Int. J. Heat Mass Transfer. Vol. 33, No. 9, pp. 2056–2059, 1990
Printed in Great Britain

0017-9310/90 \$3.00+0.00

Critical conditions for natural convection induced by a surface reaction

S. PUSHPAVANAM† and R. NARAYANAN‡
Department of Chemical Engineering, University of Florida, Gainesville, FL 32611, U.S.A.

(*Received* 6 *October* 1988 *and in final form* 11 *December* 1989)

INTRODUCTION

IN THIS note we consider the initiation of natural convection in a fluid, induced by heat generation due to the exothermicity of a zeroth-order surface reaction. The two problems of (1) initiation of natural convection due to an adverse temperature gradient and (2) ignition/extinction of a zeroth-order chemical reaction following Arrhenius kinetics have been investigated separately and extensively in the literature [1, 2]. There is one characteristic difference between these two problems. The onset of instability for natural convection is characterized by a critical disturbance with a finite non-zero wave number. In contrast, thermal ignition occurs through a disturbance with zero wave number. Consequently one observes spatial structures at the onset of instability for natural convection and none for ignition. The prime purpose of this study is to examine the interaction of these two instabilities in an effort to understand the formation and disappearance of spatial structures. It also offers a possible mechanism using a continuum approach for the occurrence of spatial structures on reacting surfaces [3, 4]. This problem is reminiscent of the classical Benard problem with heat generation now being accomplished by the exothermicity of the chemical reaction. In this note we present preliminary results on the initiation of natural convection in a quiescent fluid using a linear stability analysis of the governing nonlinear equations. Exchange of stabilities follows as a natural consequence. This ensures that the onset of convection is time independent.

MODEL ASSUMPTIONS AND GENERAL FEATURES

The model we propose to analyze is based on the following assumptions.

(1) The catalyst is coated on the surface of a slab which is of finite vertical thickness, extending to infinity in the two horizontal directions (Fig. 1). The bottom surface of the slab is maintained at a constant temperature. The reactant fluid is of finite thickness and its top surface is maintained at constant temperature.

(2) The surface catalyst coating is the site for a zeroth-order reaction. No reaction occurs in the bulk of the solid. This kind of kinetics is observed in the high concentration regimes, where concentration variation is negligible and the concentration can be effectively considered a constant.

The Boussinesq equations are used in the fluid phase [5] while the energy equation in the solid phase assumes constant properties.

The boundary conditions are given in Fig. 1 and the interface condition, aside of continuity in temperature, is

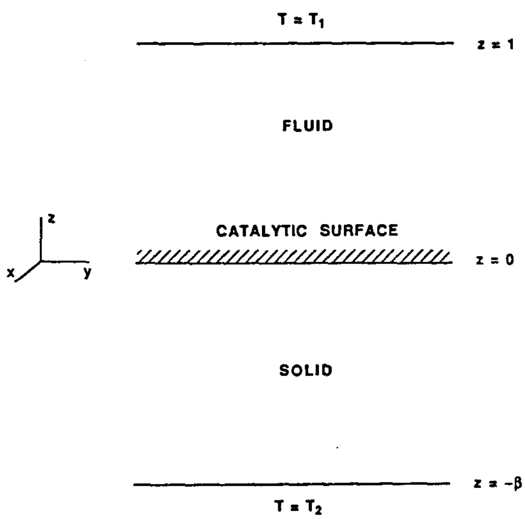

FIG. 1. Schematic diagram of the model described in the text.

$$\delta \exp\left[-\left(\frac{1}{\varepsilon_2\theta_i+\varepsilon_2}\right)\right] = GD\theta_s - D\theta_f + \alpha_i^f\frac{\partial\theta_i}{\partial\tau}. \quad (1)$$

The steady, quiescent, conduction solution gives rise to θ_{ic} (the conduction interface temperature) as a solution of

$$\delta f(\theta_{ic}) = \frac{G\theta_{ic}}{\beta} - (\varepsilon_1 - \theta_{ic}) \quad (2)$$

where

$$f(\theta_{ic}) = \exp\left[-\frac{1}{\varepsilon_2(\theta_{ic}+1)}\right]. \quad (3)$$

The subscript 'c' is used to denote the conduction solution, as here the heat transfer in the system occurs only through conduction. Equation (2) is similar to the equation describing the effluent steady-state temperature of a CSTR (continuous stirred tank reactor) supporting a zeroth-order reaction. This equation has a unique solution if and only if $\varepsilon_3 \geqslant \frac{1}{4}$. For $\varepsilon_3 < \frac{1}{4}$ the equation has three solutions for some values of P, where

$$P = (G+\beta+\varepsilon_1\beta)/\delta\beta$$

and

$$\varepsilon_3 = \varepsilon_2\left(1+\frac{\varepsilon_1\beta}{G+\beta}\right).$$

Throughout the rest of the note we set $\varepsilon_1 = 0$. The variation of θ_{ic} with δ as described by equation (2) is shown in Fig. 2(a). Branches AB and CD are stable and BC is unstable [6]. Point B is called the ignition point and C the extinction point. We observe that this base state is valid for all Rayleigh numbers. For $\varepsilon_1 = 0$, we can conclude from equation (2) that

† Present address: Department of Chemical Engineering, I.I.T. (Kanpur), U.P. 208016, India.
‡ Author to whom correspondence should be addressed.

NOMENCLATURE

a	wave number, $a^2 = a_x^2 + a_y^2$
Bi_{eq}	equivalent Biot number, $-\delta(\partial f/\partial\theta)\|_{\theta=\theta_{ic}} + Ga\coth(a\beta)$
g, G	gravitational constant, thermal conductivity ratio of solid to fluid
ΔH	heat of reaction
k_0	reaction rate constant
K_f	thermal conductivity of fluid
L	dimensional fluid depth
P_M	modified pressure
Pr	Prandtl number, ν/α
R, E	gas constant and energy of activation
Ra	Rayleigh number, $g\alpha_v L^3 T_2/\alpha_f \nu$
U, V, W	velocity components in the x-, y-, z-directions of velocity vector $\mathbf{v}$.

Greek symbols

α_i^f	thermal diffusivity ratio of interface, $\rho_i C_{pi} L^2/\nu K_f$
α_v, α_f	thermal expansion coefficient and thermal diffusivity of fluid
β	dimensionless depth of solid
δ	heat of reaction parameter, $(-\Delta H)k_0 L/K_f T_2$
$\varepsilon_{1,2}$	top and bottom plate temperature (reduced), $(T_1-T_2)/T_2$ and RT_2/E
θ	reduced dimensionless temperature, $(T-T_2)/T_2$
ν	kinematic viscosity of fluid
ρ_i, C_{pi}	density and specific heat of interface
τ	time.

Subscripts

i, f, c	interface, fluid and conduction states.

θ_{ic} must always be positive. The analog of the slope condition for stability gives the following inequality along the stable branches:

$$\frac{G}{\beta} + 1 - \delta \left.\frac{\partial f(\theta)}{\partial \theta}\right|_{\theta=\theta_{ic}} > 0.$$

Stability of the conduction or quiescent state is considered by subjecting it to an infinitesimal disturbance in the dependent variables such as $(U^*, V^*, W^*, \theta_f^*, \theta_s^*)\,e^{\sigma t}$. Linearization about the quiescent conduction state gives

$$(D^2-a^2)^3\theta_f^+ = -a^2\,Ra\,\theta_{ic}\theta_f^+ \quad (4)$$

subject to

$$(D^2-a^2)\theta_f^+(0) = D(D^2-a^2)\theta_f^+(0) = (D-B_{ieq})\theta_f^+(0) = 0 \quad (5)$$

$$\theta_f^+(1) = (D^2-a^2)\theta_f^+(1) = D(D^2-a^2)\theta_f^+(1) = 0. \quad (6)$$

Here $\theta_f^* = \theta_f^+(Z)\,e^{i(a_x x + a_y y)}$ and $D \equiv d/dz$.

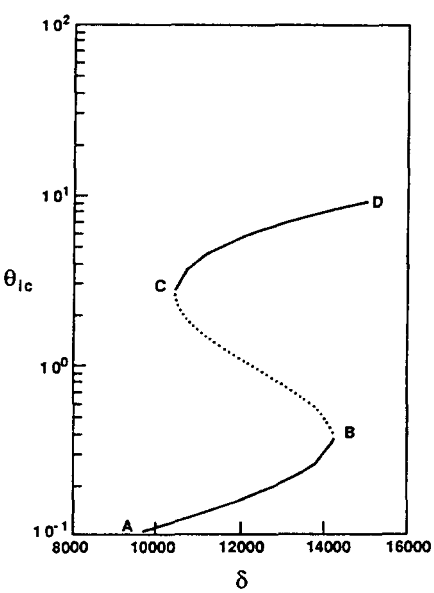

FIG. 2(a). Variation of θ_{ic} with δ. AB corresponds to low temperature steady state. CD corresponds to high temperature steady state.

In the above we have set $\sigma = 0$ since we can show that it is real (exchange of stability) and treat Ra as an eigenvalue. The minimum Ra for all values of a gives the critical condition for the onset of convection. Equations (4)–(6) are derived in a manner similar to Sparrow *et al.* [7].

DISCUSSION AND RESULTS

The Boussinesq and the associated boundary conditions are nonlinear in more than one way. The two important nonlinearities are the $\mathbf{v}\cdot\nabla\theta_f$ term in the energy equation (i.e. $\partial\theta_f/\partial\tau + \mathbf{v}\cdot\nabla\theta_f = (1/Pr)\nabla^2\theta_f$) and the exponential term in equation (1) which is a boundary condition. It is these nonlinearities that lead to bifurcation behavior and subsequent linearization helps in the calculation of these bifurcation points.

We observe that for a fixed δ we may calculate a lower or upper value of θ_{ic} (from Fig. 2(a)). This leads to a corresponding value of Bi_{eq} (see Nomenclature) which is inserted in equation (5). Thus Ra is the eigenvalue parameter and the minimum Ra with respect to a is called Ra_c. This is plotted in Fig. 2(b) as a function of δ.

As an example, if $\delta = 12\,000$ and θ_{ic} is on AB of Fig. 2(a), then Ra_c is calculated and resides on A′B′ of Fig. 2(b). To make this clear let us assume that $\delta = 12\,000$. Let Ra_{c1} be the critical Ra corresponding to the upper value of θ_{ic} and Ra_{c2} be the critical value corresponding to the lower value of θ_{ic}. If the operative value of $Ra = 200$, then we must have a stable conductive solution since we would be in Region I of Fig. 2(b) and below the critical Rayleigh numbers (Ra_c) corresponding to the lower or upper values of θ_{ic}. If $Ra = 20\,000$ we would be in a convective region (Region II) since $Ra > Ra_c$. If $Ra = 2000$, then we are in a zone where the $Ra > Ra_{c1}$ and yet $Ra < Ra_{c2}$.

We conjecture that Region III, on non-linear analysis, will lead to interesting dynamic behavior. This may well be true because departure from the high temperature steady state via convection may cause us to approach the low temperature steady state and remain there. For large perturbations it is possible to return to the high temperature convecting state. These conjectures cannot be verified with the simple linearized calculations presented here. However, our calculations are important because they bring out the peculiar bifurcation behavior in the first place. The generation of Fig. 2(b) is thus the central part of this note.

The computation of Ra_c, the critical Ra, can be carried out by two methods. The first involves solving equation (5) subject to equation (6), numerically. This can be done using the Frobenius method. The calculation involves minimizing

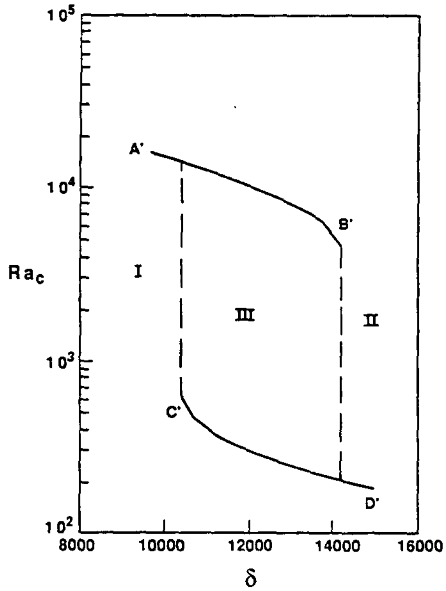

FIG. 2(b). Variation of Ra_c with δ. Region I is a region of steady stable conduction. In Region II natural convection occurs. In Region III the high temperature steady state is unstable to convection but for the low temperature steady state we have no convection. Here $G = 1000.0$, $\varepsilon_1 = 0$, $\varepsilon_2 = 0.2$, $r_T = 1.0$. C′, B′ correspond to C, B of Fig. 2(a).

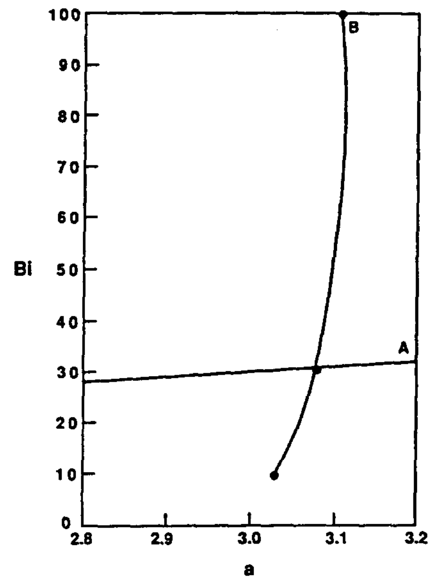

FIG. 3. Calculation of Ra_c using Sparrow *et al.*'s results. Curve A represents variation of 'Bi_{eq}' as a function of 'a'. Curve B is from Sparrow *et al.*'s table. Here $G = 10.0$, $\delta = 4170.0$, $\varepsilon_1 = 0$, $\varepsilon_2 = 0.08$, $\theta_{ic} = 0.0014$, $Ra_c = 0.1160 \times 10^7$, $a_c = 3.061$, $Bi_{eq} = 30.48$.

the eigenvalue Ra over all wave numbers 'a'. The minimum value of Ra then is the critical Rayleigh number Ra_c and the corresponding wave number 'a_c' gives the wave number of the most unstable mode.

In the second method we utilize the results of Sparrow *et al.* [7]. The parameter Bi_{eq} can be viewed as an equivalent Biot number. The calculation of Bi_{eq} as a function of 'a' needs only the knowledge of the interface temperature at the conduction state. We can then use Sparrow *et al.*'s results to help us calculate the critical wave number (a_c) and critical Rayleigh number (Ra_c), respectively. In their paper they present values of Ra_{mc} (critical Ra_m where $Ra_m = Ra\,\theta_{ic}$) and a_c for various Biot numbers. We can use these results to compute our critical parameters. The method involves plotting their Biot number as a function of a_c. Ra_{mc} is then a parameter along this curve (i.e. each point on this curve corresponds to a different Ra_{mc}). We can plot our Bi_{eq} as a function of 'a' since the functional dependence is known explicitly. The intersection of these two curves gives us the Ra_{mc}, a_c, Bi_{eq} at critical conditions. In Fig. 3 we use this method and find the numerically calculated value of Ra_{mc} to be 1667.8 and from the graph the prediction is 1667.1 for $\theta_{ic} = 0.0014$. We can use this method provided the two curves intersect. When the curves do not intersect, typically for sufficiently low G or δ close to the ignition or extinction points the equivalent critical Bi may be negative and we may have to resort to our numerical calculations. For this purpose we have extended the calculations to negative values of Bi_{eq}. The results are presented in Table 1. Boundary conditions (6) will change to reflect calculations for the case when the top surface is stress free. Using the slope condition for stability of the conduction state we get a lower bound for Bi_{eq}. Along the stable conduction branches $Bi_{eq} \geqslant -1$.

We next consider the dependence of Ra_c on 'G' (thermal conductivity ratio $= K_s/K_f$). We note that for sufficiently high values of G, the Ra_c on suitable renormalization equals 1707 [1]. Here the equivalent critical Biot number is very high and so we approximate Dirichlet boundary conditions very closely at the interface. Physically Dirichlet boundary conditions correspond to negligible resistance to heat transfer or high thermal conductivity. Increasing G has a stabilizing effect on the incidence of convection and it raises Ra_c. For intermediate values of G, Sparrow *et al.*'s [7] results may be used for comparing with our numerical calculations (Fig. 3). This corresponds to the case of intermediate Biot numbers. For low values of G (i.e. insulating solid) the effective Biot number becomes negative and we have to calculate Ra_c by a separate procedure.

We note that the pure surface reaction problem with no convection is characterized at the critical points (hereafter designated as the pure ignition and extinction) by disturbances of zero wave number or infinite wavelength. This precludes the formation of spatial structures. The introduction of convection in the surface reaction induces spatial structures along the surface of the catalyst since now the critical wave number of the disturbance is nonzero. As we move closer to the ignition and extinction points the critical wave number moves to zero and Bi_{eq} tends to -1. The

Table 1. Critical wave numbers and Rayleigh numbers for a horizontal layer of fluid with Dirichlet conditions for temperature at the top

	Top surface rigid		Top surface free	
Bi	a_c	Ra_{mc}	a_c	Ra_{mc}
0†	2.55	1295.7	2.21	816.7
−0.1	2.51	1280.8	2.18	805.5
−0.3	2.43	1246.3	2.11	779.4
−0.5	2.32	1203.4	2.01	746.6
−0.7	2.14	1146.3	1.85	702.3
−0.9	1.77	1056.8	1.51	630.8
−0.99	1.13	970.55	1.07	572.8
−0.998	0.79	949.43	0.53	535.6
−1.0‡	0.0	933.34	0.0	525.0

† Compare with Sparrow *et al.* [7].
‡ Obtained from an asymptotic analysis.

limit $a_c \to 0$, $Bi_{eq} \to -1$ satisfies the linearized equations with $\theta_f' = A_1(1-z)$ with A_1 being any arbitrary constant.

In conclusion, we have examined the onset of natural convection induced by an exothermic surface reaction with the hope of capturing the phenomena of generation of spatial thermal structures along the solid fluid interface. In so doing, we have revealed an interesting connection between the bifurcation behavior of a stirred tank reactor with an exothermic reaction and the bifurcation behavior of the classical Benard problem.

REFERENCES

1. S. Chandrasekhar, *Hydrodynamic and Hydromagnetic Stability*. Oxford University Press, Oxford (1961).
2. T. Boddington, C. G. Feng and P. Gray, Thermal explosions, criticality and the disappearance of criticality in systems with distributed temperatures. Arbitrary Biot number and general reaction rate law, *Proc. R. Soc. London* **A390**, 247 (1983).
3. K. F. Jensen and W. H. Ray, The role of surface structures in the dynamic behavior of heterogeneous catalytic systems. In *Dynamics of Non-linear Systems* (Edited by V. Hlavacek) (1986).
4. J. A. Vastano, J. E. Pearson, W. Horsthemke and H. L. Swinney, Chemical pattern formation with equal diffusion coefficients, *Phys. Lett. A* **124**, 320 (1987).
5. D. D. Joseph, *Stability of Fluid Motions*, Vol. II. Springer, Berlin (1976).
6. A. B. Poore, A model equation arising from chemical reactor theory, *Arch. Ration. Mech.* **52**, 358 (1973).
7. E. M. Sparrow, R. J. Goldstein and V. K. Jonsson, Thermal instability in a horizontal fluid layer—effect of boundary conditions and non-linear temperature profile, *J. Fluid Mech.* **18**, 513 (1964).

Int. J. Heat Mass Transfer. Vol. 33, No. 9, pp. 2059–2061, 1990
Printed in Great Britain

0017-9310/90 $3.00+0.00

The asymmetric Graetz problem in a radial capillary gap cell

RAVINDRA V. SHENOY and JAMES M. FENTON

Department of Chemical Engineering, The University of Connecticut, Storrs, CT 06269, U.S.A.

(*Received* 14 *July* 1989 *and in final form* 11 *December* 1989)

INTRODUCTION

THE RADIAL capillary gap cell (RCGC) was originally developed by Beck and Guthke [1]. The RCGC consists of two or more circular parallel plates with the electrolyte entering the cell through a central inlet and flowing outward in the radial direction as shown in Fig. 1. This cell finds application in electro-organic syntheses where the electrolyte has low conductivity and the electrodes must be placed close together to minimize ohmic resistance losses. The typical gap width for these cells range from 0.1 to 1 mm. The RCGCs are also used as coulometric cells for adsorption studies and coulometric metal detectors [2].

Dworak and Wendt [3] solved the convective diffusion equation for the mass transfer to the electrodes in an RCGC. A parabolic velocity profile was assumed which was true for creeping flow. Several other assumptions were made for convenient mathematical treatment which limited the utility of the work to the symmetric Graetz problem and for thin, non-interacting boundary layers. The local mass transfer coefficient was calculated using a Leveque type approximation. Burgi *et al.* [2] analyzed the mass transfer for an RCGC electrochemical detector. Nondimensionalization was used to transform the convective diffusion equation for the RCGC into that of the Graetz problem in rectangular ducts. Eigenvalues and eigenfunctions obtained by Brown [4] were then used to solve the problem of mass transfer in the electrochemical detector, with symmetric boundary conditions at the electrodes.

The objective of this work was to analyze the mass transfer in an RCGC with creeping flow for the asymmetric Graetz problem. Nondimensionalization was used to extend the solutions for the asymmetric Graetz problem in rectangular ducts developed by Edwards and Newman [5] to the RCGC. The variation of the local Sherwood number, as a function of Reynolds and Schmidt number, for various cases has been presented. The analysis was also extended to laminar flow with a non-parabolic velocity profile.

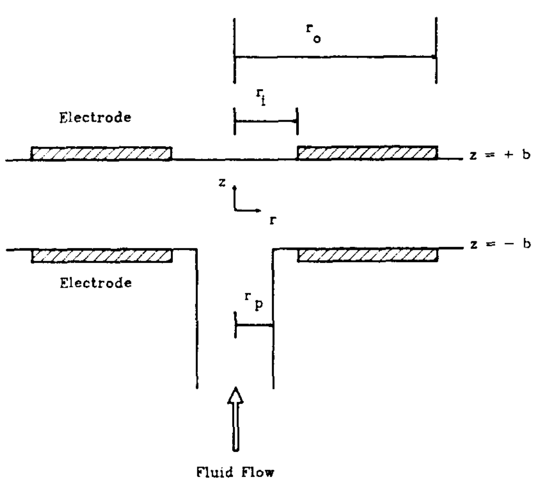

FIG. 1. Schematic of a radial capillary gap cell.

MODEL STATEMENT

The convective diffusion model for an RCGC has been discussed in detail by Dworak and Wendt [3] and Burgi *et al.* [2]. The convective diffusion equation for the RCGC, where radial diffusion is neglected, is given by

$$v_r \frac{\partial C}{\partial r} = D \frac{\partial^2 C}{\partial z^2} \tag{1}$$

where for creeping flow

$$v_r = \frac{3Q}{8\pi b r}\left(1 - \frac{z^2}{b^2}\right).$$

The model equation is nondimensionalized to the following form:

$$(1-\xi^2)\frac{\partial \Theta}{\partial \zeta} = \frac{\partial^2 \Theta}{\partial \xi^2} \tag{2}$$