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STUDIES OF MASS DIFFUSION

WITH CHEMICAL REACTION

Part I   Stagnant medium unsteady reactants' dis-
          tributions

Part II   Steady distribution finite width streams
          (Graetz)

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TIME DEPENDENT MASS-TRANSFER WITH NON-LINEAR

.CHEMICAL REACTION

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ABSTRACT

In this work the author presents two analyses of time dependent processes in which diffusion and non-linear reaction take place simultaneously. In the first case attention is focused on the distribution of a single reactant in a stagnant medium when the reaction rate is proportional to its concentration squared. In the second case there are two reactants and the reaction rate is proportional to the product of the concentrations. The analyses are carried out assuming that the space variations of the initial distributions and the diffusivities are large compared with the initial average concentrations and reaction constants. Under these circumstances, initially most of the changes in the distribution are due to diffusion. However, eventually the processes become reaction dominated. The two distinct behaviors are represented by corresponding asymptotic expansions which are matched in the usual manner.

The processes under consideration are assumed to take place in unbounded containers yet the initial concentrations are taken to have non-zero space average. The residual amount of reactant in the single component case is found to be inversely proportional to the time elapsed since the beginning of the process. The decay of a binary process is similar provided the supplied quantities of reactants are well proportioned. If there is a disproportion the decay is exponential rather than algebraic. In all events at a late stage the residual amounts are independent of the diffusivity.

INTRODUCTION

This work contains analytical solutions which represent the inter-
play between mass-diffusion and concentration-decay due to non-linear
reaction. In the first case treated here, hereafter designated by
(i), the author obtains the space and time dependence of the concen-
tration of a single component in a stagnant medium. Reaction is assumed
to be proportional to the square of the concentration. For the binary
system studied in case (ii) the reaction rate is taken to be proportional
to the product of the concentrations of the two reactants. Since attention
is focused on the relationship between diffusion and chemical reaction,
the author avoids, as much as possible, discussions of the intricacies
of the former mechanism. The complications of boundary-conditions and wall
effects are circumvented by assuming that the processes take place in
unbounded containers and that at infinity the concentrations are finite.
Since engineering practice requires an efficient use of reactors, the
amounts of reactants supplied are taken to be correspondingly large.
Accordingly, the initial concentrations of solutes are assumed to have non-
zero space averages. It is further assumed that these initial distribu-
tions are either spherically symmetric or one-dimensional and symmetric
with respect to the origin. Hopefully, it will become apparent that by
overcoming algebraic rather than fundamental difficulties the proposed
analyses could be applied to more complicated cases.

In view of the non-linear nature of the reaction rate the absorption
of the solutes is very fast wherever the concentrations are high. Therefore,
not only the diffusion mechanism but the reaction too, tend to supress the
peaks in the mass-distribution profiles. Hence, when the combined

diffusion and reaction processes have been in progress for a long time
the solutes are distributed fairly evenly throughout the container(s).
At this stage diffusion plays a minor role and the processes are domin-
ated by the effect of the reaction. It follows that the diffusion can
play a major role only at an early stage in the processes and only if
the initial concentrations are sufficiently uneven. Interest in such
cases is not only theoretical. These cases resemble those encountered
in practice when reactants are poured into a container but only a limited
effort is made to spread them evenly.

A measure of the initial relative rapidity of the reaction, as
compared with that of the diffusion, is given by a non-dimensional
parameter ε. As explained, ε is assumed to be small. This assumption
makes it possible to employ ε as a parameter in the singular perturbation
method, which is applied to the problems at hand. A power series in ε
represents the initial, 'diffusion dominated' stage of the process. It
is matched with the large time expansion which characterizes the 'reaction
dominated' stage. In that sense the author adheres to the acceptable
notion[1] that in the processes under discussion the chemicals "first
diffuse and then react". Evidently Pearson[2] was the first to point out
the correspondence between the two distinct behaviors and suitably matched
asymptotic series. By applying this method to the case at hand both useful
and instructive results are obtained. Of these the more important ones are
the apparent limited overall influence of the diffusivity and the sensi-
tivity of the binary process to disproportion in the amounts of reactants
supplied.

Toor[3] and others have shown that for case (ii) numerous significant
results can be obtained by going through much simpler calculations. However,

that shortcut is useful when the diffusivities are equal and the reaction rate is very fast, i.e. in the limiting case of $\varepsilon \to \infty$. Here ε is taken to be arbitrary but small. Again although to simplify the calculation here too the diffusivities are assumed to be equal - the analysis clearly holds when they are not. Consequently, the method and approach proposed complement those mentioned.

SINGLE COMPONENT; SECOND ORDER REACTION

Let the concentration of solute $\bar{c}$ be governed by

$$\partial \bar{c}/\partial \bar{t} + k\,\bar{c}^2 = \kappa\,\partial^2 \bar{c}/\partial \bar{x}^2 \qquad (1)$$

where $\bar{x}$ is a cartesian coordinate and $\bar{t}$ is time. The constants κ and k designate mass diffusivity and reaction coefficient, respectively. The initial concentration profile $\bar{c}(\bar{x}, 0)$ can be any function which is even in $\bar{x}$ and has a non-zero space average C_0. No generality is lost if it is expressed as follows

$$\bar{c}(\bar{x}, 0) = C_0 \left(1 + e/\hat{\gamma} \int_0^\infty G(\bar{\gamma}) \cos(\bar{\gamma}\,\bar{x})\, d\bar{\gamma} \right) \qquad (2)$$

where

$$G(0) = 0 \qquad (3)$$

The maximum value of $G(\bar{\gamma})$ is unity and it is at $\bar{\gamma} = \hat{\gamma}$. Unboundedness of the container can be interpreted as $\hat{\gamma}\ell \gg 1$, where ℓ is its characteristic dimension. Therefore, the parameter e is a measure of the initial fluctuation of $\bar{c}(\bar{x}, 0)$ with respect to the mean C_0. In terms of the non-dimensional variables

$$x = \bar{x}\,\hat{\gamma} \qquad c = \bar{c}/C_0 \qquad t = \kappa\,\hat{\gamma}^2 \bar{t} \qquad \gamma = \bar{\gamma}/\hat{\gamma}$$

the differential system under discussion reduces to

$$\partial c/\partial t + \varepsilon c^2 = \partial^2 c/\partial x^2 \qquad (1')$$

$$c(x, 0) = 1 + e \int_0^\infty g(\gamma) \cos(\gamma x) d\gamma \qquad (2')$$

where

$$\varepsilon \equiv k c_0 / k \hat{\gamma}^2 \qquad\qquad G(\gamma \hat{\gamma}) \equiv g(\gamma)$$

Let the following expansion hold at the initial stage of the process

$$c = c^{(i)} \sim c_0^{(i)} + \varepsilon c_1^{(i)} + \varepsilon^2 c_2^{(i)} \cdots \qquad (4)$$

Substitution of the latter form into equation (1') yields

$$-\partial c_0^{(i)} / \partial t + \partial^2 c_0^{(i)} / \partial x^2 = 0 , \qquad (5)$$

$$-\partial c_1^{(i)} / \partial t + \partial^2 c_1^{(i)} / \partial x^2 = (c_0^{(i)})^2 , \qquad (6)$$

$$-\partial c_2^{(i)} / \partial t + \partial^2 c_2^{(i)} / \partial x^2 = 2 c_0^{(i)} c_1^{(i)} . \qquad (7)$$

Since the right hand side of equation (2') is independent of ε, this initial condition must be imposed on $c_0^{(i)}$. Functions of higher index are made to vanish at $t=0$. Consequently, every component of the series (4) is governed by a determinate differential system. The solution for $c^{(i)}$ is therefore

$$c^{(i)} = (1 - \varepsilon t + \varepsilon^2 t^2 + \cdots) +$$

$$e (1 - 2 \varepsilon t + 3 \varepsilon^2 t^2 + \cdots) \int_0^\infty g(\gamma) \cos(\gamma x) \exp(-\gamma^2 t) d\gamma$$

$$+ \frac{e^2}{4} (\varepsilon^2 t) \int_0^\infty \int_0^\infty \frac{g(\gamma) g(\beta)}{\gamma \beta} [4 (\cos((\gamma+\beta)x) - \cos((\gamma-\beta)x)] \exp(-(\gamma^2+\beta^2) t)$$

$$- 2\cos((\gamma+\beta)x)\exp(-(\gamma+\beta)^2 t) + 2\cos((\beta-\gamma)x)\exp(-\beta-\gamma^2 t)]\, d\gamma\, d\beta$$

$$+ \frac{e^2\varepsilon^1}{4}\int_0^\infty\int_0^\infty \frac{g(\gamma)g(\beta)}{\beta\gamma}\Big[\big(\cos((\beta-\gamma)x) - \cos((\beta+\gamma)x)\big)\exp(-(\gamma^2+\beta^2)t)$$

$$+ \cos((\beta+\gamma)x)\exp(-(\beta+\gamma)^2 t) - \cos((\beta-\gamma)x)\exp(-(\beta-\gamma)^2 t)\Big]\, d\gamma\, d\beta$$

$$+ \frac{e^2\varepsilon^2}{4}\int_0^\infty\int_0^\infty \frac{g(\gamma)g(\beta)}{\beta^2\gamma^2}\Big[\cos((\gamma+\beta)x)\exp(-(\gamma+\beta)^2 t) + \cos((\beta-\gamma)x)\exp(-(\beta-\gamma)^2 t)$$

$$- \big(\cos((\beta+\gamma)x) + \cos((\beta-\gamma)x)\big)\exp(-(\beta^2+\gamma^2)t)\Big]\, d\gamma\, d\beta$$

$$+ \frac{e^3\varepsilon^2}{8}\int_0^\infty\int_0^\infty\int_0^\infty \frac{g(\alpha)g(\beta)g(\gamma)}{\gamma\beta}\Big[- \frac{1}{(\alpha\beta - \beta\gamma - \alpha\gamma)}\cos((\beta-\gamma+\alpha)x)\times$$

$$\times\Big[\exp(-(\alpha^2+\beta^2+\gamma^2)t) - \exp(-(\beta-\gamma+\alpha)^2 t)\Big]$$

$$- \frac{1}{(\alpha\gamma - \beta\gamma - \alpha\beta)}\cos((\beta-\gamma-\alpha)x)\Big[\exp(-(\alpha^2+\beta^2+\gamma^2)t) - \exp(-(\beta-\gamma-\alpha)^2 t)\Big]$$

$$+ \frac{1}{(\beta\gamma - \alpha\gamma - \alpha\beta)}\cos((\beta+\gamma-\alpha)x)\Big[\exp(-(\alpha^2+\beta^2+\gamma^2)t) - \exp(-(\beta+\gamma-\alpha)^2 t)\Big]$$

$$+ \frac{1}{(\beta\gamma + \alpha\gamma + \alpha\beta)}\cos((\alpha+\beta+\gamma)x)\Big[\exp(-(\alpha^2+\beta^2+\gamma^2)t) - \exp(-(\alpha+\beta+\gamma)^2 t)\Big]\Big] +$$

$$+ \frac{1}{\alpha(\beta+\gamma)} \cos\left((\beta+\gamma-\alpha)x\right)\left[\exp\left(-\left((\beta+\gamma)^2+\alpha^2\right)t\right) - \exp\left(-(\beta+\gamma-\alpha)^2 t\right)\right]$$

$$- \frac{1}{\alpha(\beta+\gamma)} \cos\left((\alpha+\beta+\gamma)x\right)\left[\exp\left(-\left((\beta+\gamma)^2+\alpha^2\right)t\right) - \exp\left(-(\alpha+\beta+\gamma)^2 t\right)\right]$$

$$+ \frac{1}{\alpha(\beta-\gamma)} \cos\left((\beta-\gamma+\alpha)x\right)\left[\exp\left(-\left((\beta-\gamma)^2+\alpha^2\right)t\right) - \exp\left(-(\beta-\gamma+\alpha)^2 t\right)\right]$$

$$- \frac{1}{\alpha(\beta-\gamma)} \cos\left((\beta-\gamma-\alpha)x\right)\left[\exp\left(-\left((\beta-\gamma)^2+\alpha^2\right)t\right) - \exp\left(-(\beta-\gamma-\alpha)^2 t\right)\right]\right] d\alpha\, d\beta\, d\gamma \tag{8}$$

follows
It from the arguments brought in the introduction that when the
process is reaction-dominated both time and space variations are much
smaller than at the initial stage. This is reflected by the appropriate
scaling of the corresponding independent variables. There are various in-
dications that the appropriate scaling ratios are given by

$$X = \varepsilon^{1/2} x \qquad\qquad T = \varepsilon t \tag{9}$$

However, the author knows of no chain of rigorous arguments which leads
to relationship (9) as the unique choice. The fact that it yields an asymp-
totic expansion for large t, $c^{(\ell)}$, which matches with $c^{(i)}$, offers some
a posteriori justification.

When rewritten in terms of X and T and rearranged as a se-
quence of terms of descending orders of magnitude, equation (8) reduces to

$$c_0^{(i)} + \varepsilon c_1^{(i)} + \varepsilon^2 c_2^{(i)} = \left(1 - T + T^2\right)$$

$$+ \left(1 - 2T + 3T^2\right)\left[\varepsilon^{3/2} e(1/2) g''(0) x\right.$$

$$\times \int_0^\infty \zeta^2 \cos(\zeta X)\exp(-\zeta^2 T)d\zeta + \varepsilon^{5/2} \ell\,(1/24)\, g^{\overline{IV}}(0) \int_0^\infty \zeta^4 \cos(\zeta X)\exp(-\zeta^2 T)d\zeta \Big] \qquad (10)$$

In obtaining the latter, use is made of the following change of variable:

$$\zeta = \varepsilon^{1/2}\gamma$$

and of the Taylor expansion

$$g\left(\varepsilon^{1/2}\zeta\right) = g(0) + \varepsilon^{1/2}\zeta\, g'(0) + 1/2\,\varepsilon\zeta^2 g''(0) \cdots$$

Note that in view of equation (3) and the symmetry of $c(x,0)$ with respect to the origin $g(0)$ and the odd derivatives $g'(0)$, $g'''(0)$ vanish. The form (10) suggests that the "late" expansion is given by

$$c \doteq c^{(\ell)} \sim c_0^{(\ell)}(T) + \varepsilon^{3/2} c_1^{(\ell)}(X,T) + \varepsilon^{5/2} c_2^{(\ell)}(X,T) \qquad (11)$$

It is substituted into the governing equation, which is rewritten in the form

$$\partial c/\partial T \;+\; c^2 \;=\; \partial^2 c/\partial X^2 \qquad (1'')$$

and the components $c_i^{(\ell)}$ are found to be governed by

$$\partial c_0^{(\ell)}/\partial T \;+\; \left(c_0^{(\ell)}\right)^2 \;=\; 0 \qquad (12)$$

$$-\partial c_1^{(\ell)}/\partial T \;-\; 2 c_0^{(\ell)} c_1^{(\ell)} \;+\; \partial^2 c/\partial X^2 = 0 \qquad (13)$$

$$-\partial c_2^{(\ell)}/\partial T \;-\; 2c_0^{(\ell)} c_2^{(\ell)} \;+\; \partial^2 c_2^{(\ell)}/\partial X^2 \;=\; 0 \tag{14}$$

The solution of equation (12) is

$$c_0^{(\ell)} \;=\; A\big/(1 + AT) \tag{15}$$

where A is a constant of integration. By matching $c_0^{(\ell)}$ with $c_0^{(i)}$ one finds that A is unity. The matching of higher order terms is in agreement with this result.

Once $c_0^{(\ell)}$ is known the solution for the higher terms in the expansion is immediate. The general solution of equations (13) and (14) is

$$c_n^{(\ell)} \;=\; (1 + T)^{-2} \int_0^{\infty} f_n(\zeta)\cos(\zeta X)\exp(-\zeta^2 T)\,d\zeta, \quad n = 1, 2. \tag{16}$$

The transforms $f_n(\zeta)$ are obtained by matching with $c^{(ii)}$. The expansion $c^{(\ell)}$ is thus found to be

$$c^{(\ell)} \;=\; (1 + T)^{-1} \;+\; \ell(1 + T)^{-2}\int_0^{\infty}\big[\varepsilon^{3/2} g''(0)\,\zeta^2/2!$$

$$+\; \varepsilon^{5/2} g^{IV}(0)\,\zeta^4/4!\big]\cos(\zeta X)\exp(-\zeta^2 T)\,d\zeta \tag{17}$$

Solution for the spherically symmetric case can be constructed in a similar manner. With r as the non-dimensional radial coordinate, the initial condition is

$$c(r,0) = 1 + e F(r),$$ (18)

where $F(r)$ is a function even in r which satisfies

$$4\pi \int_0^\infty r^2 F(r)\, dr = 0 .$$ (19)

Up to terms of $O(\varepsilon^4)$ the initial expansion is found to be

$$c = c^i = (1 - \varepsilon t) + e(1$$

$$- 2\varepsilon t)\int_0^\infty f(\alpha) r^{-1} \sin(\alpha r) \exp(-\alpha^2 t)\, d\alpha + \varepsilon e^2 \int_0^\infty\int_0^\infty f(\alpha) f(\beta) r^{-1} \times$$

$$\times\left[\chi(r; \alpha,\beta)\cos(\lambda r) - H(\alpha,\beta)\sin(\lambda r)\right]\exp(-\lambda^2 t)\, d\alpha\, d\beta$$ (20)

In this expression λ is $(\alpha^2+\beta^2)^{1/2}$ and the transforms are given by

$$f(\alpha) = (2/\pi)\int_0^\infty F(r)\, r \sin(\alpha r)\, dr ,$$

$$\chi(r; \alpha,\beta) = (1/4)\int_0^r \cos^{-2}(\lambda\tilde{r})\left[C_i\left((\alpha-\beta+\lambda)\tilde{r}\right) \right.$$

$$\left. + C_i\left((\alpha-\beta-\lambda)\tilde{r}\right) - C_i\left((\alpha+\beta+\lambda)\tilde{r}\right) - C_i\left((\alpha+\beta-\lambda)\tilde{r}\right)\right]\, d\tilde{r} ,$$

$$H(\alpha,\beta) = (2/\pi)\int_0^\infty \sin(\lambda r)\cos(\lambda r)\,\chi(r; \alpha,\beta)\, dr .$$ (21)

The scaling scheme (9) is adopted here too, hence the leading term in the "late" expansion is again $(1 + T)^{-1}$. However, since in the present case the mass diffuses in more than one direction, one can expect uniformity to be attained earlier in the process. Thus, while in the one-dimensional

case the X variations of $c^{(\ell)}$ are of $O(\varepsilon^{3/2})$, the corresponding radial variation $(R = \varepsilon^{\frac{1}{2}} r)$ in the present case are of $O(\varepsilon^{5/2})$. This is a consequence of the facts that $f(\alpha)$ is odd in α and that $f'(o)$ is proportional to the left hand side of equation (18). The "late" expansion is given by

$$
c = c^{(\ell)} = (1 + T)^{-1} +
$$

$$
+ (1 + T)^{-2} \ell \, \varepsilon^{5/2} \left(f'''(o) / 3! \right) \int_0^\infty \zeta^3 R^{-1} \sin(\zeta R) \exp(-\zeta^2 T) \, d\zeta \tag{22}
$$

BINARY SYSTEM; REACTION RATE PROPORTIONAL TO THE PRODUCT OF CONCENTRATIONS

A nondimensionatization scheme similar to that employed in the previous section reduces the differential system which governs the present case to

$$\partial a / \partial t \; - \; \partial^2 a / \partial x^2 \; = \; - \, \varepsilon \, a b \, , \tag{23}$$

$$\partial b / \partial t \; - \; \partial^2 b / \partial x^2 \; = \; - \, \delta \varepsilon \, a b \, , \tag{24}$$

where

$$a(x, o) \; = \; 1 \; + \; \ell_a \int_o^\infty h(\gamma) \cos(\gamma x) \, d\gamma \, , \tag{25}$$

$$b(x, o) \; = \; 1 \; + \; \ell_b \int_o^\infty m(\gamma) \cos(\gamma x) \, d\gamma \, . \tag{26}$$

The diffusivities, κ, and the length characterizing the initial space variations, $\hat{\gamma}^{-1}$, are assumed to be the same for the two components. The parameter ε is the initial ratio between the rate absorbed in the reaction to the rate diffused -- for component a. The product $\varepsilon\delta$ is the corresponding ratio for component b.

As in the analysis of the single component here too both ε and $\delta\varepsilon$ depend on the initial average concentrations of reactants a and b. The parameter δ is associated with the proportion of the initial quantities of reactants. When δ is unity these amounts are chemically balanced so that both will eventually be completely absorbed in the reaction. The cases $\delta > 1$ and $\delta < 1$ correspond to binary systems with excess amounts of reactants a and b, respectively.

The initial, diffusion dominated behavior is again represented by

regular power series in ε. Up to terms of $O(\varepsilon^4)$ these are given by:

$$a = a^{(ii)} = (1 - \varepsilon t) + \ell_a (1 - \varepsilon t) \times$$

$$\times \int_0^\infty h(\gamma)\cos(\gamma x)\exp(-\gamma^2 t)\,d\gamma \; - \; \ell_b\,(\varepsilon t)\int_0^\infty m(\gamma)\cos(\gamma x)\exp(-\gamma^2 t)\,d\gamma$$

$$+ \; \frac{\varepsilon\,\ell_a\,\ell_b}{4}\int_0^\infty\int_0^\infty \frac{h(\gamma_1)\,m(\gamma_2)}{\gamma_1\,\gamma_2}\Big[\cos\big((\gamma_1-\gamma_2)x\big)\big(\exp\big(-(\gamma_1^2+\gamma_2^2)t\big)$$

$$- \exp\big(-(\gamma_1-\gamma_2)^2 t\big)\big) \; - \; \cos\big((\gamma_1+\gamma_2)x\big)\big(\exp\big(-(\gamma_1^2+\gamma_2^2)t\big)$$

$$- \exp\big(-(\gamma_1+\gamma_2)^2 t\big)\big)\Big]\,d\gamma_1\,d\gamma_2 \tag{27}$$

$$b = b^{(ii)} = (1 - \zeta\varepsilon t) + \ell_b (1 - \zeta\varepsilon t)\times$$

$$\times \int_0^\infty m(\gamma)\cos(\gamma x)\exp(-\gamma^2 t)\,d\gamma \; - \; \ell_a\,(\zeta\varepsilon t)\int_0^\infty h(\gamma)\cos(\gamma x)\exp(-\gamma^2 t)\,d\gamma$$

$$+ \; \frac{\zeta\varepsilon\,\ell_a\,\ell_b}{4}\int_0^\infty\int_0^\infty \frac{h(\gamma_1)\,m(\gamma_1)}{\gamma_1\,\gamma_2}\Big[\cos\big((\gamma_1-\gamma_2)x\big)\big(\exp\big(-(\gamma_1^2+\gamma_2^2)t\big)$$

$$- \exp\big(-(\gamma_1-\gamma_2)^2 t\big) \; - \; \cos\big((\gamma_1+\gamma_2)x\big)\big(\exp\big(-(\gamma_1^2+\gamma_2^2)t\big)$$

$$- \exp\big(-(\gamma_1+\gamma_2)^2 t\big)\big)\Big]\,d\gamma_1\,d\gamma_2 \tag{28}$$

By rewriting these in terms of the scaled variables X and T, one finds that as in the single reactant process the mathematical form of the late expansion is:

$$a = a^{(\ell)} \sim a_o^{(\ell)}(T) + \varepsilon^{3/2} a_1^{(\ell)}(X,T) \left.\vphantom{\begin{matrix}a\\b\end{matrix}}\right\} \quad (29)$$
$$b = b^{(\ell)} \sim b_o^{(\ell)}(T) + \varepsilon^{3/2} b_1^{(\ell)}(X,T)$$

However, it will be shown that, under certain circumstances, the manner of the reaction-dominated decay is substantially different.

It follows from the governing equations that $a_o^{(\ell)}$ and $b_o^{(\ell)}$ are governed by

$$\partial a_o^{(\ell)} / \partial T + a_o^{(\ell)} b_o^{(\ell)} = 0 \qquad (30)$$

$$\partial b_o^{(\ell)} / \partial T + \zeta \, a_o^{(\ell)} b_o^{(\ell)} = 0 \qquad (31)$$

Subtraction and integration yields

$$\zeta \, a_o^{(\ell)} - b_o^{(\ell)} = C$$

where C is a constant. By substituting the latter result into equation (30) or equation (31) one gets

$$a_o^{(\ell)} = (1/\zeta)(B+T)^{-1} \qquad b_o^{(\ell)} = (B+T)^{-1} \quad \text{if} \quad C = 0 \qquad (32)$$

$$a_o^{(\ell)} = \frac{C/\delta}{1 - D \exp(-CT)} \quad , \quad b_o^{(\ell)} = \frac{CD\exp(-CT)}{1 - D\exp(-CT)} \quad , \quad if \ C \neq 0 \quad (33)$$

Here, D and B are also constants of integration which, together with C, are determined by matching $(a_o^{(\ell)}, b_o^{(\ell)})$ with $(a_o^{(i)}, b_o^{(i)})$. These constants are thus found to be governed by:

$$(\delta B)^{-1} = 1, \qquad\qquad B^{-1} = 1, \ C = 0, \qquad (34)$$

$$C/\delta(1-D) = 1, \qquad\qquad CD/(1-D) = 1, \ C \neq 0 \qquad (35)$$

Since C may be either positive of negative, equations (32) and (33) represent three different asymptotic solutions for large t. Evidently, the asymptotic behavior depends on δ. For $\delta = 1$, equation (35) has no solution while equation (34) is satisfied provided B is unity. Consequently, in this case, $a_o^{(\ell)}$ and $b_o^{(\ell)}$ are given by:

$$a_o^{(\ell)} = b_o^{(\ell)} = (1 + T)^{-1} \qquad for \qquad \delta = 1 \qquad (36)$$

so that indeed eventually, the entire amounts of reactants are absorbed in the reaction. Again, when δ is bigger or smaller than unity, there is, respectively, deficiency and an excess of the reactant b. Indeed, for $\delta \neq 1$, equation (34) cannot be satisfied; the solution (32) is ruled out.

It follows from equation (35) and (33) that the following holds:

$$a_o^{(\ell)} = \frac{1 - \delta^{-1}}{1 - \delta^{-1} exp(-(\delta-1)T)} \quad , \quad b_o^{(\ell)} = \frac{(1 - \delta^{-1}) exp(-(\delta-1)T)}{1 - \delta^{-1} exp(-(\delta-1)T)} \quad , \quad \delta \neq 1 \quad (37)$$

so that for $\delta > 1$, a approaches the final value $(1 - \delta^{-1})$ while b vanishes. For $\delta < 1$, b approaches $(1 - \delta)$ while a vanishes. The analysis will now be completed recognizing the distinction between the cases of $\delta > 1$ and $\delta = 1$. Clearly, the case of $\delta < 1$, or excess in the amount of the reactant b, does not deserve a special treatment.

Whether the amounts of reactants are well proportioned or not, the terms of $O(\varepsilon^{3/2})$ in the late expansions are governed by

$$\partial a_1^{(\ell)}/\partial T - \partial^2 a_1^{(\ell)}/\partial X^2 = -\left(a_o^{(\ell)} b_1^{(\ell)} + a_1^{(\ell)} b_o^{(\ell)}\right) \quad (38)$$

$$\partial b_1^{(\ell)}/\partial T - \partial^2 b_1^{(\ell)}/\partial X^2 = -\delta \left(a_o^{(\ell)} b_1^{(\ell)} + a_1^{(\ell)} b_o^{(\ell)}\right) \quad (39)$$

The right hand side of these is eliminated and then a general solution is obtained for the combination $\left(\delta a_1^{(\ell)} - b_1^{(\ell)}\right)$. By substituting the solution for this group into equation (38) the latter reduces to

$$\partial a_1^{(\ell)}/\partial T + \left(b_o^{(\ell)} + \delta a_o^{(\ell)}\right) a_1^{(\ell)}$$

$$- \partial^2 a_1^{(\ell)}/\partial X^2 = a_o^{(\ell)} \int_0^\infty U(\xi) \cos(\xi X) exp(-\xi^2 T) d\xi \quad (40)$$

Therefore for the case $\delta = 1$ the solution for $a_1^{(\ell)}$ and $b_1^{(\ell)}$ has the form

$$a_1^{(\ell)} = (1/2) \int_0^\infty U(\xi) \cos(\xi X) \exp(-\xi^2 T) d\xi + (1+T)^{-2} \int_0^\infty V(\xi) \cos(\xi X) \exp(\xi T) \quad (41)$$

$$b_1^{(\ell)} = -(1/2) \int_0^\infty U(\xi) \cos(\xi X) \exp(-\xi^2 T) d\xi + (1+T)^{-2} \int_0^\infty V(\xi) \cos(\xi X) \exp(-\xi T) \quad (42)$$

By matching either $a^{(\ell)}$ with $a^{(i)}$ or $b^{(\ell)}$ with $b^{(i)}$ the transform functions $U(\xi)$ and $V(\xi)$ are evaluated. It is found that the late behavior of the chemically well balanced process is given by

$$\left. \begin{array}{c} a \\ b \end{array} \right\} = \left. \begin{array}{c} a^{(\ell)} \\ b^{(\ell)} \end{array} \right\} \sim (1+T)^{-1} + (1/4) \varepsilon^{3/2} \Big[\pm \Big(\ell_a h''(0)$$

$$- \ell_b m''(0) \Big) + \Big(\ell_a h''(0) + \ell_b m''(0) \Big)(1+T)^{-2} \Big] \int_0^\infty \xi^2 \cos(\xi X) \exp(-\xi^4 T) d\xi \quad (43)$$

It can be similarly shown that when there is an excess of reactant the late time and space dependence of the concentrations is (approximately) given by

$$a = a^{(\ell)} \sim \frac{(\delta - 1)/\delta}{1 - \delta^{-1} \exp(-(\delta-1)T)} - \frac{1}{2} \varepsilon^{3/2} \frac{\delta^{-1} \exp(-(\delta-1)T)}{(1 - \delta^{-1} \exp(-(\delta-1)T))^2} \times$$

$$\times \left[(2\delta - 1) \delta^{-1} \ell_a h''(0) - \ell_b m''(0) \right] \int_0^\infty \xi^2 \cos(\xi x) \exp(-\xi^2 T) d\xi$$

$$+ \frac{1}{2} \varepsilon^{3/2} \frac{1 - (\delta-1)\delta^{-1}T \exp(-(\delta-1)T)}{\delta(1 - \delta^{-1} \exp(-(\delta-1)T))^2} \times$$

$$\times \left[\delta \ell_a h''(0) - \ell_b m''(0) \right] \int_0^\infty \xi^2 \cos(\xi x) \exp(-\xi^2 T) d\xi \tag{44}$$

$$b = b^{(\ell)} \sim \frac{(1 - \delta^{-1})\exp(-(\delta-1)T)}{1 - \delta^{-1} \exp(-(\delta-1)T)} - \frac{1}{2} \varepsilon^{3/2} \frac{\exp(-(\delta-1)T)}{(1 - \delta^{-1} \exp(-(\delta-1)T))^2} \times$$

$$\times \left[(2\delta - 1) \delta^{-1} \ell_a h''(0) - \ell_b m''(0) \right] \int_0^\infty \xi^2 \cos(\xi x) \exp(-\xi^2 T) d\xi$$

$$+ \frac{1}{2} \varepsilon^{3/2} \frac{\exp(-(\delta-1)T)\left[(2 - (\delta-1)T) - \delta^{-1}\exp(-(\delta-1)T) \right]}{\delta(1 - \delta^{-1} \exp(-(\delta-1)T))^2} \times$$

$$\times \left[\delta \ell_a h''(0) - \ell_b m''(0) \right] \int_0^\infty \xi^2 \cos(\xi x) \exp(-\xi^2 T) d\xi \tag{45}$$

DISCUSSION

In theory, the processes under consideration never subside. In practice, they are terminated when the rates at which the residual amounts of reactant decay is suitably small. Therefore, it is useful to be able to predict what will be the residual amounts at an arbitrarily large time $\bar{t}$. In the single component case the following holds

$$ c\,(\vec{x},\,\bar{t}\,) \quad\longrightarrow\quad \left(k\,\bar{t}\,\right)^{-1}, \qquad \bar{t} \longrightarrow \infty \qquad (46) $$

This known result[4,5] is rederived by writing $c^{(\ell)}$ in a dimensional form and approximating it for large $\bar{t}$. It implies that late in the process the concentration is independent of the amount of reactant supplied initially and of the initial distribution. It is worthwhile noting that when the reaction is of the first order the residual concentration is proportional to the initial average and the timewise decay is exponential rather than algebraic.

On the other hand in the binary process the residual amount depends both qualitatively and quantitatively on the initial conditions. In the event that the initial amounts are well proportioned, $\delta=1$, the residual amounts approach zero. The decay is again algebraic and the concentrations of both components are inversely proportional to $\left(k\bar{t}\right)$. If there is an excessive amount of one reactant, $\delta\neq1$, a residual amount of one component will be left unabsorbed when the concentration of the other component vanishes. The inherent disproportion makes the process comparatively fast so that the timewise decay is exponential. The quantitities $\delta,(\delta-1)$ and $(1-\delta)$ which are associated with the initial disproportion are reflected in the large $\bar{t}$ concentration

distribution.

Both for the single component and binary processes the concentrations at large $\bar{t}$ are independent of the diffusivity. Indeed in view of the scaling (9) and the nondimensionalization scheme adopted, T is independent of κ. Therefore inasmuch as $a^{(\ell)}$ $b^{(\ell)}$ and $c^{(\ell)}$ are, to within a certain error, functions of T only then the late stage distribution are independent of the diffusivity. This conclusion implies that as they subside, the processes become reaction dominated. In fact, the anticipation of this result motivated the scaling choice (9). The fact that the two expansions match shows that the choice is correct and that the solution is valid. It would have been considerably more difficult to construct the solutions by adopting a pure mathematical approach.

Though the expressions for the residual amounts do not show it, in practice diffusion plays a very important role. The governing equations adopted are based on the implicit assumption that the reactants are completely dissolved. However when, in practice, the reactant(s) is (are) poured into a container this is not so. It takes time (and somethimes effort) to have the concentrations everywhere below the saturation point. In this initial mixing stage the diffusivity is very important but this stage is not accounted for here.

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CEAS # 127

The Graetz Problem for Combined Diffusion
Convection and Second Order Chemical Reaction

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ABSTRACT

The author analyses steady-state reactant concentration distri-
butions throughout finite-width streams, when convection conduction and
second order chemical reaction take place simultaneously. This is done
by recognizing that the process under consideration has two distinct be-
haviors at the inlet and downstream, and developing two asymptotic ex-
pansions to represent these. Downstream, the reaction is spread more-
or-less evenly across any transverse section so that the reaction is
responsible for most of the changes in the concentrations. Upstream,
the effect of diffusion is dominant. It is found that once the reac-
tant is completely dissolved, the diffusion mechanism has very little
additional overall influence on the process. Thus, at any section
downstream, the residual amount of reactant is independent of the dif-
fusivity and of the quantity supplied at the inlet. The decay is such
that this residual amount is inversely proportional to the distance
of the section from the inlet.

INTRODUCTION

In this work, the author analyzes a process in which a reactant diffuses across a stream, gets convected along it, and is absorbed in a chemical reaction. The stream is of finite width and is bounded by impregnable surface or surfaces. At the inlet, the flow is fully developed, the reactant is completely dissolved, and its concentration has an arbitrary non-uniform profile. Axial conduction is neglected. The amount of mass absorbed in the reaction per unit time is proportional to the concentration squared. This non-linearity makes the mathematical analysis difficult. The author considers two geometrical patterns: a circular pipe and a two-dimensional channel. The flow profiles are taken to be parabolic in both cases. The distribution of reactant at the inlet, and hence also across any transverse sections downstream, are assumed to be, respectively, rotationally symmetric and one-dimensional. It will, hopefully, become apparent that the method of solution used here is not restricted to these geometries.

A matched asymptotic expansions type of solution is developed. The perturbation parameter employed, ε, is the ratio between the characteristic reaction rate and the characteristic time change due to diffusion near the inlet. In many cases which are of practical interest, ε is small, and this enables one to employ the method of singular perturbations. Smallness of ε corresponds to the cases in which the reactant is injected into a finite number of spots in the stream, and due to diffusion the injected mass spreads across it. It is less often that pains are taken, or can be taken, to spread the reactant evenly across the inlet. Thus, attention is focused here on the more common case in which the diffusion is dominant

near the inlet. Far downstream, the transverse mass distribution is more or less uniform, and hence there the process is reaction dominated. The two distinct behaviors are characterized by the asymptotic expansions constructed here. The results are compared with those of the solution for the limiting case of zero diffusivity.

Treatments of processes in which diffusion, reaction and either time-dependence or convection take place simultaneously are often based on the premise that mass "first diffuses then reacts"[1]. Hence, the implicit recognition of the two stages, discussed herewith, is anything but new. Furthermore, the correspondence between two such regimes and two asymptotic expansions has already been exploited[2]. However, the author is unaware of any work in which the suitability of this method to the Graetz[3] type of problem is pointed out. The proposed application could be of help in design. It yields information about the amount of reactants that is absorbed in the reaction over a given length of conduit and about the overall influence of diffusion on the process.

ANALYSIS

The differential system governing the concentration $\bar{c}\left(\bar{x}_1, \bar{x}_2, \bar{x}_3\right)$ is

$$\bar{U}_3(\bar{x}_1, \bar{x}_2)\, \partial\bar{c}/\partial\bar{x}_3 \quad + \quad k\,\bar{c}^2 = \kappa\left(\partial^2/\partial\bar{x}_1^2 + \partial^2/\partial\bar{x}_2^2\right)\bar{c} \qquad (1)$$

$$\bar{c}\left(\bar{x}_1, \bar{x}_2, 0\right) = c_0 f \qquad (2)$$

$$\partial\bar{c}/\partial\bar{n} = 0 \qquad \text{at}\quad H(\bar{x}_1, \bar{x}_2) = 0 \qquad (3)$$

Here, $(\bar{x}_1, \bar{x}_2, \bar{x}_3)$ are cartesian coordinates with $(+\bar{x}_3)$ pointing along the conduit axis. The velocity in that direction is $\bar{v}_3$. The stream is bounded by the surface $H=0$ and $\bar{n}$ is the normal to it. Here, κ is the diffusivity and k is the reaction coefficient. c_0 is the 'mixed-cup' average concentration at the inlet, and the distribution there is characterized by the function $f(\bar{x}_1, \bar{x}_2)$.

In terms of the maximum velocity, V, and the length associated with the transverse cross section ℓ, the following non-dimensional variables are defined:

$$\left(x, y, n\right) \equiv \left(\bar{x}_1, \bar{x}_2, \bar{n}\right)\ell^{-1} \qquad z \equiv \bar{x}_3\kappa/V\ell^2 \qquad c \equiv \bar{c}/c_0 \qquad U \equiv \bar{U}_3/V$$

Using these, equations (1)-(3) reduce to

$$U\left(\partial c/\partial z\right) \quad + \quad \varepsilon c^2 = \left(\partial^2/\partial x^2 + \partial^2/\partial y^2\right)c \qquad (1')$$

$$c(x, y, 0) = f(x, y), \qquad\qquad (2')$$

$$\partial c / \partial n = 0, \qquad\qquad at \quad H(\bar{x}_1, \bar{x}_2) = 0. \qquad (3')$$

Here, the parameter ε is defined thus:

$$\varepsilon \equiv k c_0^2 \ell^2 / c_0 \kappa$$

As explained, ε is small and sufficiently close to the inlet region, the influence of the reaction is of $O(\varepsilon^1)$. This is taken as an indication that at this region the following holds:

$$c = c^{(i)} \sim c_0^{(i)} + \varepsilon c_1^{(i)} + \varepsilon^2 c_2^{(i)} \qquad\qquad (4)$$

By combining this form with the governing equation, one obtains:

$$- U \left(\partial c_0^{(i)} / \partial z \right) + \left(\partial^2 / \partial x^2 + \partial^2 / \partial y^2 \right) c_0^{(i)} = 0 \qquad (5)$$

$$- U \left(\partial c_1^{(i)} / \partial z \right) + \left(\partial^2 / \partial x^2 + \partial^2 / \partial y^2 \right) c_1^{(i)} = \left(c_0^{(i)} \right)^2 \qquad (6)$$

and so on. Since the condition (2') is independent of ε, the following initial conditions must be satisfied:

$$\left.\begin{array}{l} c_0^{(i)} (x, y, 0) = f \\[2em] c_j^{(i)} (x, y, 0) = 0 \qquad\qquad j \neq 0 \end{array}\right\} (7)$$

It is similarly clear that every component is governed by a well posed

differential system. These can be solved consecutively. An expression

for the space distribution of c near the inlet, correct to within an

error of $O(\varepsilon^m)$, is given by the sum of the first m components. However,

regardless of the number of terms retained, expansion (4) will not be a

valid representation of c far downstream. For this region, the under-

lying assumption that the process is diffusion dominated holds no longer.

A quantitative demonstration of the failure of this assumption when z is

large emerges once a couple of terms $c_j^{(i)}$ are calculated. Solution of

these for the case of a two dimensional channel of width 2ℓ will now be

presented.

Clearly, $c_o^{(i)}$ is a solution of a Graetz type problem. It can be

expressed in terms of the eigenvalues λ_n^2 and the eigenfunctions ϕ_n gene-

rated by

$$\varphi_n'' + \lambda_n^2 \left(1 - x^2\right)\varphi_n = 0 , \qquad \varphi_n'(\pm 1) = 0 , \qquad (8)$$

as follows:

$$c_o^{(i)} = \sum_{n=0}^{\infty} A_n^0 \, \varphi_n(x) \exp\left(-\lambda_n^2 z\right) . \qquad (9)$$

The constants A_n^0 are given by

$$A_n^0 \int_{-1}^{1} \left(1 - x^2\right)\varphi_n^2 \, dx = \int_{-1}^{1} \left(1 - x^2\right)\rho \, \varphi_n \, dx . \qquad (10)$$

The first solution of the Sturm Louiville system (8) is $\lambda_o = 0$ and $\phi_o = $ const.

It, therefore, follows from (10) and the definition of 'mixed-cup' average

that the first term in expansion (9) is unity. Therefore, equation (6) reads

$$- v \, \partial c_1^{(i)}/\partial z \quad + \quad \partial^2 c_1^{(i)}/\partial x^2 \quad = \quad 1 \quad +$$

$$+ \quad 2 \sum_{n=1}^{\infty} A_n^o \, \varphi_n(x) \, exp(- \lambda_n^2 z) \quad +$$

$$+ \quad \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} A_n^o A_m^o \, \varphi_n \varphi_m \, exp(- (\lambda_n^2 + \lambda_m^2) z) \tag{6'}$$

so that $c_1^{(i)}$ has the form:

$$c_1^{(i)} \quad = \quad -(3/2) z \quad + \quad (1/8)(1 - x^2)^2 \quad +$$

$$+ \quad 2 \sum_{n=1}^{\infty} A_n^o \, \psi_n \, exp(- \lambda_n^2 z) \quad +$$

$$+ \quad \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} A_n^o A_m^o \, \chi_{nm} \, exp(- (\lambda_n^2 + \lambda_m^2) z) \quad +$$

$$+ \quad A_o' \quad + \quad \sum A_n' \, \varphi_n \, exp(- \lambda_n^2 z) \; . \tag{11}$$

In this expansion, ψ_n and χ_{nm} are solution of the systems:

$$\psi_n'' \quad + \quad \lambda_n^2 (1 - x^2) \psi_n \; = \; \varphi_n \quad , \quad \psi_n'(\pm 1) = 0 \tag{12}$$

$$\chi_{nm}'' \quad + \quad (\lambda_n^2 + \lambda_m^2)(1 - x^2) \chi_{nm} = \varphi_n \varphi_m \; , \quad \chi_{nm}'(\pm 1) = 0 \tag{13}$$

Note that ψ_n is determinable to within a constant times ϕ_n, but since A_n^1 are adjusted so as to make $c_1^{(i)}(x,o)$ vanish, the form (11) contains no

ambiguity. Higher terms $c_j^{(i)}$ will not be calculated. Nevertheless, it can be easily shown that the expression for $c_2^{(i)}$ contains a term which is proportional to z^2.

The perturbation technique employed in generating the components $c_j^{(i)}$ is based on the premise that the term $\varepsilon_m c_m^{(i)}$ is of an order of magnitude smaller than the term $\varepsilon^{m-1} c_{m-1}^{(i)}$. Therefore, the terms proportional to z and z^2 in the expression for $c_1^{(i)}$ and $c_2^{(i)}$, respectively, limits the validity of expansion (4) to the small z range. Moreover, the emergence of the products $\varepsilon^2 z^2$ suggests that an asymptotic expansion for large z, $c^{(\ell)}$, can be constructed by adopting the following scaling scheme:

$$Z \equiv \varepsilon z \tag{14}$$

Rigorous proof that this is the correct and unique choice of scaling will not be offered. We propose to justify this choice on the grounds that it produces an expansion $c^{(\ell)}$ which matches $c^{(i)}$.

Writing $c^{(i)}$ in terms of $(x, Z)^{(4)}$, one gets:

$$c^{(i)} \sim \left(1 - 3/2\, Z\right) + \varepsilon(1/8)\left((1-x^2)^2 + 8A_o'\right) + O(\varepsilon^2)$$

If $c^{(\ell)}$ matches $c^{(i)}$, it must have the form:

$$c^{(\ell)} \sim c_o^{(\ell)}(x, Z) + \varepsilon c_1^{(\ell)}(x, Z) \tag{15}$$

The governing equation, written in terms of x and Z, yields:

$$0 = \partial^2 c_o^{(\ell)} / \partial x^2 \tag{16}$$

$$(1 - x^2)\, \partial c_0^{(\ell)}/\partial Z \;+\; \left(c_0^{(\ell)}\right)^2 \;=\; \partial^2 c_1^{(\ell)}/\partial x^2 \;, \tag{17}$$

$$(1 - x^2)\, \partial c_1^{(\ell)}/\partial Z \;+\; 2\, c_0^{(\ell)} c_1^{(\ell)} \;=\; \partial^2 c_2^{(\ell)}/\partial x^2 \;, \tag{18}$$

while it follows from condition (3') that $c_j^{(\ell)}$ satisfy:

$$\partial c_j^{(\ell)}/\partial x \;=\; 0 \;, \qquad\qquad x = \pm 1 \;. \tag{19}$$

Equations (16) and (19) imply that $c_0^{(i)}$ is independent of x. Therefore, integration of equation (17) over the range $-1 < x < 1$ yields:

$$(2/3)\, \partial c_0^{(\ell)}/\partial Z \;+\; \left(c_0^{(\ell)}\right)^2 \;=\; 0 \tag{20}$$

The general solution of the last relationship is:

$$c_0^{(\ell)} \;=\; \left(C \;+\; 3/2\, Z\right)^{-1} \tag{21}$$

When $c_0^{(\ell)}$ is matched with $c_0^{(i)}$, it is found that the constant of integration C is unity. By combining the last result with equations (17) and (19) one finds that the solution for $c_1^{(\ell)}$ has the following form:

$$c_1^{(\ell)} \;=\; \frac{(1 - x^2)^2}{8\,(1 + 3/2\, Z)^2} \;+\; F(Z) \tag{22}$$

where $F(Z)$ is independent of x. It is evaluated by substituting the last result into equation (18) and integrating over the range $-1 < x < 1$. In view of equation (19), integration of the right hand side of equation (18) vanishes.

Hence, $F(Z)$ is governed by:

$$3 F(Z)(1 + 3/2 Z)^{-1} - (2/35)(1 + 3/2 Z)^{-3} + F'(Z) = 0 \qquad (23)$$

The solution for $F(Z)$ is:

$$F(Z) = F(0)(1 + 3/2 Z)^{-2}$$

$$+ (4/105) \ln (1 + 3/2 Z)(1 + 3/2 Z)^{-2} \qquad (24)$$

By matching two terms of $c^{(\ell)}$ with two terms of $c^{(i)}$, one can show that the initial value $F(0)$ is equal to A_0^1. In view of equations (12) and (13), the latter can be expressed in terms of quantities which are associated with the Graetz problem (5) as follows:

$$F(0) = -\frac{3}{16} \int_{-1}^{1} (1 - x^2) dx - 3 \sum_{n=1}^{\infty} A_n^0 \frac{1}{\lambda_n^2} \int_{-1}^{1} \varphi_n \, dx$$

$$- \frac{3}{2} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} A_n^0 A_m^0 \frac{1}{\lambda_n^2 + \lambda_m^2} \int_{-1}^{1} \varphi_n \varphi_m \, dx \qquad (25)$$

In the rotationally symmetric case, the forms of solutions for $c_0^{(i)}(x,z)$ and $c_1^{(i)}(r,z)$ are given by equations (9) and (11) with minor modifications. The eigenfunctions and eigenvalues are generated by:

$$\frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial \varphi_n}{\partial r} + \lambda_n^2 (1 - r^2) \varphi_n = 0 \qquad \varphi_n(0) = \text{fin.t}, \quad \varphi_n'(1) = 0 \quad (26)$$

The same operator and boundary conditions appear again in the systems governing $\psi_n(r)$ and $\chi_{nm}(r)$ which correspond to equations (12) and (13). Again, in the case at hand, the integration over the area implicit in the evaluations of A_n^j, $j=0,1$ has a slightly different form. Finally, the first term in the expression for $c_1^{(i)}(r,z)$ is $(-2z)$ rather than $(-3/2\ z)$. In view of the matching requirements, this change of factor must recur in the expansion $c^{(\ell)}$. It is shown below that this is so.

Clearly, the expansion $c^{(\ell)}(r,z)$ has the form (15) and $c_j^{(\ell)}$ are obtained by a set of equations similar to (16)-(18). However, the integration over the area implicit in the reduction of equation (17) to (20) yields a different factor for the case at hand. Therefore, in the rotationally symmetric case, $c_o^{(\ell)}$ is given by:

$$c_o^{(\ell)} = \left(1 + 2Z\right)^{-1} \tag{27}$$

Again, $c_1^{(\ell)}$ is given by:

$$c_1^{(\ell)} = \frac{(1 - \gamma^2)^2}{8(1+2Z)^2} + F(Z) \tag{28}$$

In this case, $F(Z)$ is governed by:

$$F' + 4F\left(1 + 2Z\right)^{-1} - (1/12)\left(1 + 2Z\right)^{-3} \tag{29}$$

Hence, its solution is:

$$F(Z) = F(0)\left(1 + 2Z\right)^{-2} + (1/24)\,\ln\left(1+2Z\right)\left(1+2Z\right)^{-2} \tag{30}$$

where

$$F(0) = -\frac{1}{2}\int_0^1 (1-r^2)^3 r\, dr + 8\sum_{n=1}^{\infty} A_n^0 \frac{1}{\lambda_n^2}\int_0^1 r\, \varphi_n(r)\, dr$$

$$+ 4\sum_{n=1}^{\infty}\sum_{m=1}^{\infty} A_n^0 A_m^0 \frac{1}{\lambda_n^2 + \lambda_m^2}\int_0^1 r\, \varphi_n\, \varphi_m\, dr \qquad (31)$$

DISCUSSION

From the analysis, it is obvious that the diffusion plays an important role near the inlet. We shall now show that the influence of this effect is not restricted to this domain. Note that the evidence of effective diffusion downstream does not contradict the basic premise that the process is reaction dominated there. Dominancy of an effect is taken (see Introduction) to imply that it is responsible for most of the changes in the reactant concentration. Indeed, to within an error of $O(\varepsilon)$, $c^{(\ell)}$ is uniform over any transverse cross-section so that changes in $c^{(\ell)}$ are mainly due to the chemical reaction. However, were it not for the diffusion, $c_o^{(\ell)}$ would not have been uniform over the section $Z=\text{const}$. In fact, this uniformity is due to the fact that the highest order equation governing the expansions in the downstream region, (16), represents the influence of this and no other effect.

The overall influences of diffusion will now be examined. This is done by comparing the solution obtained here, which holds for arbitrarily large κ, with the solution for $\kappa=0$. The latter is given by

$$\bar{c}(\bar{x}_1, \bar{x}_2, \bar{x}_3) = \bar{c}(\bar{x}_1, \bar{x}_2, 0)\,\bar{v}_3\left(\bar{v}_3 + k\,\bar{x}_3\,\bar{c}(\bar{x}_1, \bar{x}_2, 0)\right)^{-1} \tag{32}$$

In view of equations (21), (27), and (32), for large $\bar{x}_3$, $\bar{c}$ can be approximated by:

$$\bar{c} \sim \begin{cases} \bar{v}_3(\bar{x}_1, \bar{x}_2)(k\,\bar{x}_3)^{-1} & \kappa=0 & \text{arbitrary section} \\ (2/3)V(k\,\bar{x}_3)^{-1} & k\neq 0 & \text{channel} \\ (1/2)V(k\,\bar{x}_3)^{-1} & k\neq 0 & \text{circular pipe} \end{cases} \tag{33}$$

Thus, the average residual reactant over the conduit cross-section is the same in all cases. Since for $\kappa=0$ the stream is richer at the center, the 'mixed cup' average is slightly higher in this case. However, the differences are minute so that the diffusion mechanism appears to have very little overall influence on the process at hand. Of course, in practice, this is not so. The results (33) hold when $\overline{x}_3$ is measured from a somewhat fictitious inlet, namely, a section in which the reactant is completely dissolved. However, at the point where pure reactant is injected into the stream, its concentration is often above the saturation point. Clearly, L, the length of conduit required to have the reactant completely dissolved depends markedly on the diffusivity. In the limiting case of vanishing κ, L will be indefinitely large. Consequently, at the section $(\overline{x}_3 + L)$ downstream of the 'true' inlet, the amount of residual reactant is a much more sensitive function of κ than implied by equation (33).

In Graetz's case, and for processes in which convection diffusion and first order reactions are in effect simultaneously, the residual amount of mass is proportional to the average concentration at the inlet. The residual amount decays exponentially with x_3. However, in the non-linear case at hand, the residual amount is (within an error of $O(\varepsilon)$) independent of $\overline{c}(\overline{x}_1,\overline{x}_2,o)$, or c_o, and its dacay is much slower, like $\overline{x}_3^{-1}$. This result, combined with the appropriate interpretation of 'true' conduit length $\overline{x}_3=L$, could be of importance in engineering design.

Acknowledgement

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