

## Non-isothermal catalytic wall reactions

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### Summary

A reacting gas flows along a tube and passes over a catalytic coating which begins at  $x = 0$ . A strong exothermic reaction which is temperature dependent occurs at the wall of the tube leading to a local "hot spot" near  $x = 0$ . It is assumed that the surface temperature of the catalyst is controlled by conduction of heat through the metal wall of the tube, heat transfer into the gas being negligible. The equations governing the gas concentration and the metal temperature are reduced to a pair of coupled integral equations which are solved numerically. The temperature distribution at the wall of the tube is determined and axial conduction of heat in the metal casing is shown to be important.

### 1. Introduction

Catalytic wall reactors are widely used in industry when the gas/solid catalytic reaction produces a large amount of heat. This heat can be efficiently removed by conduction through the metal wall of the reactor, leading to its quasi-isothermal operation [1]. Temperature effects are most likely to be important where the gas first comes into contact with the catalytic coating. The existence of a "hot spot" in the reactor may lead to an unwanted volume reaction or to local degrading of the catalyst. The purpose of this paper is to determine analytically the surface temperature of the catalyst in this region, when the reaction is so strong that significant temperature rises occur. As the quantity of heat produced at the wall in the chemical reaction is temperature dependent, there will be a strong coupling between the concentration field in the gas and the heat conduction problem in the metal casing.

Many authors have considered laminar boundary layer flow over a catalytic surface under isothermal conditions. Chambre [2] formulated the more general problem including the non-isothermal aspects of the reaction. A review of the relevant literature has been given by Chung [3]. More recently, work in this field has been concerned with the possible multiplicity of steady state solutions in flows involving an exothermic reaction at the solid boundary [4].

### 2. The mathematical model

We shall consider the fully developed, steady Poiseuille flow of a single reacting gas through a tube of circular cross-section, bounded by a thin metal wall. The outer surface

of the metal wall is maintained at a uniform temperature. If  $z$  is the co-ordinate measured down the tube we shall assume that the catalytic coating, which is of negligible thickness, is applied to the region  $z \geq 0$ . When the gas first passes over the catalytic coating, a strong reaction occurs at the gas/metal interface close to  $z = 0$ , which rapidly reduces the gas concentration and releases a large amount of heat per unit area. In a steady state the surface temperature of the catalyst, which greatly influences the speed of the reaction, must be such that the heat released at the wall can be conducted away, both axially and radially, by the metal. We shall show that the heat flux into the gas is relatively small. Downstream of  $z = 0$ , the gas concentration at the wall is small and the rate at which heat is released will be determined by the rate at which unreacted gas can diffuse to the wall from the centre of the channel, that is, the reaction is diffusion limited. In this region only moderate temperature rises are required to conduct the heat away across the metal wall.

As is usual in these problems, concentration and temperature boundary layers begin in the gas at  $z = 0$  and spread until they meet at the centre of the tube some distance downstream. We shall assume that this entry length is large compared with the  $z$  length scale of the region where the greatest reaction occurs. A boundary layer analysis is therefore appropriate.

We shall consider the case in which the wall reaction is first order, but it is clear that the techniques used here may be applied equally well to the case of higher order reactions.

### 3. The governing equations

We consider the Poiseuille flow of a reacting gas down a long tube of radius  $a$  bounded by a metal wall of thickness  $l$ . We shall suppose that  $l$  is small compared with  $a$ , as this is the case of practical interest. The outer surface of the metal is maintained at the constant temperature  $T_0$ . We assume that axial diffusion of mass and heat is small compared with axial convection. Thus in the region  $z < 0$ , where there is no catalytic wall reaction, the gas concentration will take the constant value  $c_0$ .

If  $c(\rho, z)$  and  $T_g(\rho, z)$  are the concentration and temperature of the gas respectively, where  $\rho$  is the radial co-ordinate, then in the gas

$$2u_0 \left\{ 1 - \left( \frac{\rho}{a} \right)^2 \right\} \frac{\partial c}{\partial z} = \frac{D}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial c}{\partial \rho} \right), \quad (1)$$

$$2u_0 \left\{ 1 - \left( \frac{\rho}{a} \right)^2 \right\} \frac{\partial T_g}{\partial z} = \frac{\alpha}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial T_g}{\partial \rho} \right) \quad (2)$$

where  $u_0$  is the mean velocity of the gas flow and  $D$  and  $\alpha$  are the constant values of the molecular diffusivity and thermal diffusivity respectively.

As we are concerned with thin, laminar boundary layers on  $\rho = a$ , Eqns. (1) and (2) may be written in the boundary layer form

$$\frac{4u_0}{a} (a - \rho) \frac{\partial c}{\partial z} = D \frac{\partial^2 c}{\partial \rho^2}, \quad (3)$$

$$\frac{4u_0}{a} (a - \rho) \frac{\partial T_g}{\partial z} = \alpha \frac{\partial^2 T_g}{\partial \rho^2}. \quad (4)$$

Within the metal wall, the temperature  $T(\rho, z)$  satisfies the steady heat conduction equation

$$\frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial T}{\partial \rho} \right) + \frac{\partial^2 T}{\partial z^2} = 0. \quad (5)$$

The boundary conditions are:

(i) The temperature is prescribed at the outer edge of the metal

$$T = T_0 \text{ at } \rho = a + l, \text{ all } z$$

and tends to its undisturbed value as  $|z| \rightarrow \infty$  in the metal i.e.

$$T \rightarrow T_0 \text{ as } |z| \rightarrow \infty, \quad a < \rho < a + l. \quad (6)$$

(ii) In the gas

$$c = c_0 \text{ at } z = 0, \quad 0 \leq \rho < a,$$

$$T_g \rightarrow T_0 \text{ as } z \rightarrow -\infty, \quad 0 \leq \rho < a. \quad (7)$$

Note that we cannot assume  $T_g = T_0$  at  $z = 0$ , because the metal wall is heated in  $z < 0$  by axial conduction and is not therefore at uniform temperature in this region.

(iii) The temperature is continuous at the gas/metal interface

$$T_g = T \text{ at } \rho = a, \quad \text{all } z. \quad (8)$$

(iv) As we are considering the flow in a boundary layer on  $\rho = a$ , both the concentration and the temperature of the gas must tend to their mainstream values at the edge of the boundary layer. (9)

(v) We assume that the catalytic wall reaction in the region  $z > 0$  is first order in concentration

$$-D \frac{\partial c}{\partial \rho} = \begin{cases} r(T_w) \cdot c & z > 0 \\ 0 & z < 0 \end{cases} \text{ on } \rho = a \quad (10)$$

where

$$r(T_w) = r_0 \exp \left\{ -\frac{E}{R} \left( \frac{1}{T_w} - \frac{1}{T_0} \right) \right\} \quad (11)$$

is the Arrhenius form of the reaction rate and  $T_w(z)$  is the temperature at the wall. In Eqn. (11),  $r_0$  is the rate constant,  $E$  is the activation energy and  $R$  is the gas constant. Note that  $r_0$  is the effective reaction rate parameter at the undisturbed temperature  $T_0$  and has the dimension of a velocity.

(vi) The jump in the transverse heat flux at  $\rho = a$  equals the rate at which heat is produced there by the chemical reaction

$$-K \frac{\partial T}{\partial \rho} + k \frac{\partial T_g}{\partial \rho} = \begin{cases} -qD \frac{\partial c}{\partial \rho} & z > 0 \\ 0 & z < 0 \end{cases} \text{ on } \rho = a \quad (12)$$

where  $K$  and  $k$  are the constant thermal conductivities of the metal and the gas respectively and  $q$  is the heat of reaction.

At this stage, we can make a major simplification by assuming that the heat flux into the gas is much smaller than that into the metal. From boundary condition (12), we can see that this is valid if

$$\frac{kl}{K\delta} \ll 1 \quad (13)$$

where  $\delta \sim D/r$  is a typical boundary layer thickness in the gas. A representative value for  $k/K$  is  $2.5 \times 10^{-3}$  and therefore condition (13) holds provided  $\delta/l$  is not too small. Obviously condition (13) cannot be uniformly valid in the boundary layer as  $\delta$  vanishes at  $z = 0$ , however it can be checked a posteriori that the heat flux into the gas from this very small region (where  $\delta \approx kl/K$ ) is negligible. Assuming that condition (13) holds, then almost all the heat generated at the gas/metal interface is conducted away by the metal and we do not need to consider the temperature problem in the gas any further. The heat flux into the gas can be calculated using a perturbation method, taking the present problem as the zeroth order solution.

The equations governing the concentration problem in the gas and the temperature problem in the metal can be written in terms of the dimensionless variables

$$y^* = \frac{a - \rho}{l}, \quad x^* = \frac{z}{l}, \quad c^* = \frac{c}{c_0},$$

$$\theta^* = N \left( \frac{T}{T_0} - 1 \right) \text{ where } N = \frac{E}{RT_0}. \quad (14)$$

We can see from boundary condition (10) that there is a natural length scale for  $\rho$  in the gas of  $D/r$  and hence from Eqn. (3) that the natural length scale for  $z$  in the gas is  $4u_0 D^2/ar^3$ . As both these length scales depend upon the unknown reaction rate, we have chosen to scale all lengths on  $l$ , the natural length scale for  $\rho$  and  $z$  in the metal.

Dropping the starred notation, Eqns. (3) and (5) become

$$\beta^3 y \frac{\partial c}{\partial x} = \frac{\partial^2 c}{\partial y^2} \quad (15)$$

and

$$\frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} = 0 \quad (16)$$

where

$$\beta^3 = \frac{4u_0 l^2}{aD}. \quad (17)$$

In the derivation of Eqn. (16), we have assumed that  $l \ll a$ .

From the Eqns. (6)–(12), the dimensionless boundary conditions satisfied by  $c(x, y)$  and  $\theta(x, y)$  are

$$\theta = 0 \text{ at } y = -1, \quad \text{all } x, \quad (18)$$

$$\theta \rightarrow 0 \text{ as } |x| \rightarrow \infty, \quad -1 < y < 0, \quad (19)$$

$$c = 1 \text{ at } x = 0, \quad y > 0, \quad (20)$$

$$c \rightarrow 1 \text{ as } y \rightarrow \infty, \quad x > 0, \quad (21)$$

$$\frac{\partial c}{\partial y} = \begin{cases} \lambda(\theta_w)c & x > 0 \\ 0 & x < 0 \end{cases} \quad \text{on } y = 0, \quad (22)$$

where

$$\lambda(\theta_w) = \lambda_0 \exp\left\{\frac{\theta_w}{1 + \frac{\theta_w}{N}}\right\}, \quad \lambda_0 = \frac{r_0 l}{D} \quad (23)$$

and  $\theta_w(x)$  is the dimensionless wall temperature,

$$\frac{\partial \theta}{\partial y} = \begin{cases} Q \frac{\partial c}{\partial y} & x > 0 \\ 0 & x < 0 \end{cases} \quad \text{on } y = 0 \quad (24)$$

where

$$Q = \frac{qDc_0E}{KRT_0^2}. \quad (25)$$

We can see that the nature of the solution is determined by 4 independent dimensionless parameters:  $N$ ,  $\lambda_0$ ,  $Q$  and  $\beta$ . The parameter  $N$  measures the dependence of the reaction on temperature,  $\lambda_0$  determines the speed of the reaction at the constant temperature  $T_0$  and  $Q$  measures the strength of the reaction. The parameter  $\beta^3$  is a measure of the relative effects of convection and diffusion in the boundary layer when the spacial variables are scaled on  $l$ . In practice  $\beta^3$  is large which reflects the fact that the length  $l$  is not the appropriate length scale in the boundary layer.

The method of solution that we shall adopt is to derive two coupled integral equations for the temperature  $\theta_w(x)$  and the mass flux  $(\partial c / \partial y)_{y=0}$  at the wall. These equations will be solved numerically and it is then straightforward matter to determine both the concentration distribution in the gas and the temperature distribution in the metal. However the quantity of most practical importance is  $\theta_w(x)$ .

The gas concentration problem can be readily reduced to an integral equation by using Laplace transforms. Defining the Laplace transform

$$\bar{c}(p, y) = \int_0^\infty c(x, y) e^{-px} dx \quad (26)$$

we find that  $\bar{c}(p, y)$  is given by

$$\bar{c}(p, y) = \frac{1}{p} + \beta^{-1} p^{-1/3} \frac{\partial \bar{c}}{\partial y}(p, 0) \frac{A_i(\beta p^{1/3} y)}{A_i'(0)} \quad (27)$$

where  $A_i(\xi)$  is the Airy function [5].

Using the convolution theorem, we can formally invert Eqn. (27) and so by putting  $y = 0$  and using boundary condition (22), we obtain the integral equation

$$\frac{f(x)}{\lambda(\theta_w(x))} = 1 - \frac{1}{\beta 3^{1/3} \Gamma(\frac{2}{3})} \int_0^x f(t) (x-t)^{-2/3} dt \quad (28)$$

where  $f(x) = (\partial c / \partial y)_{y=0}$  is the dimensionless mass flux at the wall and  $\lambda(\theta_w(x))$  is given by Eqn. (23). Equation (28) is a weakly singular Volterra integral equation of the second kind for  $f(x)$  and may be solved numerically for a given  $\theta_w(x)$ , [6].

The solution to the heat conduction problem in the metal, defined by Eqn. (16) with the boundary conditions (18), (19) and (24), can be written in the form

$$\theta(x, y) = Q \int_0^\infty f(X) G(x - X, y) dX \quad (29)$$

where  $G(x - X, y)$  is the Green's function for the problem, that is, the solution to the heat conduction equation which satisfies the boundary conditions (18) and (19), but replaces condition (24) by a unit point source of heat at  $x = X$ , the rest of the surface  $y = 0$  being insulated. It may be shown by the method of images that

$$G(x - X, y) = \frac{1}{2\pi} \operatorname{Re} \left[ \ln \coth^2 \left\{ \frac{1}{4} \pi (x - X + iy) \right\} \right]. \quad (30)$$

Hence by putting  $y = 0$  in Eqn. (29), we find that

$$\theta_w(x) = \frac{Q}{2\pi} \int_0^\infty f(X) \ln \left\{ \coth^2 \frac{1}{4} \pi (x - X) \right\} dX. \quad (31)$$

This integral equation may be solved numerically to determine  $\theta_w(x)$  provided  $f(x)$  is known. Hence we have obtained two coupled integral equations (28) and (31).

For the purpose of illustration we have chosen the following numerical values:  $N = 6.8$ ,  $\lambda_0 = 7.2$ ,  $Q = 3.7 \times 10^{-1}$  and  $\beta = 4.2$ .

#### 4. The solution for infinite reaction rate

This represents an important limiting case of the previous theory in which the concentration at the wall is zero for  $x > 0$  because the gas at the wall is completely destroyed by the reaction. The results obtained are therefore independent of the assumed form of the reaction kinetics.

Formally taking  $\lambda_0 = \infty$ , Eqn. (28) becomes

$$\frac{1}{\beta 3^{1/3} \Gamma(\frac{2}{3})} \int_0^x f(t)(x-t)^{-2/3} dt = 1 \tag{32}$$

which has the solution

$$f(x) = \frac{\beta \Gamma(\frac{2}{3}) 3^{5/6}}{2\pi} x^{-1/3}. \tag{33}$$

This result can of course be obtained directly from Eqn. (15) by looking for a similarity solution. Using Eqn. (31), the corresponding wall temperature may be written in the form

$$\theta_w^\infty(x) = \frac{Q\beta \Gamma(\frac{2}{3}) 3^{5/6}}{4\pi^2} \int_0^\infty X^{-1/3} \ln\{\coth^2 \frac{1}{4}\pi(x-X)\} dX. \tag{34}$$

It is evident from this equation that  $\theta_w^\infty(x)$  has magnitude  $\beta Q$  and that the corresponding dimensional temperature rise is of order

$$(\Delta T)_\infty = \frac{qDc_0}{K} \left[ \frac{u_0 l^2}{aD} \right]^{1/3}. \tag{35}$$

Thus  $(\Delta T)_\infty$  is proportional to  $l^{2/3}$  and so as expected, decreases as the thickness of the metal wall decreases. The temperature rise also depends upon the radius of the tube  $a$ , via the shear of the velocity profile;  $u_0/a$ , however  $(\Delta T)_\infty$  is not sensitive to this parameter.

The graph of  $\theta_w^\infty(x)/\beta Q$  is shown in Fig. 1. The temperature profile has a sharp

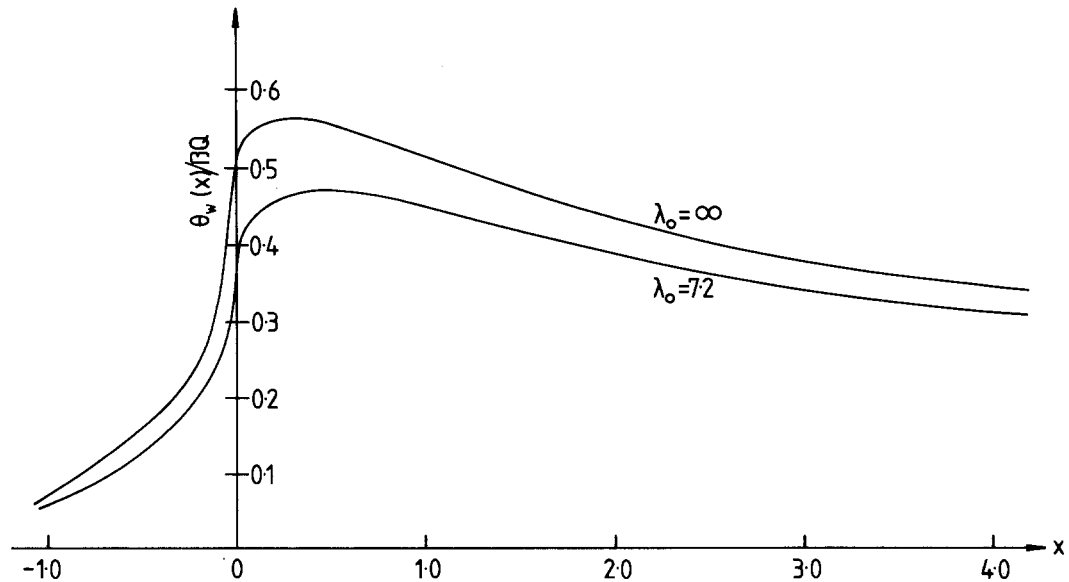


Figure 1. The variation of  $\theta_w^\infty(x)/\beta Q$  with  $x$  for  $\lambda_0 = \infty$ ,  $\lambda_0 = 7.2$ .

maximum near  $x = 0.3$  and the effect of axial conduction of heat can be seen in the region  $x < 0$ . It is worth noting that if the effect of axial conduction in the metal is ignored, then the temperature rise at  $x = 0$  is infinite. Hence axial conduction plays a crucial role in the determination of the maximum temperature in this case.

We can easily show that if the reaction rate is finite, then the maximum temperature rise is reduced and consequently  $\theta_w^\infty(x)$  gives an upper estimate of the dimensionless temperature rise. The temperature in the interior of the metal may be determined from Eqns. (29) and (30) if it is required.

### 5. The surface temperature for a first order wall reaction

To obtain the temperature at the gas/metal interface we have to solve two coupled integral equations, (28) and (31). The numerical procedure that we adopted involved approximating  $f(x)$  by a piecewise linear function and then evaluating the integral in Eqn. (28) analytically. In this way we were able to generate a recurrence relation for the values of  $f(x)$  at the end of each interval, provided that  $\theta_w(x)$  was given [6]. Having obtained this result, Eqn. (31) was evaluated using a standard integration routine, to give us the value of  $\theta_w(x)$  at the end of each interval. The final solution was then obtained by iteration.

The graph of  $\theta_w(x)/\beta Q$  against  $x$  is shown in Fig. 1 for a typical value of  $\lambda_0$ . It was found that of the four dimensionless parameters the quantity  $\theta_w(x)/\beta Q$  was most sensitive to  $\lambda_0$ , the main dependence of  $\theta_w(x)$  on  $\beta$  and  $Q$  being given by the factor  $\beta Q$ . Fig. 2 illustrates how the maximum value of  $\theta_w(x)/\beta Q$  varies with  $\lambda_0$ . It was found that the position of the maximum temperature rise is 0.3 for  $\lambda_0 = \infty$  and moves slowly away from  $x = 0$  as  $\lambda_0$  decreases.

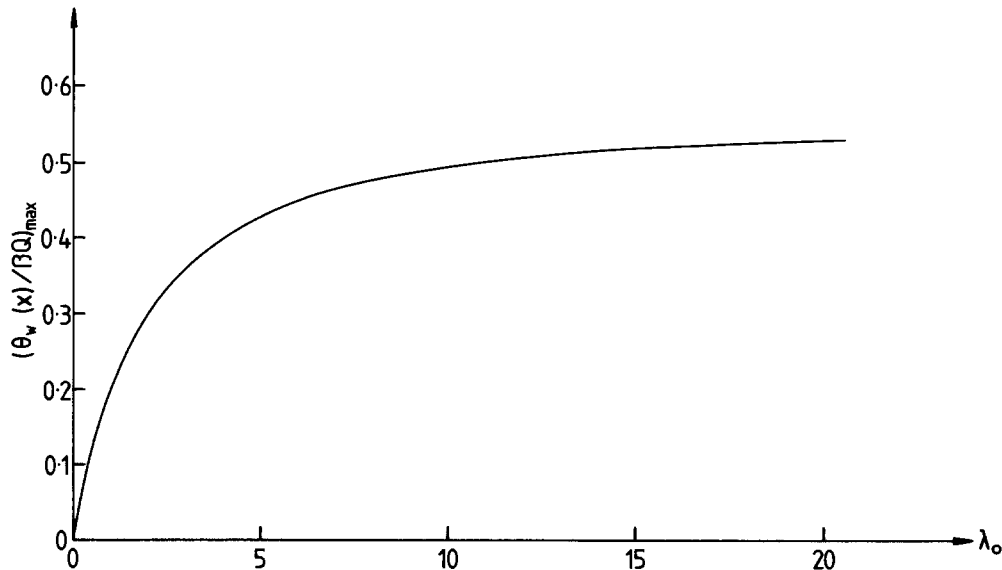


Figure 2. The variation of the maximum value of  $\theta_w(x)/\beta Q$  with  $\lambda_0$ .



## 6. Conclusions

We have determined the temperature distribution which may be expected when a reacting gas flows over a catalytic coating of negligible thickness, assuming that the reaction is first order and that the heat flow into the gas is small compared with the flux into the metal wall. In this problem, the quantity of heat generated is a sensitive function of the wall temperature and so there exists a strong coupling between the concentration field in the gas and the heat conduction problem in the metal casing. The maximum temperature rise possible occurs when the reaction rate is infinite and in this case, the results are independent of the assumed kinetics. The position and magnitude of the temperature maximum are determined by axial and radial conduction of heat in the metal wall surrounding the gas.

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