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The effects of flow rate and particle shape on the convective diffusion to a solid catalytic particle

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SUMMARY

The flow of a fluid, containing a reactant, past a solid catalytic particle on which a reaction takes place is considered for large Péclet number. The concentration of the reactant is given by the diffusion boundary-layer equation, and this is solved in the case when the rate of reaction on the particle surface and the rate of diffusion of reactant onto the surface are of the same order of magnitude.

For a spherical particle, a series solution for the concentration is found for the case of Stokes flow, and numerical solutions are found for Stokes flow and for flow at higher Reynolds numbers (up to Re = 10). To examine the effect of particle shape, numerical solutions are found for prolate and oblate spheroids in Stokes flow.

1. Introduction

An operation often used in chemical engineering is one in which a fluid containing several chemical species flows over a solid surface on which a reaction takes place. The solid itself may take part in the reaction or it may only act as a catalyst.

In such situations the calculation of the rate of surface reaction is the main interest. This rate is determined by both the kinetic laws which govern the chemical reaction and the hydrodynamically induced transport mechanisms near the surface. The coupling between the kinetics and the flow arises because before the substances can react they must first reach the surface – by convection with the fluid and by diffusion. The effect of the flow becomes appreciable when the reaction rate constant is very large, since in this case the limiting factor is how fast the chemical substances are transported to the surface (the reaction is then said to be diffusion limited).

In this paper we consider the steady flow of an inert fluid containing a single reactant past a solid particle. We assume that a first order reaction (with rate constant k) takes place on its surface and that far from the particle the flow is a uniform stream U_0 and the concentration of the reactant is a constant c_f. The velocity of the fluid (taken to be viscous and incompressible) is determined by the Navier-Stokes equations with appropriate boundary conditions, and the concentration c of the reactant is given by the convective diffusion equation. On making the realistic assumption that the Péclet number $\mathrm{Pe} = U_0 a/D$ is large (where D is the diffusion coefficient and a is a typical length scale), the effects of diffusion are confined to a boundary-layer region next to the particle surface. On the particle the rate of reaction must equal the rate of diffusion onto the surface, which, for a first order reaction, leads to the boundary condition

$$D\mathbf{n}\cdot\nabla c = kc, \tag{1}$$

($\boldsymbol{n}$ is the outward unit normal).

In previous work on this problem Sih and Newman [1] and Chambré and Acrivos [2] assumed the process to be diffusion limited, that is $k \to \infty$, and so boundary condition (1) becomes $c = 0$. In [1] the Reynolds number $\mathrm{Re} = U_0 a/\nu$ (ν is the kinematic viscosity of the fluid) was assumed small, the flow being given by Stokes flow, and the particle was spherical, in [2] Re was assumed to be very large, the flow now being described by the boundary-layer equations, and the geometry considered was that of a flat plate. General reaction kinetics have been discussed by Polyanin and Sergeev [3] (for $\mathrm{Re} \ll 1$) and by Acrivos and Chambré [4] (for $\mathrm{Re} \gg 1$), again both in the diffusion limited case.

Here we assume that the reaction and diffusion rates are of the same order, so that the full form of (1) is used. Firstly Stokes flow is considered, and then the effect of increasing Re up to $\mathrm{Re} = 10$, just prior to the onset of separation (where the assumption of a concentration boundary-layer on the surface no longer holds). The basic geometry considered is that of a sphere, but the effect of particle shape on the reaction rate is also discussed – the shapes considered being prolate and oblate spheroids.

2. The basic equations

Consider the case of a spherical particle of radius a, the modification for prolate and oblate spheroids will be discussed later. The situation is axisymmetric and so the convective diffusion equation can be written in the spherical coordinates r', θ ($\theta = 0$ being the direction of the free stream at infinity). Expressing the velocity components in terms of a stream function and then non-dimensionalising with respect to length a, velocity U_0 and concentration c_f gives

$$\frac{1}{\sin\theta}\left(\frac{\partial\psi}{\partial\theta}\frac{\partial C}{\partial r} - \frac{\partial\psi}{\partial r}\frac{\partial C}{\partial\theta}\right) = \mathrm{Pe}^{-1}\left\{\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial C}{\partial\theta}\right)\right\}, \tag{2}$$

where $r = r'/a$, and $C = c/c_f$. The non-dimensional velocity components U_r, U_θ, in the radial and azimuthal directions respectively, are given by

$$\begin{aligned} U_r &= (r^2\sin\theta)^{-1}\frac{\partial\psi}{\partial\theta}, \\ U_\theta &= -(r\sin\theta)^{-1}\frac{\partial\psi}{\partial r}. \end{aligned} \tag{3}$$

The boundary conditions are,

$$\left(\frac{D}{ka}\right)\frac{\partial C}{\partial r} - C = 0 \qquad \text{on} \qquad r = 1 \quad \text{(from (1))}, \tag{4}$$

and

$$C \to 1 \qquad \text{as} \qquad r \to \infty. \tag{5}$$

There is also a symmetry condition

$$\frac{\partial C}{\partial \theta} = 0 \qquad \text{on} \qquad \theta = 0, \pi.$$

Letting $\mathrm{Pe} \to \infty$ in (2) leaves only the convective terms, indicating that C is a constant on streamlines and hence $C = 1$ everywhere. But in that case the boundary condition on $r = 1$ cannot be satisfied. This suggests the presence of a boundary-layer region close to the sphere where the concentration varies rapidly from its depleted value at the sphere surface to its outer value 1. This region can be investigated by stretching the r coordinate. Sih and Newman [1] have shown that for $\mathrm{Pe} \gg 1$ the flow field can be divided into several regions characterised by different dominant methods of mass transfer. In each region (2) is approximated by appropriate stretching of coordinates and then retaining the largest terms as $\mathrm{Pe} \to \infty$. Sih and Newman found six regions: an outer region, $(r-1) > O(\mathrm{Pe}^{-1/3})$, $\theta > O(\mathrm{Pe}^{-1/3})$; a diffusion boundary-layer, $(r-1) < O(\mathrm{Pe}^{-1/3})$, $\theta > O(\mathrm{Pe}^{-1/3})$; and four regions in the wake, $\theta < O(\mathrm{Pe}^{-1/3})$.

In the outer region convection dominates as the method of transfer, and in the boundary layer, convection and diffusion perpendicular to the sphere surface are dominant. It was shown in [3] that the concentration field near the rear stagnation point (i.e. in the region $\theta < O(\mathrm{Pe}^{-1/3})$) contributes very little to the total reaction on the sphere, and so the problem of finding the rate of total surface reaction reduces to that of solving the equation which is valid in the diffusion boundary layer.

Since $U_r = U_\theta = 0$ on the sphere, then near $r = 1$, ψ will have the approximate form

$$\psi = b(\theta)(r-1)^2 + O((r-1)^3) \tag{7}$$

for some function $b(\theta)$. To derive the diffusion boundary-layer equation, we put this expression for ψ into (2), make the transformation $y = (r-1)\mathrm{Pe}^{1/3}$ and take the terms which are largest as $\mathrm{Pe} \to \infty$. Putting $x = \pi - \theta$ for convenience then gives,

$$2yB(x)\frac{\partial C}{\partial x} - B'(x)y^2\frac{\partial C}{\partial y} = \sin x \frac{\partial^2 C}{\partial y^2} \tag{8}$$

with boundary conditions

$$\alpha_0 \frac{\partial C}{\partial y} - C = 0 \qquad \text{on} \qquad y = 0,$$

$$C \to 1 \qquad \text{as} \qquad y \to \infty$$

and symmetry condition

$$\frac{\partial C}{\partial x} = 0 \qquad \text{on} \qquad x = 0,$$

where $B(x) = b(\theta(x))$, and $\alpha_0 = U_0 \mathrm{Pe}^{-2/3}/k$ is a constant of order 1.

Having found the surface concentration, C_s, from (8) the total rate of reaction on the sphere, Q, (non-dimensionalised with respect to rate $4\pi k$) is given by

$$Q = \frac{1}{4\pi} \int_S C_s dS, \tag{9}$$

where S is the sphere surface.

3. Series solution

Since $U_\theta = 0$ at $x = 0$ then $B(x)/x \to 0$ as $x \to 0$, and so $B(x)$ has the general form

$$B(x) = x^2(b_0 + b_2 x^2 + b_4 x^4 + \ldots), \qquad b_0 \neq 0. \tag{10}$$

This suggests an expansion for the concentration $C(x, y)$ in the form

$$C(x,y) = \sum_{i=0}^{\infty} C_{2i}(y) x^{2i}. \tag{11}$$

Substituting (10) and (11) into equation (8), together with the Taylor series for $\sin x$, and equating coefficients of powers of x gives a set of ordinary differential equations for the $C_{2i}(y)$. The equations and boundary conditions for C_0, C_2 and C_4 are

$$C_0'' + 2b_0 y^2 C_0' = 0, \tag{12}$$

$$C_2'' + 2b_0 y^2 C_2' - 4b_0 y C_2 = \tfrac{1}{6} C_0'' - 4b_2 y^2 C_0', \tag{13}$$

$$C_4'' + 2b_0 y^2 C_4' - 8b_0 y C_4 = \tfrac{1}{6} C_2'' - 4b_2 y^2 C_2' + 4b_2 y C_2 - \tfrac{1}{120} C_0'' - 6b_4 y^2 C_0', \tag{14}$$

$$\alpha_0 C_{2i}'(0) - C_{2i}(0) = 0, \qquad i = 0, 1, 2,$$

$$C_0 \to 1, C_{2i} \to 0 (i \geqslant 1) \qquad \text{as} \qquad y \to \infty.$$

Equation (12) is easily integrated to give

$$C_0(y) = \frac{3\alpha_0 + (3/2b_0)^{1/3} \gamma(\tfrac{1}{3}; (2b_0/3)y^3)}{3\alpha_0 + (3/2b_0)^{1/3} \Gamma(\tfrac{1}{3})} \tag{15}$$

where $\gamma(a,y) = \int_0^y e^{-t}t^{a-1}\,dt$ is the incomplete gamma function.

To solve (13) we first consider the associated homogeneous equation. Making the transformation $t = 2b_0y^3/3$ and putting $C_2(t) = e^{-t}v_2(t)$ gives

$$tv_2'' + (\tfrac{2}{3} - t)v_2' - \tfrac{4}{3}v_2 = 0.$$

This is a particular case of Kummer's equation, the solutions of which are confluent hypergeometric functions. In particular the solution we require is $v_2(t) = K_2U(\tfrac{4}{3};\tfrac{2}{3};t)$, K_2 constant, where U, defined by Slater [5], is not exponentially large at infinity.

A particular integral of (13) is sought in the form $A_0yC_0'(y)$, A_0 constant, and K_2 is determined from the boundary condition at $y = 0$. The complete solution for $C_2(y)$ is,

$$C_2(y) = e^{-2b_0y^3/3}\left\{K_2U\left[\frac{4}{3};\frac{2}{3};\frac{2b_0y^3}{3}\right] + A_0K_0y\right\},$$

where

$$A_0 = (b_0 + 12b_2)/30b_0,$$

$$K_0 = 3/(3\alpha_0 + (3/2b_0)^{1/3}\Gamma(\tfrac{1}{3})),$$

$$K_2 = 2\alpha_0A_0K_0G_0/(18\alpha_0(2b_0/3)^{1/3} + 3G_0^2),$$

$$G_0 = \Gamma(\tfrac{1}{3})/\Gamma(\tfrac{2}{3}).$$

The equation for $C_4(y)$ is solved in a similar way to that for $C_2(y)$, a particular integral being sought in the form

$$(D_1y + E_1)p + (F_1y + G)p' + (H_1y + J_1y^4)C_0',$$

where

$$p = e^{-2b_0y^3/3}v_2(2b_0y^3/3)$$

and D_1 to J_1 are constants. The solution is

$$C_4(y) = e^{-2b_0y^3/3}\;K_4U\left[2;\frac{2}{3};\frac{2b_0y^3}{3}\right] + E_1p + F_1yp' + (H_1y + J_1y^4)C_0',$$

where

$$E_1 = (3b_2 - b_0)/15b_0,$$

$$F_1 = (b_0 + 12b_2)/30b_0,$$

$$H_1 = 13/12600 + 8b_2/(525b_0) + 3b_4/(7b_0) - 24b_2^2/(175b_0^2),$$

$$J = -A_0(b_0 + 12b_2)/30,$$

$$K_4 = [2\alpha_0H_1K_0G_0 - 18(E_1 + F_1)\alpha_0K_2(2b_0/3)^{1/3} - 3E_1K_2G_0^2]/[6\alpha_0(2b_0/3)^{1/3}\Gamma(\tfrac{1}{3}) + 9G_0/2].$$

As an approximation (denoted by $C^*(x,y)$), valid for small x, the series for $C(x,y)$ is truncated after the x^4 term. The corresponding approximation for Q is then

$$Q^* = \tfrac{1}{2}\int_0^\pi C^*(x,0)\sin x dx. \tag{16}$$

For Stokes flow the non-dimensional stream function is known to be $(2r^4 - 3r^3 + r)\sin^2 x/4r^2$, and hence

$$B(x) = \tfrac{3}{4}\sin^2 x. \tag{17}$$

In this case $C^*(x,0)$ is

$$C^*(x,0) = C_0(0) + C_2(0)x^2 + C_4(0)x^4,$$

where

$$C_0(0) = \alpha_0/(\alpha_0 + 2^{1/3}\Gamma(\tfrac{1}{3})/3), \tag{18i}$$

$$C_2(0) = -C_0(0)/(10 + 60\alpha_0/2^{1/3}G_0^2), \tag{18ii}$$

$$C_4(0) = \frac{(7/G_0^2 - 8\Gamma(\tfrac{2}{3})/9)(\alpha_0 C_2(0)/5.2^{1/3}) - C_0(0)/4200}{(1 + 4\alpha_0\Gamma(\tfrac{2}{3})/(3.2^{1/3}))}. \tag{18iii}$$

It can easily be seen from equations (18) above that $C_0(0)\to 1$, $C_2(0)\to 0$ and $C_4(0)\to 0$ as $\alpha_0\to\infty$, and that $C_{2i}(0)\to 0$, $i = 0, 1, 2$ as $\alpha_0\to 0$. This behaviour is consistent since $\alpha_0\to\infty$ leads to the boundary condition $\partial C/\partial y = 0$ on $y = 0$ (and consequently a solution of the form $C = 1 + O(\alpha_0^{-1})$), and $\alpha_0\to 0$ leads to the boundary condition $C = 0$ on $y = 0$ (which has been solved by [1]).

With $\alpha_0 = 1$, for example, and Stokes flow,

$$C^*(x,0) = 0.47056 - 0.21228x^2 - 0.00086x^4,$$

which is a decreasing function over the range $0 \leqslant x \leqslant \pi$.

$C^*(x,0)$ for Stokes flow is compared to a numerical solution of (8) in the next section.

4. The numerical solution for Stokes flow

With $B(x)$ as given in (17), equation (8) becomes

$$y\sin x\frac{\partial C}{\partial x} - y^2\cos x\frac{\partial C}{\partial y} = \frac{2}{3}\frac{\partial^2 C}{\partial y^2}. \tag{19}$$

This was solved numerically using a Crank-Nicholson scheme, accurate to order (k^2, h^2) where k and h are the steplengths in the x- and y-directions respectively. A regularly spaced grid of points was used, $x_i = ik$, $i = 0$ to M, $y_j = jh$, $j = 0$ to N. The outer boundary condition was applied at $y_N = Nh$. Equation (15) was used to obtain a set of values at points $i = 0, j = 0, 1 \ldots$ for the concentration profile at $x = 0$ and using this as initial data the Crank-Nicholson scheme steps forward in the x direction. Q was then found by numerical integration of (9) using Simpson's rule.

Although (19) was solved in the range $0 \leqslant x \leqslant \pi$ it is really only applicable for $(\pi - x) > O(\mathrm{Pe}^{-1/3})$, and so values of the surface concentration obtained for points very close to, or at $x = \pi$ should not be given too much credence. They are in fact very small and so any errors that they contain will produce only a small percentage error in Q (particularly since the integrand in (9) will contain a sin x term which is also small near $x = \pi$). The nature of the solution near $x = \pi$ is discussed in detail in the Appendix.

The effects of altering radial and angular stepsizes and the value of N on the accuracy of the numerical results for C_s were investigated. Values of $h = 0.05$, $k = \pi/60$ and $N = 60$ were used, giving results accurate (except very close to the rear stagnation point) to three decimal places.

Figure 1 shows $C^*(x, 0)$ and the numerical solution for C_s at $\alpha_0 = 0.5$, 1 and 2. For each value of α_0 the two solutions are in good agreement up to $x = \pi/2$, but diverge thereafter the difference at $x = 5\pi/6$ for example, being 7–8% of the numerical value. Q and Q^* (shown in

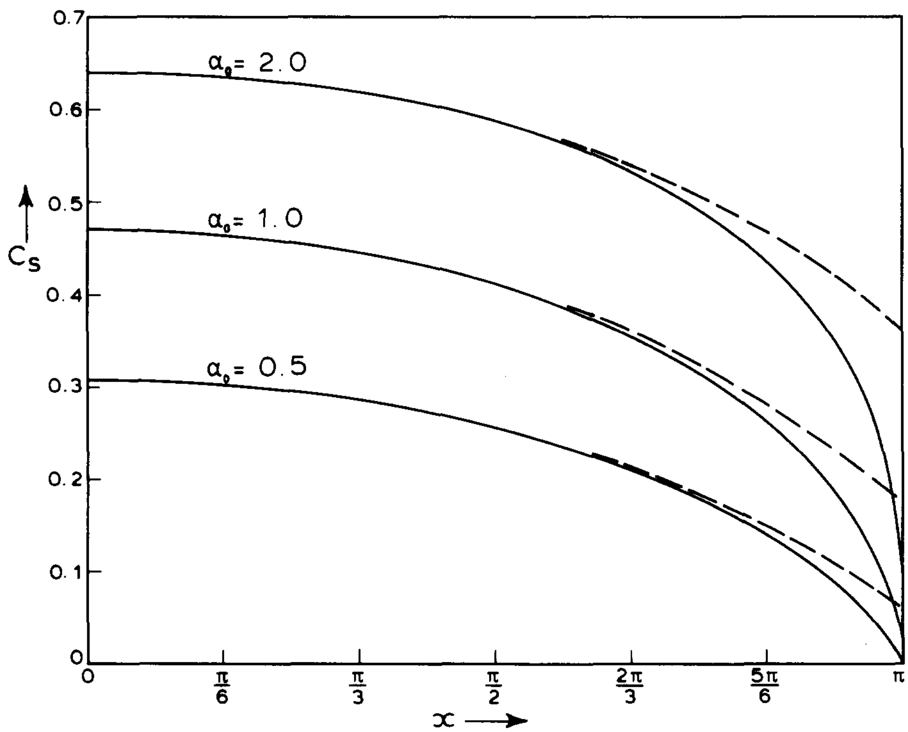

Figure 1. Series approximation and numerical solution for the surface concentration, C_s, on a sphere in Stokes flow, for various values of α_0 : – – – – series approximation; ——— numerical solution.

Table 1. Q and Q^* for a sphere in Stokes flow for various α_0.

α_0	Q	Q^*
0.5	0.241	0.244
1.0	0.392	0.397
2.0	0.565	0.573

Table 1) differ by less than 2% of Q at each α_0. Thus it can be seen that the approximation $C^*(x, 0)$ is adequate for the purposes of obtaining a good estimate for the total rate of surface reaction.

5. The numerical solution for higher Reynolds numbers

For higher Reynolds numbers $B(x)$ was calculated at regular intervals of x, using numerically determined values of the vorticity (ω) at the sphere surface, and the relationship

$$\omega(x, 0) = 2B(x)/\sin x.$$

The surface vorticity was found by solving the full Navier-Stokes equations using an iterative numerical scheme which followed closely that of Hamielec et al. [6]. The main difference between the scheme used and that in [6] was in the finite-difference expression used for the boundary condition on ω at the sphere surface. The form of this expression is believed to be a critical factor in the convergence of the scheme. The expression used was accurate to second order in the steplength in the radial direction and was derived using the method indicated by Ingham [7].

As well as $B(x)$, the concentration profile at $x = 0$ is needed in order to use the Crank-Nicholson scheme. This is given by (15) if b_0 is known, and the latter can be calculated to a good approximation as shown below

$$\frac{B(x_i)}{(ik)^2} = b_0 + b_1(ik) + O(k^4), \qquad x_i = ik, \qquad i = 1, 2;$$

$$b_0 = \frac{1}{12k^2}(16B(x_1) - B(x_2)) + O(k^4).$$

Results were found for a range of Reynolds numbers from 0.1 to 10, and these are shown in Figure 2. At $\mathrm{Re} = 0.1$ the surface concentration is very close to that for Stokes flow, as would be expected. As the Reynolds number is increased C_s is increased over the range $x = 0$ to $x = 2\pi/3$, and is decreased for $x > 2\pi/3$, with the result that the total rate of surface reaction Q is increased (this is shown in Table 2).

At $\mathrm{Re} = 10$ there is some unusual behaviour of C_s near the rear stagnation probably due to the approach to separated flow in this region.

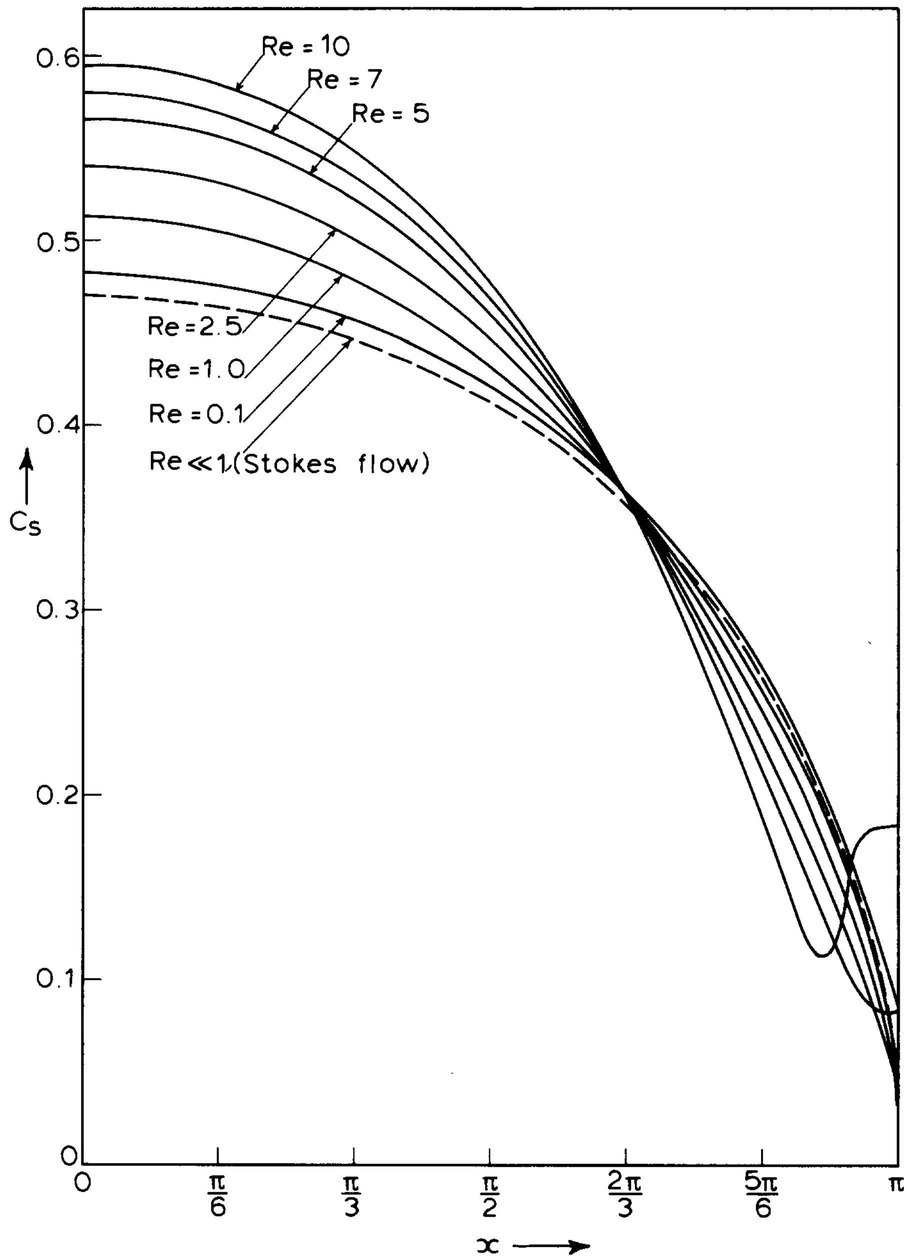

Figure 2. Surface concentration, C_s, on a sphere in flow at various Reynolds numbers, up to Re = 10, and with $\alpha_0 = 1.0$.

6. The prolate and oblate spheroids in Stokes flow

The effect of the shape of the catalytic particle on the total surface reaction was investigated by considering a prolate and an oblate spheroid in Stokes flow.

If X and Y are Cartesians, X being the direction of the free stream, then the case of a prolate

Table 2. Q at various Reynolds numbers (with $\alpha_0 = 1.0$).

Re	Q
0.1	0.400
0.5	0.404
1.0	0.410
2.5	0.421
5.0	0.431
7.0	0.435
8.0	0.437
9.0	0.439
10.0	0.441

spheroid can be dealt with by making the transformation $X + iY = \beta \cosh(\xi + i\eta)$, where β is a constant. The curve $\xi = \xi_0$ is an ellipse in the X-Y plane, given parametrically by

$$\left.\begin{array}{ll} X = a\cos\eta, & a = \beta\cosh\xi_0 \\ Y = b\sin\eta, & b = \beta\sinh\xi_0 \end{array}\right\} 0 \leqslant \eta \leqslant 2\pi.$$

Rotation of this curve about the X axis generates a prolate spheroid.

The convective diffusion equation is written in terms of the coordinates ξ, ϕ, η (ϕ being azimuthal angle), and is non-dimensionalised, this time using a length scale of $\beta \cosh \xi_0$. This means that the non-dimensional figure is contained within a sphere of unit radius, and as $\xi_0 \to \infty$ (i.e. $a \to b$) the particle tends to a unit sphere. The velocity components are written in terms of a stream function which has near $\xi = \xi_0$, the approximate form

$$\psi = b(\eta)(\xi - \xi_0)^2 + O((\xi - \xi_0)^3). \tag{20}$$

Using (20), making the transformations $x = \pi - \eta$ and $\bar{\xi} = (\xi - \xi_0)\,\mathrm{Pe}^{1/3}$ (where now $\mathrm{Pe} = U_0 \beta \cosh \xi_0 / D$) and taking the largest terms as $\mathrm{Pe} \to \infty$ gives the diffusion boundary-layer equation in elliptic coordinates

$$2B(x)\bar{\xi}\frac{\partial C}{\partial x} - B'(x)\bar{\xi}^2\frac{\partial C}{\partial x} = \tanh\xi_0 \sin x \frac{\partial^2 C}{\partial \bar{\xi}^2}, \tag{21}$$

$$\alpha_0 \coth\xi_0 \frac{\partial C}{\partial \bar{\xi}} - C = 0, \qquad \text{on } \bar{\xi} = 0,$$

$$C \to 1 \quad \text{as} \quad \bar{\xi} \to \infty, \qquad \frac{\partial C}{\partial x} = 0 \quad \text{on} \quad x = 0,$$

$$B(x) = b(\eta(x)).$$

Payne and Pell [8] give an expression for ψ for a prolate spheroid; their expression appears to be in error, but using a corrected version we find

$$B(x) = \frac{B_0}{\cosh^2 \xi_0} \sin^2 x, \tag{22}$$

where

$$B_0 = \frac{-s_0}{s_0 - \frac{1}{2}(s_0^2 + 1) \ln\left(\frac{s_0+1}{s_0-1}\right)}, \qquad s_0 = \cosh \xi_0.$$

So (21) becomes

$$\sin x\, \bar{\xi} \frac{\partial C}{\partial x} - \cos x\, \bar{\xi}^2 \frac{\partial C}{\partial \bar{\xi}} = \frac{\sinh \xi_0 \cosh \xi_0}{2B_0} \frac{\partial^2 C}{\partial \bar{\xi}^2}. \tag{23}$$

This is the same as equation (19) for a sphere except for the coefficient on the right-hand side. As expected (since the shape of the particle tends to a unit sphere as $\xi_0 \to \infty$) this coefficient tends to 2/3 as $\xi_0 \to \infty$.

The oblate spheroid is given by the transformation $X + iY = \beta \sinh(\xi + i\eta)$. The curve $\xi = \xi_0$ is now an ellipse similar to that which generates the prolate spheroid, but rotated through 90°. In this case the boundary-layer diffusion equation (derived in exactly the same way as for (23)) is

$$\sin x\, \bar{\xi} \frac{\partial C}{\partial x} - \cos x\, \bar{\xi}^2 \frac{\partial C}{\partial \bar{\xi}} = \frac{\cosh^2 \xi_0}{2B_0} \frac{\partial^2 C}{\partial \bar{\xi}^2}, \tag{24}$$

$$\alpha_0 \frac{\partial C}{\partial \bar{\xi}} - C = 0 \qquad \text{on} \qquad \bar{\xi} = 0,$$

$$B_0 = \frac{\tau_0}{\tau_0 + (1 - \tau_0^2) \cot^{-1}(\tau_0)}, \qquad \tau_0 = \sinh \xi_0.$$

Equations (23) and (24) were solved numerically, using a Crank-Nicholson scheme, for a range of values of ξ_0 to give in each case the surface concentration C_s, and hence the total rate of reaction (this time non-dimensionalised with respect to the rate $S_A k$, where S_A is the surface area of the particle in question).

In order to obtain results of a similar accuracy to those in the case of a sphere in Stokes flow, the step lengths were taken to be $k = \pi/60$ and $h = 0.05$. $N = 60$ was used for the prolate spheroid at all values of ξ_0. For the oblate spheroid $N = 60$ was a suitable value except where ξ_0 was small – at $\xi_0 = 0.05$, for example, $N = 200$ was needed to obtain the required accuracy.

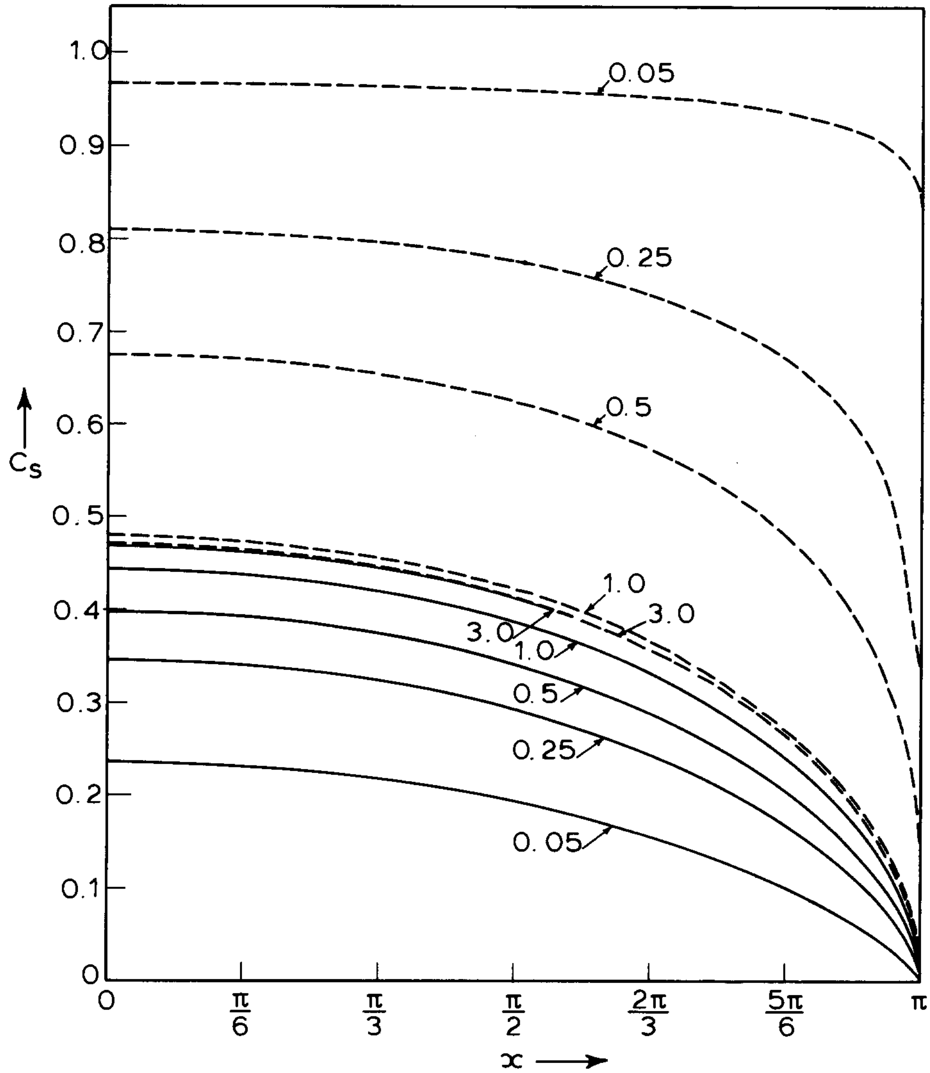

Figure 3. Surface concentration, C_s, for the prolate and oblate spheroids at various values of ϵ_0, and with $\alpha_0 = 1.0$, Re < 1: ---- prolate spheroid; ——— oblate spheroid.

The results for C_s are shown in Figure 3. At any value of ξ_0 the solution for the prolate spheroid lies above that for the sphere which in turn lies above that for the oblate spheroid. As ξ_0 is increased the two solutions for the two types of spheroid approach each other and, as is expected, converge on the solution for a sphere. A corresponding trend is seen in the values of Q shown in Table 3.

Appendix: The solution near $x = \pi$

To examine the behaviour of the solution of (8) near $x = \pi$ we work in terms of $\theta\,(\theta = \pi - x)$. Since $b(\theta) = D_0\theta^2$ near $\theta = 0$ (for some constant D_0) then equation (8) gives, on retaining

Table 3. Q for the prolate and oblate spheroids for various values of ξ_0 and with $\alpha_0 = 1.0$, Re $\ll 1$.

ξ_0	Q	
	Prolate	Oblate
0.05	0.957	0.174
0.1	0.905	0.211
0.25	0.764	0.269
0.5	0.607	0.318
0.75	0.517	0.347
1.0	0.466	0.364
2.0	0.401	0.388
3.0	0.393	0.391
5.0	0.391	0.391
∞ (sphere)	0.391	0.391

only leading terms,

$$\frac{\partial^2 C}{\partial y^2} - 2D_0 y^2 \frac{\partial C}{\partial y} + 2D_0 y\theta \frac{\partial C}{\partial \theta} = 0. \tag{25}$$

$C(\theta, y)$ is now expanded in the form

$$C(\theta, y) = \theta^m (g_0(y) + \dots), \tag{26}$$

where m is a constant, as yet unknown. The equation for $g_0(y)$ is

$$g_0'' - 2D_0 y^2 g_0' + 2mD_0 y g_0 = 0 \tag{27}$$

which has the solution (which is not exponentially large at infinity)

$$g_0 = A_0 U\left(\frac{-m}{3}; \frac{2}{3}; \frac{2D_0 y^3}{3}\right) \tag{28}$$

for some constant A_0.

The boundary condition on $y = 0$ gives $\alpha_0 g_0'(0) = g_0(0)$, so that from Slater [5] we find that

$$\frac{\alpha_0 \Gamma\left(\frac{1-m}{3}\right)}{\Gamma\left(\frac{-m}{3}\right)} = \frac{1}{D_0^{1/3}} \frac{\Gamma(1/3)}{\Gamma(-1/3)} \left(\frac{3}{2}\right)^{1/3}. \tag{29}$$

Equation (29) determines the value of m for a given value of α_0, if D_0 is known. For Stokes flow (i.e. $D_0 = 3/4$) (29) was solved numerically by evaluating the left-hand side as a function of m, at various α_0. Graphs of the log of the numerical solution for C_s (for Re $\ll 1$) against log (θ), for small θ, at various α_0 were found to be straight lines – thus confirming that $C_s(\theta)$ behaves

Table 4. Values of m, at various α_0, for the solution at the rear stagnation point.

α_0	m	
	(i)	(ii)
0.25	0.80	0.81157
0.5	0.66	0.67666
0.75	0.57	0.57769
1.0	0.50	0.50285
1.25	0.44	0.44462
1.5	0.39	0.39817
1.75	0.35	0.36034
2.0	0.32	0.32898

(i) Values obtained graphically
(ii) Values obtained from equation (29)

like θ^m near the rear stagnation point. The values of m obtained from these graphs (m being the gradient) agreed fairly closely with those obtained from (29). Some results are shown in Table 4.

A_0 is indeterminate, but since the above is an asymptotic expansion of a parabolic equation as described by Stewartson [9] we do expect some indeterminancy in the solution.

The form for $g_0(y)$ given above does not satisfy the outer boundary condition, and so (26) must be regarded as an inner solution holding for $y = O(1)$. The asymptotic form of g_0 as $y \to \infty$ gives

$$C \sim \left(\frac{2D_0}{3}\right)^{m/3} A_0 y^m \theta^m \left(1 - \frac{m(m-1)}{6D_0 y^3} + \frac{m(m-1)(m-3)(m-4)}{72D_0^2 y^6} + \ldots\right) \qquad (30)$$

This suggests we put $\mu = y\theta$ to obtain a solution which will hold when $y = O(\theta^{-1})$. Equation (25) then becomes

$$\theta^2 \frac{\partial^2 C}{\partial \mu^2} + 2D_0 \mu \frac{\partial C}{\partial \theta} = 0. \qquad (31)$$

Expanding C in the form $C = C_0(\mu) + \theta^3 C_1(\mu) + \ldots$, we find that $C_1 = -C_0''/(6D_0\mu)$ and (as expected) $C_0(\mu)$ is indeterminate.

However we know from (30) that

$$C_0(\mu) \sim \left(\frac{2D_0}{3}\right)^{m/3} A_0 \mu^m \qquad \text{as} \qquad \mu \to 0.$$

Also, as a check, the term of order θ^3 in the outer expansion agrees to leading order, as $\mu \to 0$, with the $O(\theta^3)$ term in (30).

This form of the solution of (8) near $\mu = 0$ as inner and outer expansions matches onto the form of the solution of the full convective diffusion equation near $\theta = 0$ as described by [1].

Since the surface concentration is $O(\theta^m)$, and $m > 0$, near $\theta = 0$ then (as asserted earlier) the contribution to the total surface reaction from this region is small. For the prolate and oblate spheroids the analysis of the boundary-layer diffusion equation near the r.s.p. is essentially that given above, leading to the same conclusion.

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