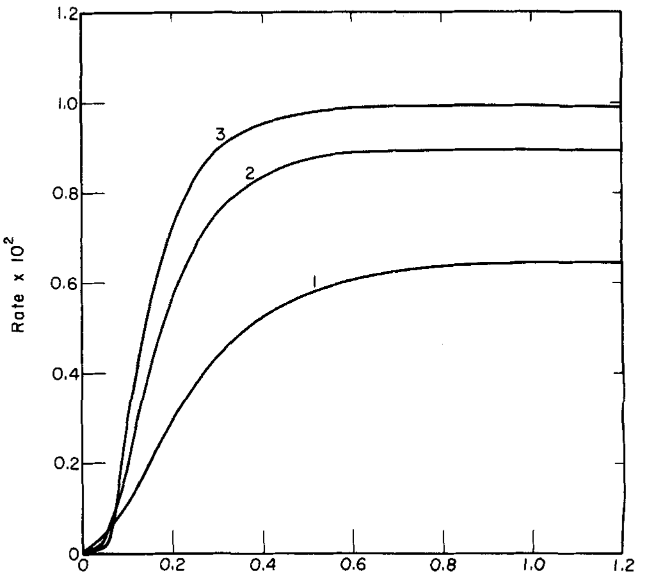

Fig. 1. Dimensionless reaction rate, hydrogenation of ethylene. Average mole fractions 0.2, 0.6, and 0.2 for hydrogen, ethylene, and ethane. (1) $K_{11}^* = 1.87$, $K_{12}^* = 0$, $K_{21}^* = -1.87$, $K_{22}^* = 0$. (2) $K_{11}^* = 9.35$, $K_{12}^* = 0$, $K_{21}^* = -9.35$, $K_{22}^* = 0$. (3) $K_{11}^* = \infty$, $K_{12}^* = 0$, $K_{21}^* = -\infty$, $K_{22}^* = 0$.

where $\left[\sinh\sqrt{\frac{s}{\lambda}}\,y\right]$ and $\left[\cosh\sqrt{\frac{s}{\lambda}}\,y\right]$ are diagonal matrices given by

$$\left[\sinh\sqrt{\frac{s}{\lambda}}\,y\right] = \begin{bmatrix} \sinh\sqrt{\frac{s}{\lambda_1}}\,y & & \\ & \sinh\sqrt{\frac{s}{\lambda_2}}\,y & \\ & & \ddots \end{bmatrix} \tag{8}$$

and similarly for $\left[\cosh\sqrt{\frac{s}{\lambda}}\,y\right]$. (a) and (b) are column vectors of arbitrary constants which will be determined from the boundary conditions. From (6a) the vector (b) is found to be

$$(b) = \frac{1}{s}(w^o) \tag{9}$$

Substituting (7) and (9) into (6b) one gets

$$[C](a) = -\frac{1}{s}(d) \tag{10}$$

where

$$[C] = \left[\sqrt{\frac{s}{\lambda}}\cosh\sqrt{\frac{s}{\lambda}}\right] + [B]\left[\sinh\sqrt{\frac{s}{\lambda}}\right] \tag{11}$$

and

$$(d) = \left[\sqrt{\frac{s}{\lambda}}\sinh\sqrt{\frac{s}{\lambda}}\right](w^o) + [B]\left[\cosh\sqrt{\frac{s}{\lambda}}\right](w^o) \tag{12}$$

The components of the vector (a) may now be determined from (10). Defining $[C^r]$ as the matrix derived from $[C]$ by replacing its r^{th} column by (d), and $|C^r|$ as the determinant of $[C^r]$, one obtains by Cramer's rule

$$(a) = \frac{-(\,|C^i|\,)}{s\,|C|} \tag{13}$$

In (13), $(\,|C^i|\,)$ is a column vector whose i^{th} component is given by the determinants $|C^i|$. The solution for $(\overline{w})$ is therefore given by (7), (9), and (13). $(\overline{w})$ is therefore given as the inverse of $(\overline{w})$, or

$$(w) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}\left\{\frac{-\left[\sinh\sqrt{\frac{s}{\lambda}}\,y\right](\,|C^i|\,)}{s\,|C|} + \frac{1}{s}\left[\cosh\sqrt{\frac{s}{\lambda}}\,y\right](w^o)\right\}e^{s\tau}\,ds \tag{14}$$

In order to evaluate (14) it will first be shown that there are no branch points. Each term of the determinant $|C|$ is an odd function of $s^{1/2}$. $|C|$ will therefore be odd or even in $s^{1/2}$ as N is odd or even. On the other hand, $|C^i|$ is formed by replacing one odd column by an even column. The ratio of $|C^i|$ to $|C|$ will therefore always be an odd function of $s^{1/2}$. This multiplied by $\left[\sinh \sqrt{\frac{s}{\lambda}}\, y\right]$ will be an even function of $s^{1/2}$, and the entire first term in brackets has no branch point. The second term in brackets is easily seen to have no branch points, and (14) may be evaluated by summing the residues. The vector (w) is therefore given by

$$(w) = (w^o) + \sum_{n=0}^{\infty} \lim_{\eta \to \eta_n} \frac{\eta^2 - \eta_n{}^2}{\eta^2} \, \frac{(\sin \eta \beta_i y \, |E^i| \,)}{|E|} \, e^{-\eta^2 t} \tag{15}$$

where

$$\eta = (-s)^{1/2}, \qquad \beta_i = (\lambda_i)^{-1/2}$$
$$[E] = [\eta\beta \cos \tau\beta] + [B] \; [\sin \eta\beta] \tag{16}$$

and $[E^r]$ is the matrix derived from $[E]$ by replacing the r^{th} column by

$$(e) = [\eta\beta \sin \eta\beta] \; (w^o) - [B] \, [\cos \eta\beta] \; (w^o) \tag{17}$$

The roots η_n are given by the zeros of $|E|$ for $n \geqq 1$. There is also a root at $\eta = 0$.

Consider first the root $\eta_o = 0$. The determinant $|E|$ has an N^{th} order zero at $\eta = 0$, since each term in $|E|$ goes to zero. $|E^i|$ has an $N - 1^{\text{th}}$ order zero, since one column of $|E|$ has been replaced by a nonzero quantity. Since $|E^i|$ is multiplied by $\sin \eta\beta_i y$, both the numerator and denominator have N^{th} order zeroes. Application of L'Hospital's rule N times gives the residue at $\eta_o = 0$ as

$$\frac{y \, (\, |G^i| \,)}{|G|} \tag{18}$$

where

$$[G] = [B] + [I] \tag{19}$$

and $[G^i]$ is $[G]$ with the i^{th} column replaced by $[B] \; (w^o)$.

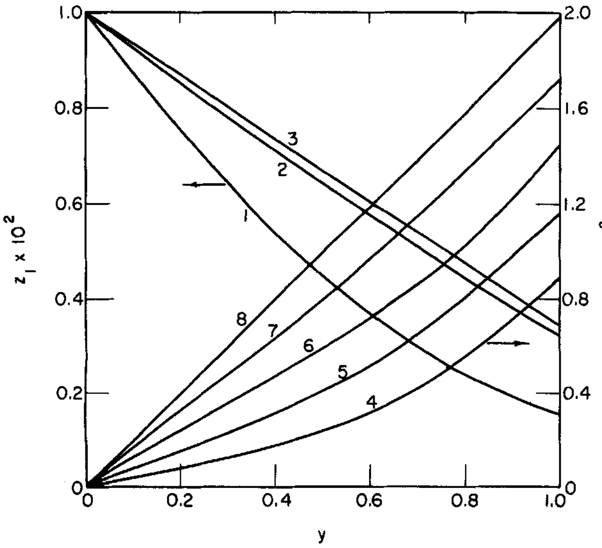

Fig. 2. Mole fraction deviation from steady state, hydrogenation of ethylene. Average mole fractions 0.2, 0.6, and 0.2 for hydrogen, ethylene, and ethane. $K_{11}{}^* = 1.87$, $K_{12}{}^* = 0$, $K_{21}{}^* = -1.87$, $K_{22}{}^* = 0$. z_1 and z_2 represent hydrogen and ethane. *(1)* z_1; $\tau = 0.2$. *(2)* z_1; $\tau = 0.6$. *(3)* z_1; $\tau = 1.0$. *(4)* z_2; $\tau = 1.0$. *(5)* z_2; $\tau = 1.4$. *(6)* z_2; $\tau = 2.0$. *(7)* z_2; $\tau = 3.0$. *(8)* z_2; $\tau = 6.0$.

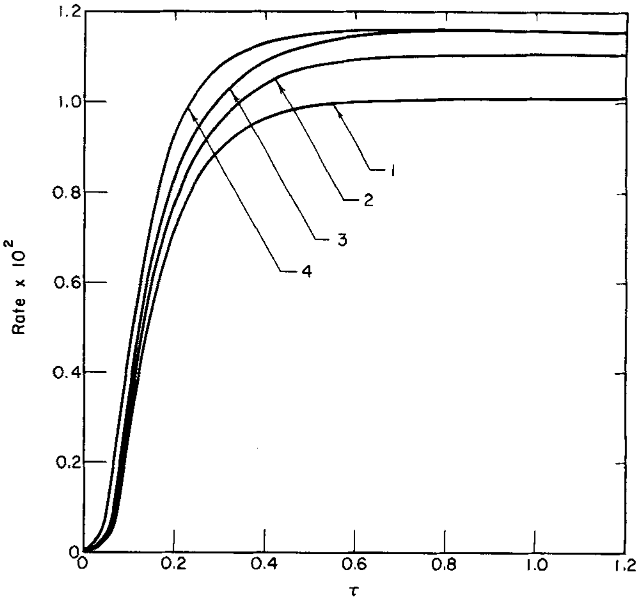

Fig. 3. Dimensionless reaction rate for diffusion-controlled catalytic cracking 1 → 2 + 3. *(1)* $\mathcal{D}_{23}/\mathcal{D}_{12} = 1.5$; $\mathcal{D}_{23}/\mathcal{D}_{13} = 2$. *(2)* $\mathcal{D}_{23}/\mathcal{D}_{12} = 1.5$; $\mathcal{D}_{23}/\mathcal{D}_{13} = 6$. *(3)* $\mathcal{D}_{23}/\mathcal{D}_{12} = 1.5$; $\mathcal{D}_{23}/\mathcal{D}_{13} = 10$. *(4)*. $D_{\text{eff}} = 0.01157$.

Since the other roots of $|E|$ are simple, the residues are easily determined, and (w) is found to be

$$(w) = (w^o) - \frac{y \, (\, |G^i| \,)}{|G|} + \sum_{n=1}^{\infty} \frac{2}{\eta_n} \, \frac{(\sin \eta_n \beta_i y \, |E^i| \,) \, e^{-\eta_n{}^2 \tau}}{\sum\limits_{j=1}^{N} |j_E|} \tag{20}$$

The determinant $|j_E|$ is obtained from $|E|$ by differentiating the j^{th} column with respect to η. The vector (z), which is the deviation of the mole fractions from the initial condition, is given as

$$(z) = [A] \; (w) \tag{21}$$

where $[A]$ is known and (w) is given by (20). The first two terms of (20) are the steady state solution, and the third is the transient part.

The rate of reaction with respect to the initial rate is equal to the flux at $y = 1$ with respect to the initial flux

$$(R') = -c \, [D'] \, \frac{\partial(z)}{\partial y'} \bigg|_{y'=\delta}$$

or, in dimensionless terms

$$(R) = - \, [D] \, \frac{\partial(z)}{\partial y} \bigg|_{y=1}$$

From (20) and (21), there is

$$(R) = [D] \, [A] \, \frac{(\, |G^i| \,)}{|G|} - [D] \, [A] \sum_{n=1}^{\infty} \frac{2 \, (\beta_i \cos \eta_n \beta_i \, |E^i| \,) \, e^{-\eta_n{}^2 \tau}}{\sum\limits_{j=1}^{N} \; |j_E|} \tag{22}$$

DISCUSSION

The solution given by (20), (21), and (22) holds for an arbitrary number of components. If some of these species are inert, zero entries appear in the matrix $[K^*]$; the solution still holds.

The vectors (z) and (R), which represent the deviation of mole fraction and reaction rate from the initial steady state, are zero for $\tau = 0$ and progress to a new steady state. Because of the coupled nature of the equations there may be maxima or minima in these curves.

Expressions (20), (21), and (22) are evaluated for the ternary reacting system:

$$H_2 + C_2H_4 \rightarrow C_2H_6$$

Jenkins and Rideal (*4*) give rate data for the reaction on a nickel catalyst. Below 160°C. the rate is first order in hydrogen and independent of ethylene and ethane concentrations. From their data on reaction rate and activation energy (10.2 kcal./mole) the reaction rate constant is found to be 1.92 cm./sec. at 150°C.; this value was used in the calculations. The components of the diffusivity matrix $[D']$ are given by expressions of the form

$$D'_{12} = \frac{x_1\mathcal{D}_{23}\,[\mathcal{D}_{31} - \mathcal{D}_{12}]}{x_1\mathcal{D}_{23} + x_2\mathcal{D}_{13} + x_3\mathcal{D}_{12}}$$

with similar expressions for the other components (*1*). The $\mathcal{D}$ are the binary diffusivities, and the mole fractions x are average mole fractions in the system. The subscripts 1, 2, and 3 refer to hydrogen, ethane, and ethylene, respectively. Results are presented here for $x_1 = 0.2$, $x_2 = 0.2$, and $x_3 = 0.6$. It is noted that it is necessary to neglect the volume change of reaction in applying the analytical solution to this reaction. The dimensionless reaction rate matrix $[K^*]$ is varied by changing the pressure P or the film thickness δ. The dimensionless surface reaction rate deviation from initial steady state is presented in Figure 1 as a function of dimensionless time. The mole fraction perturbation at the edge of the film is $z_1 = 0.01$, $z_2 = 0.0$. The lower curve ($K_1^* = 1.87$) represents, for example, $P = 5$ atm., $\delta = 0.2$ cm. or $P = 1$ atm., $\delta = 1.0$ cm. Each of the three curves passes through a maximum before reaching steady state, but this maximum is too small to be seen graphically. The relative maximum increases with increasing dimensionless rate constant. The mole fraction deviations from initial steady state are presented in Figure 2 with parameter τ.

Diffusion controlled catalytic cracking, for which the steady state rates have been determined (3), is now considered. The parameters chosen correspond to values used in Figure 4 of reference 3. The binary diffusivity ratio $\mathcal{D}_{23}/\mathcal{D}_{12}$ is held at 1.5, while the ratio $\mathcal{D}_{23}/\mathcal{D}_{13}$ is 2, 6, and 10 for the three lowest curves with the rate increasing with increasing ratio. The reaction rate was also calculated by using effective diffusivities, and that corresponding to the ratio $\mathcal{D}_{23}/\mathcal{D}_{13} = 10$ is shown in Figure 3. It is noted that employing the effective diffusivity results in a faster approach to the steady state; the steady state is, however, the same.

From the above analytical solution for transient multicomponent diffusion of an arbitrary number of components with heterogeneous reaction, it is seen that considerable error can be introduced by the use of an effective diffusivity. The solution also gives some indication of the effects which will be found in other two-dimensional systems in which the second independent variable is another spacial variable rather than time.

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NOTATION

(a) = vector of constants
$[A]$ = matrix of eigenvectors of $[D]$
(b) = vector of constants
$[B]$ = $[A]^{-1}\,[K][A]$
c = molar concentration, moles/cc.
$[C]$ defined by Equation (15)
$[C^r]$ = matrix derived from $[C]$ by replacing the r^{th} column by (d)
(d) defined by Equation (16)
$[D]$ = matrix of dimensionless diffusivities = $[D']/D'_{11}$
$[D']$ = matrix of diffusivities, sq.cm./sec.
$\mathcal{D}$ = binary diffusivity, sq.cm./sec.
(e) defined by Equation (21)
$[E]$ defined by Equation (20)
$[E^r]$ = matrix derived from $[E]$ by replacing the r^{th} column by (e)
(f) = vector of initial steady state mole fractions
$[G]$ defined by Equation (23)
$[G^i]$ = matrix derived from $[G]$ by replacing the i^{th} column by $[B]$ (w^o)
$[K]$ = $[D]^{-1}\,[K^*]$
$[K^*]$ = matrix of dimensionless reaction rate constants = $[K']\,\delta/D'_{11}$
$[K']$ = reaction rate constant matrix, cm./sec.
(R') = reaction rate vector, moles/(sec.)(sq.cm.)
(R) = dimensionless rate vector = $(R')\delta/c\,D'_{11}$
s = Laplace transform variable
(w) = $[A]^{-1}\,(z)$
(w^o) = $[A]^{-1}\,(z^o)$
(x) = vector of mole fractions
(x^o) = (x) evaluated at $y = 0$
y' = distance from edge of film, cm.
y = dimensionless position = y'/δ
(z) = $(x) - (f)$
(z^o) = $(x^o) - [f\,(0)]$

Greek Letters

β = $\lambda^{-1/2}$
δ = film thickness, cm.
η = $\{-s\}^{1/2}$
λ = component of $[\Lambda]$
$[\Lambda]$ = $[A]^{-1}\,[D][A]$
τ = dimensionless time = $\tau' D'_{11}/\delta^2$
τ' = time, sec.

Superscript

— = Laplace-transformed quantity

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