Influence of Secondary Flows on the Stability of Chemically Reacting Systems

A model is presented for convection and chemical reacton in porous media. An irreversible chemical reaction of arbitrary order is considered. Reactant depletion allows for basic solutions in either the kinetic or the diffusion regime. The cases of forced flow parallel to the lateral walls of the cavity and a closed system are addressed. A linear stability analysis of the basic states is performed and critical values of the thermal Rayleigh number for the onset of natural convection are determined. A dispersion relation is derived and a graphical representation of the linear stability analysis results is provided for typical values of the system parameters. Analytical predictions are verified by results obtained by numerical integration of the complete set of nonlinear partial differential equations. The effect of natural convection is discussed when the basic state is either in the kinetic or in the diffusion regime. For large gradients, associated with the diffusion regime, chemical reaction can drive free convection even for low values of the Rayleigh number. In forced flow systems, natural convection can change substantially the flow pattern of the system.

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Introduction

Natural convection in confined porous media has received much attention in the last decades (Combarnous and Bories, 1975). Most of the work has been devoted to the case of a global driving force that results from a thermal gradient applied to the boundaries of the system.

As changes in the density lead to natural convection, chemical reactions can provide a distributed driving force for free convection phenomena. Usually it is assumed that there is no free convection in chemical reactors, and that the effect of variable density can be safely neglected. Experimental evidence in chemically reacting systems (Mikus et al., 1979) indicates that in many important situations the influence of the natural convection cannot be overlooked. Indeed, recent studies have shown that under certain conditions the influence of the flow field can be important and that reaction fronts, apparently planar, can be corrugated due to the variable-density effect (Sivashinsky and Matkowsky, 1981).

The conditions for the onset of convective instabilities are represented by the critical value of the Rayleigh number. Thus, occurrence of natural convection instabilities can be neglected only for systems with subcritical values of the Rayleigh number.

Two problems are manifested in studying the progress of a chemical reaction under natural convection conditions: First, the onset and development of natural convection because of the chemical reaction and, second, the influence of the development of the free convection on the progress of the reaction. An example of the first problem is the transition from a conduction-reaction regime to a conduction-convection-reaction regime. An example of the second problem is the operation of a chemical vapor deposition (CVD) reactor, where the existence of natural convection could be a potential source of film nonuniformities.

A large volume of information has been published on the onset of convection in nonreacting systems. However, there is need for a systematic study of the effect of chemical reaction on the occurrence of convective instabilities. Gatica et al. (1987) addressed the special cases of isothermal *reactions and zero*-order reactions without reactant depletion. A linear stability analysis was performed and neutral stability conditions were confirmed by numerical results. Steinberg and Brand (1983) investigated the instabilities of a binary mixture with fast chemical reaction when heated from below or from above. They found that oscillatory modes can exist, depending on the sign and mag-

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nitude of the heat of reaction. Viljoen and Hlavacek (1987) studied the nonlinear interaction between different convective models and the conduction state for the case of zero-order reaction. This is a natural extension of the linear stability analysis and useful information on the stability of the convective state is extracted from this analysis. A similar approach was used by Bdzil and Frisch (1980) to treat the case of a dissociating fluid superimposed on the Benard problem. Their results indicate the effect of a chemical reaction on the conventional Benard results. In this study an irreversible chemical reaction of arbitrary order is considered. Reactant depletion is taken into consideration and thus different basic states can exist. Solutions in the kinetic regime are characterized by quasi-linear temperature profiles. Temperature profiles in the diffusion regime are typically nonlinear, and as the heat released increases, boundary layers are formed.

Most of the work on the onset of convection in porous media (with or without chemical reaction) has assumed that the fluid in the basic equilibrium state is motionless. The treatment of flow instabilities for systems with throughflow is incomplete (Jones and Persichetti, 1986). Both closed and flow systems are analyzed in this paper. In the rest of the text, "closed system" refers to a confined porous medium saturated with reactive fluid. The two lateral walls as well as the bottom are considered nonpermeable and adiabatic. The upper plane is kept at a constant temperature and allows fresh reactant to diffuse into the system. Figure 1 presents the scheme of the reaction system.

Model Formulation

The analysis of flow and heat and mass transfer processes in chemically reacting systems is usually based on the transport equations resulting from the differential balance laws. Detailed information on the velocity profiles and the concentration and temperature fields is extracted from the solution of the associated transport equations subject to the pertinent boundary conditions. When reactive flow through a complex structure such as a porous medium is involved, these equations are still valid inside the pores, but the geometric complexity prevents general solutions of the detailed velocity profiles and the concentration and temperature fields. Instead, some form of macroscopic balance based on the average over a small volumetric element must be employed.

For the mathematical treatment of the heat and mass transfer processes in fixed beds, with or without chemical reaction, two general types of models have been developed:

1. The one-phase, known as pseudohomogeneous, model; where the reactor is approximated by a quasi-continuum medium
2. The two-phase, also called heterogeneous, model; where both phases, solid and fluid, exchange heat and/or mass, and such transport processes are accounted for separately

Of these two models, the second is clearly more realistic. However, Vortmeyer et al. (1974) have shown that a reliable *description of the* temperature and concentration fields in packed beds can be attained through a pseudohomogeneous model if the transport coefficients are chosen appropriately.

It is well known that in flow through a porous medium the pressure drop caused by the frictional drag is directly proportional to the fluid velocity (low-speed flow). This is the familiar Darcy's law, which relates the pressure drop and the velocity of a fluid in an unbounded porous medium. At higher velocities, however, inertial effects become appreciable, causing an increase of the drag coefficient. Experimental observations indicated that the pressure drop in the bulk of a porous medium can be approximated by a quadratic function of the flow velocity. Thus, for high Reynolds number flow calculations in a porous medium, Darcy's law is usually replaced by the scalar nonlinear Ergun equation (Ergun, 1952). However, the inertial term, associated with microscale inertial effects, can be neglected if the particle Reynolds number is small. This assumption is made here and non-Darcy effects are neglected.

There is still some controversy about the boundary effect inclusion for the treatment of flow in porous medium (Nield, 1983). This subject will not be addressed in this work.

The present analysis is based on the assumption that the medium has a constant porosity. The effect of porosity variation near the walls, as discussed by Chandrasekhara and Vortmeyer (1979), is neglected.

Finally, the Boussinesq approximation, which states that the fluid density is constant everywhere except in the external forces term, is also considered valid.

Under these assumptions, mass, and momentum transfer processes for a chemical reaction system, as visualized in Figure 1, will be governed by the following dimensionless equations.

Mass Balance

$$\frac{\partial y}{\partial t} = \underline{u} + \underline{\nabla} y + Le\nabla^2 y + Da\,R(y,\theta) \qquad (1)$$

Energy Balance

$$\sigma \frac{\partial \theta}{\partial t} = -\underline{u} \cdot \underline{\nabla}\theta + \nabla^2\theta + B\,Da\,R(y,\theta) \qquad (2)$$

where $R(y,\theta) = (1-y)^n \exp[\theta/(1+\theta/\gamma)]$
subject to

$$\frac{\partial y}{\partial z} = \frac{\partial \theta}{\partial z} = 0 \quad \text{at } z = 0, 0 \le x \le 1$$

$$y = \theta = 0 \quad \text{at } z = 1, 0 \le x \le 1$$

$$\frac{\partial y}{\partial x} = \frac{\partial \theta}{\partial x} = 0 \quad \text{at } 0 \le z \le 1, \text{x} = 0, 1$$

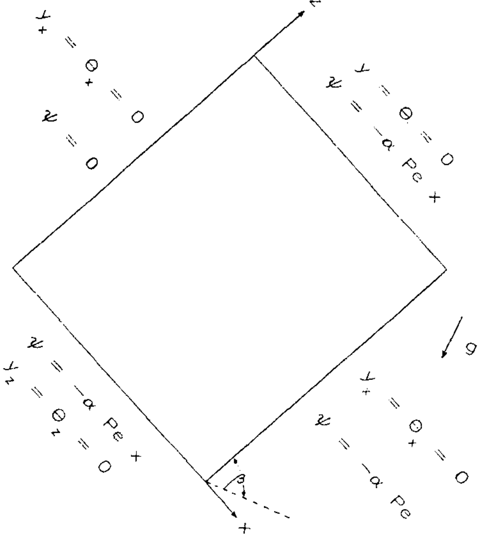


Figure 1. Scheme of the reaction system.

while the flow field will be described by

Continuity Equation

$$\underline{\nabla}\cdot\underline{u} = 0 \tag{3}$$

Momentum Balance

$$\frac{1}{Pr_p}\left(\frac{\partial \underline{u}}{\partial t} + \frac{1}{\epsilon}\underline{u}\cdot\underline{\nabla u}\right) = -\underline{\nabla p} - \underline{u} + (Ra_1\theta + Ra_2 y)(\sin\beta\,\dot{z} + \cos\beta\,\dot{x}) \tag{4}$$

Equations 3 and 4 are known as the Darcy-Boussinesq-Oberbeck model for flow through a porous medium. They can be simplified by eliminating the time dependency, since for most situations of interest $Pr_p \gg 1$ (Straus, 1974).

As shown in the literature (Bird et al., 1960), the elimination of the pressure in the equation of motion leads to an equation that can be handled more easily than the original set of Eqs. 3 and 4. The pressure is eliminated by making use of the stream function definition

$$\xi = \underline{\nabla}\times\underline{u}\cdot\dot{x}\times\dot{z} = \nabla^2\psi$$

Here ξ denotes vorticity and Eqs. 3 and 4 become

$$\nabla^2\psi = \frac{\sin\beta}{\alpha}\left(Ra_1\frac{\partial\theta}{\partial x} + Ra_2\frac{\partial y}{\partial x}\right) + \cos\beta\left(Ra_1\frac{\partial\theta}{\partial z} + Ra_2\frac{\partial y}{\partial z}\right) \tag{5}$$

Equation 5 will be referred to as the vorticity equation.

The boundary conditions can be written in terms of the stream function as

$$\psi = -\alpha Pex \quad \text{at } z = 0, 1 \quad 0 \le x \le 1$$
$$\psi = 0 \quad \text{at } 0 \le z \le 1, \quad x = 0$$
$$\psi = -\alpha Pe \quad \text{at } 0 \le z \le 1, \quad x = 1$$

Simplification of the Model

Equations 1 to 4 are to be solved to establish flow, concentration, and temperature fields. This general formulation can be simplified for two particular situations, isothermal and nonisothermal reactions.

Isothermal Reaction Problem. It is no longer necessary to consider the energy balance. The mass balance becomes

$$\frac{\partial y}{\partial t} = -\underline{u}\cdot\underline{\nabla}y + Le\nabla^2 y + \Phi^2 Le R(y) \tag{6}$$

Here, Φ^2 stands for the effectiveness factor.

Nonisothermal Zero-order Reaction without Reactant Depletion. This is the typical problem referred to as thermal explosion. Since there is no change in the concentration the energy balance is decoupled from the mass balance, which is no longer considered.

The energy balance becomes

$$\sigma\frac{\partial\theta}{\partial t} = -\underline{u}\cdot\underline{\nabla}\theta + \nabla^2\theta + FK\exp\left(\frac{\theta}{1+\theta/\gamma}\right) \tag{7}$$

where $FK = B\,Da$.

In the latter case the vorticity equation, Eq. 5, can now be written as

$$\nabla^2\psi = Ra_1\left(\frac{\sin\beta}{\alpha}\frac{\partial\theta}{\partial x} + \cos\beta\frac{\partial\theta}{\partial z}\right)$$

These two situations were analyzed in previous contributions (Gatica et al., 1987; Viljoen and Hlavacek, 1987). In this study we will concentrate on a general nonisothermal case.

Linear Stability Analysis

For subcritical values of the Rayleigh numbers, $Ra_1 < Ra_{1c}$ or $Ra_2 < Ra_{2c}$, convective instabilities do not exist. Thus the temperature, concentration, and flow fields are described by a basic state (θ_o, y_o, ψ_o), which results from

$$\frac{1}{\alpha}\left(\frac{\partial\psi_o}{\partial z}\frac{\partial y_o}{\partial x} - \frac{\partial\psi_o}{\partial x}\frac{\partial y_o}{\partial z}\right) + Le\nabla^2 y_o + FK/B\,R(y_o, \theta_o) = 0 \tag{8}$$

$$\frac{1}{\alpha}\left(\frac{\partial\psi_o}{\partial z}\frac{\partial\theta_o}{\partial x} - \frac{\partial\psi_o}{\partial x}\frac{\partial\theta_o}{\partial z}\right) + \nabla^2\theta_o + FK\,R(y_o, \theta_o) = 0 \tag{9}$$

$$-\nabla^2\psi_o + Ra_1\left(\frac{\sin\beta}{\alpha}\frac{\partial\theta_o}{\partial x} + \cos\beta\frac{\partial\theta_o}{\partial z}\right) + Ra_2\left(\frac{\sin\beta}{\alpha}\frac{\partial y_o}{\partial x} + \cos\beta\frac{\partial y_o}{\partial z}\right) = 0 \tag{10}$$

with $\psi_o = -\alpha\,Pex$. Any small perturbation imposed on the system will disappear, and the system will return to the basic state.

For certain critical values of the Rayleigh numbers, namely $Ra_1 = Ra_{1c}$ or $Ra_2 = Ra_{2c}$, small perturbations will drive the system toward a new state (y, θ, ψ). It can easily be seen that the basic solution, $\psi_o = -\alpha Pex$, will only hold (and so will Eqs. 8–10) if $\cos\beta = 0$. If $\cos\beta \neq 0$, this basic state will only be valid for $Ra_1 = Ra_2 = 0$. [We neglect the exceptional situation where $Ra_1 \cdot (d\theta_o/dz) = -Ra_2\,(dy_o/dz)$, $0 \le z \le 1$.] Since we are not interested in the trivial solution, we will only analyze the two cases $\beta = \pi/2$ and $\beta = 3\pi/2$. As a result, the term containing $\cos\beta$ can be eliminated in the vorticity equation, Eq. 5.

Let us now consider the situation where the system in the basic state, and $Ra_1 = Ra_{1c}$ or $Ra_2 = Ra_{2c}$, is perturbed as

$$y = y_o + \epsilon y_1 + \epsilon^2 y_2 + \cdots$$
$$\theta = \theta_o + \epsilon\theta_1 + \epsilon^2\theta_2 + \cdots$$
$$\psi = \psi_o + \epsilon\psi_1 + \epsilon^2\psi_2 + \cdots$$

with

$$Ra_1 = Ra_{1c}^o + \epsilon Ra_1^1 + \epsilon^2 Ra_1^2 + \cdots$$

or

$$Ra_2 = Ra_{2c}^o + \epsilon Ra_2^1 + \epsilon^2 Ra_2^2 + \cdots$$

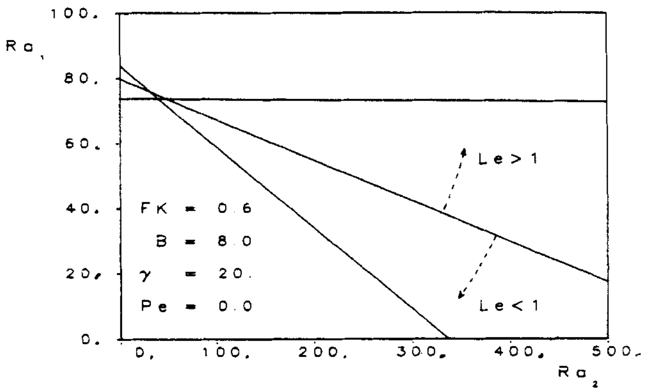


Figure 2. Influence of Lewis number on neutral stability condition.

(In this section ϵ denotes a small expansion parameter and is not to be confused with the void fraction used in later sections.) The dynamic behavior of the system will be governed by Eqs. 1, 2, and 5.

To make the problem more tractable, the reaction term is expanded around the basic state as

$$R(y,\theta) = R(y_o,\theta_o) + R_y(y_o,\theta_o)(\epsilon y_1 + \epsilon^2 y_2 + \cdots) + R_\theta(y_o,\theta_o)(\epsilon\theta_1 + \epsilon^2\theta_2 + \cdots) + \cdots$$

In the rest of the paper we will consider the thermal Rayleigh number Ra_1 as the bifurcation parameter. The mass Rayleigh number Ra_2, like the rest of the system parameters, will remain constant.

Thus the first-order perturbation equations are

$$\frac{\partial y_1}{\partial t} = -\frac{1}{\alpha}\left(-\alpha Pe\frac{\partial y_1}{\partial z} + \frac{\partial \psi_1}{\partial x}\frac{\partial y_o}{\partial z}\right) + Le\nabla^2 y_1 + FK/B[R_y(y_o,\theta_o)y_1 + R_\theta(y_o,\theta_o)\theta_1] \quad (11)$$

$$\sigma\frac{\partial \theta_1}{\partial t} = -\frac{1}{\alpha}\left(-\alpha Pe\frac{\partial \theta_1}{\partial z} + \frac{\partial \psi_1}{\partial x}\frac{\partial \theta_o}{\partial z}\right) + \nabla^2\theta_1 + FK[R_y(y_o,\theta_o)y_1 + R_\theta(y_o,\theta_o)\theta_1] \quad (12)$$

$$-\nabla^2\psi_1 + \frac{\sin\beta}{\alpha}\left(Ra^o_{1c}\frac{\partial \theta_1}{\partial x} + Ra_2\frac{\partial y_1}{\partial x}\right) = 0 \quad (13)$$

subject to the following boundary conditions

$$y_1 = \theta_1 = 0, \quad \text{at } 0 \le x \le 1, z = 1$$

$$\frac{\partial y_1}{\partial z} = \frac{\partial \theta_1}{\partial z} = 0 \quad \text{at } 0 \le x\ 1, z = 0$$

$$\frac{\partial y_1}{\partial x} = \frac{\partial \theta_1}{\partial x} = 0 \text{ at } x = 0, 1, 0 \le z \le 1$$

$$\psi_1 = 0 \quad \text{along the boundaries}$$

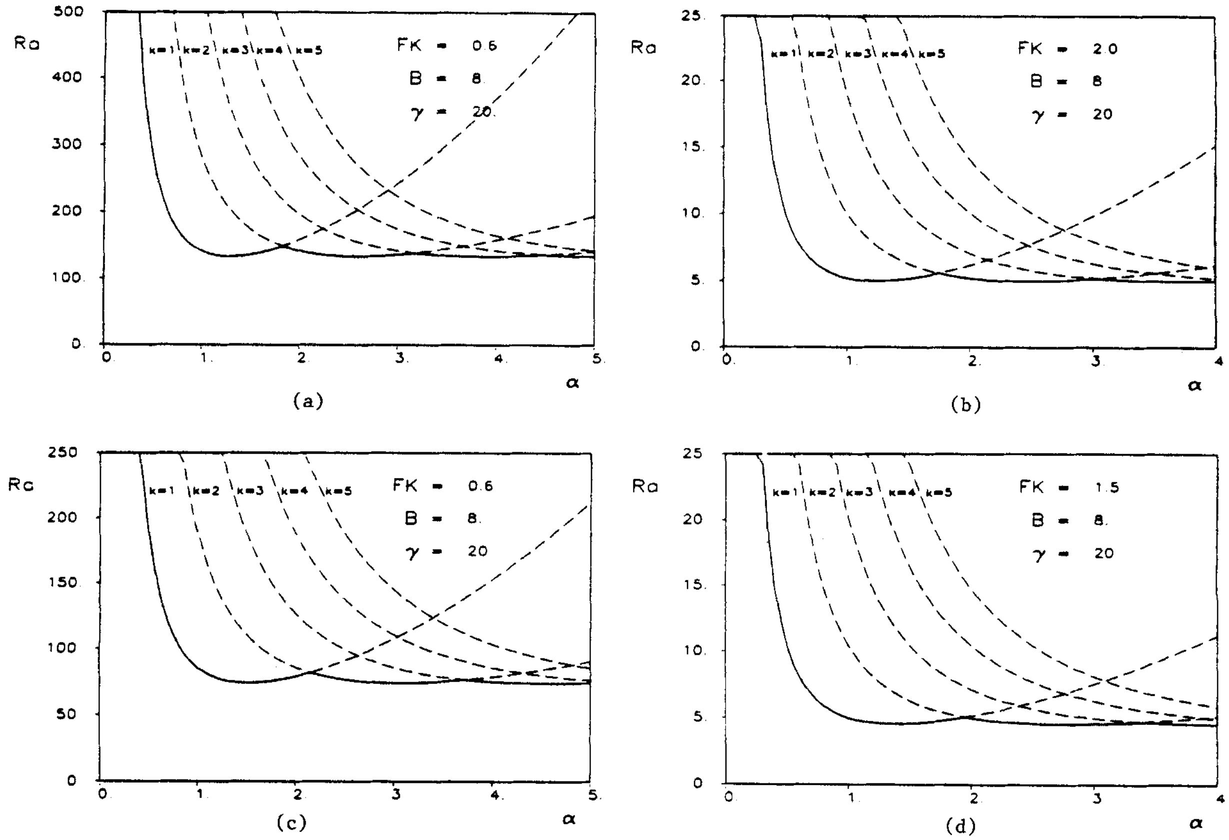


Figure 3. Neutral stability curves for *Le* = 1.

(a) Kinetic regime *Pe* = 1; (b) Diffusion regime *Pe* = 1
(c) Kinetic regime *Pe* = 0; (d) Diffusion regime *Pe* = 0

Suitable trial functions for the perturbation solutions are

$$y_1 = Y \cdot \cos\,[(2m-1)\pi/2z]\,\exp\,(ik\pi x + \omega t)$$

$$\theta_1 = T \cdot \cos\,[(2m-1)\pi/2z]\,\exp\,(ik\pi x + \omega t)$$

$$\psi_1 = F \cdot \sin\,(m\pi z)\,\exp\,[i(k\pi x - \pi/2) + \omega t]$$

Using a variational formulation, the weak form of the system of Eqs. 11 to 13 is:

$$\omega Y = -Pe^*(2m-1)\frac{\pi}{2}Y - Le\left[(2m-1)^2\frac{\pi^2}{4} + \frac{k^2\pi^2}{\alpha^2}\right]Y - \frac{k^2}{(m^2\alpha^2+k^2)}\sin\beta D_2^*(Ra_{1c}^o T + Ra_2 Y) + FK/B(E_1^* T + E_2^* Y) \quad (14)$$

$$\sigma\omega T = -Pe^*(2m-1)\frac{\pi}{2}T - \left[(2m-1)^2\frac{\pi^2}{4} + \frac{k^2\pi^2}{\alpha^2}\right]T - \frac{k^2}{(m^2\alpha^2+k^2)}\sin\beta D_1^*(Ra_{1c}^o T + Ra_2 Y) + FK(E_1^* T + E_2^* Y) \quad (15)$$

where

$$\bar{y}_1 = \int_\Omega v y_1\, d\Omega = Y c_1$$

$$\bar{\theta}_1 = \int_\Omega v\theta_1\, d\Omega = T c_1$$

$$Pe^* = \frac{Pe}{c_1}\int_\Omega v \sin\left[(2m-1)\frac{\pi}{2}z\right]\exp\,(ik\pi x + \omega t)\, d\Omega$$

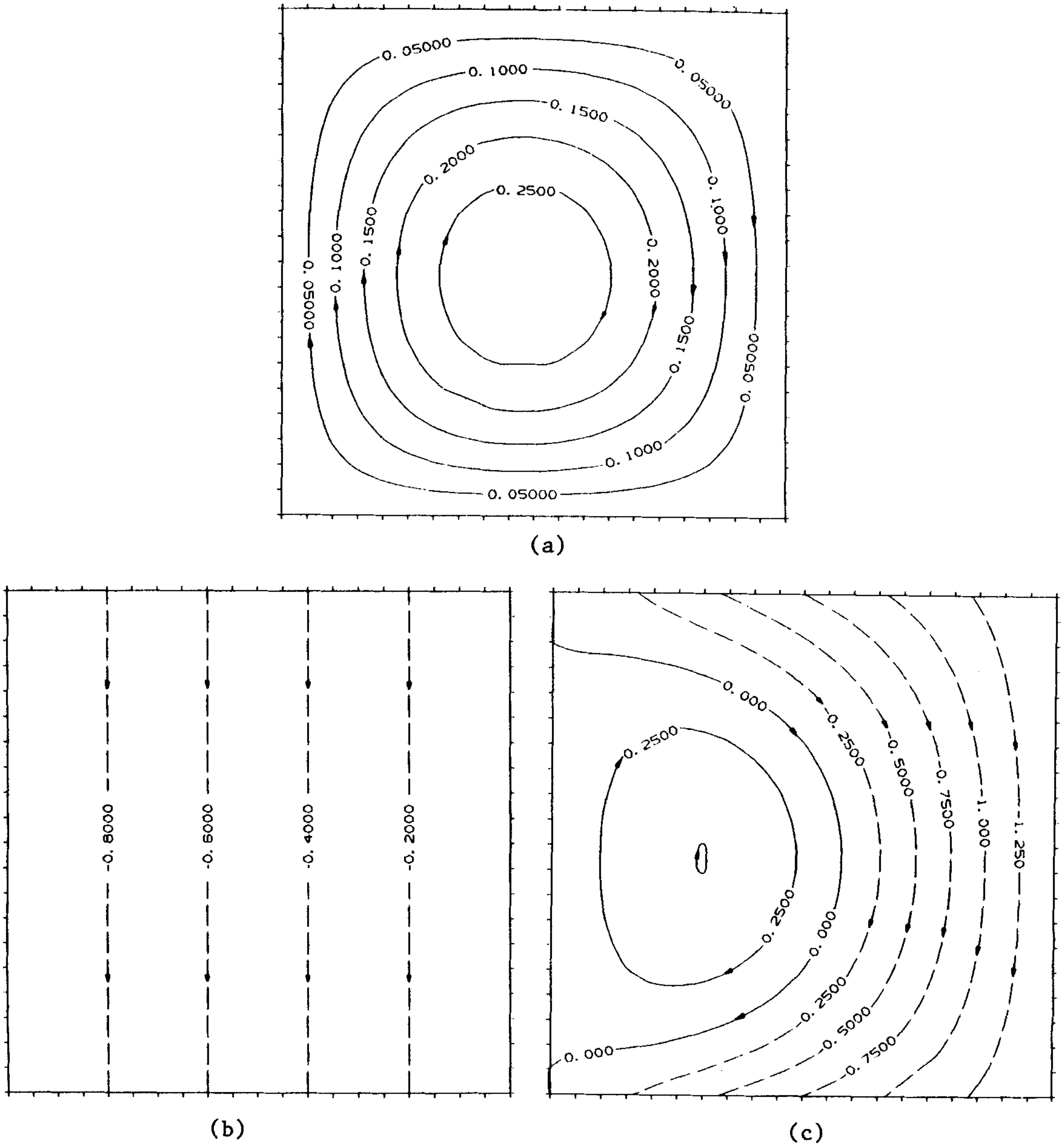


Figure 4a. Flow fields for kinetic regime in region I (α = 1.5).
(a) Ra = 75, Pe = 0; (b) Basic solution Pe = 1; (c) Ra = 135, Pe = 1

$$D_1^* = \frac{1}{c_1}\int_\Omega v\,\frac{\partial\theta_o}{\partial z}\frac{\theta_1}{T}\,d\Omega$$

$$D_2^* = \frac{1}{c_1}\int_\Omega v\,\frac{\partial y_o}{\partial z}\cdot\frac{y_1}{y}\,d\Omega$$

$$E_1^* = \frac{1}{c_1}\int_\Omega vR_\theta(y_o, \theta_o)\,\frac{\theta_1}{T}\,d\Omega$$

$$E_2^* = \frac{1}{c_1}\int_\Omega vR_y(y_o, \theta_o)\,\frac{y_1}{Y}\,d\Omega$$

Here $v = v(x, z)$, stands for a weighting function.

Then, provided the principle of exchange of stabilities holds (Jones, 1973) for $\omega = 0$, the neutral stability condition is given by the eigenvalues of the system of Eqs. 14 and 15.

The dispersion relation is

$$\begin{aligned}(\overline{Pe} + C)[\overline{Pe} + C + \overline{D}_1 Ra_{1c}^o + \overline{D}_2 Ra_2 - FK(E_1^* + E_2^*/B)]\\ = (1 - Le)C(\overline{Pe} + C + \overline{D}_1 Ra_{1c}^o + \overline{D}_2 Ra_2 - FK\cdot E_1^*)\\ + FK(E_1^* Ra_{1c}^o - E_2^* Ra_2)(\overline{D}_1/B - \overline{D}_2) \qquad (16)\end{aligned}$$

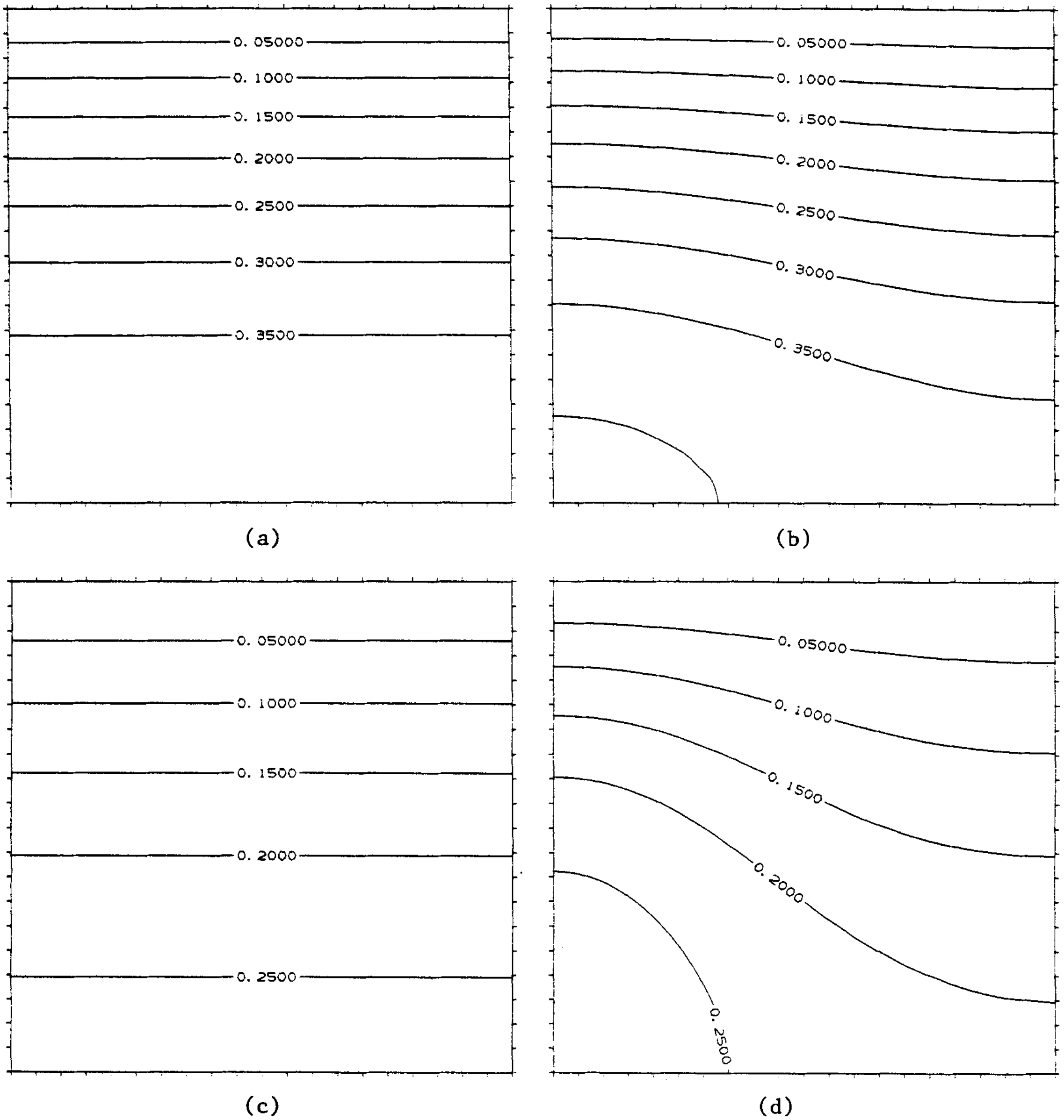
where

$$\overline{Pe} = (2m - 1)\pi/2Pe^*$$

$$C = [(2m - 1)^2\pi^2/4 + k^2\pi^2/\alpha^2]$$

$$\overline{D}_1 = \frac{k^2}{(m^2\alpha^2 + k^2)}\sin\beta\cdot D_1^*$$

$$\overline{D}_2 = \frac{k^2}{(m^2\alpha^2 + k^2)}\sin\beta\cdot D_2^*$$



(a) (b)

(c) (d)

Figure 4b. Temperature fields for kinetic regime in region I (α = 1.5).

(a) Basic solution Pe = 0; (b) Ra = 75, Pe = 0
(c) Basic solution Pe = 1; (d) Ra = 135, Pe = 1

In Figure 2, for a typical set of system parameters, the influence of the Lewis number on the neutral stability condition is shown. As a result of our choice of trial functions, a linear relation between both Rayleigh numbers results. The region above the lines represents the convection regime; below the line only conduction is possible. As the Lewis number deviates from unity two limits are observed. For $Le \ll 1$, the critical values approach the limit of convection driven by concentration only (Ra_2). For $Le > 1$ the influence of the mass driven convection (Ra_2) becomes weaker, converging to the limit case of thermally driven convection (Ra_1) only, for $Le \gg 1$.

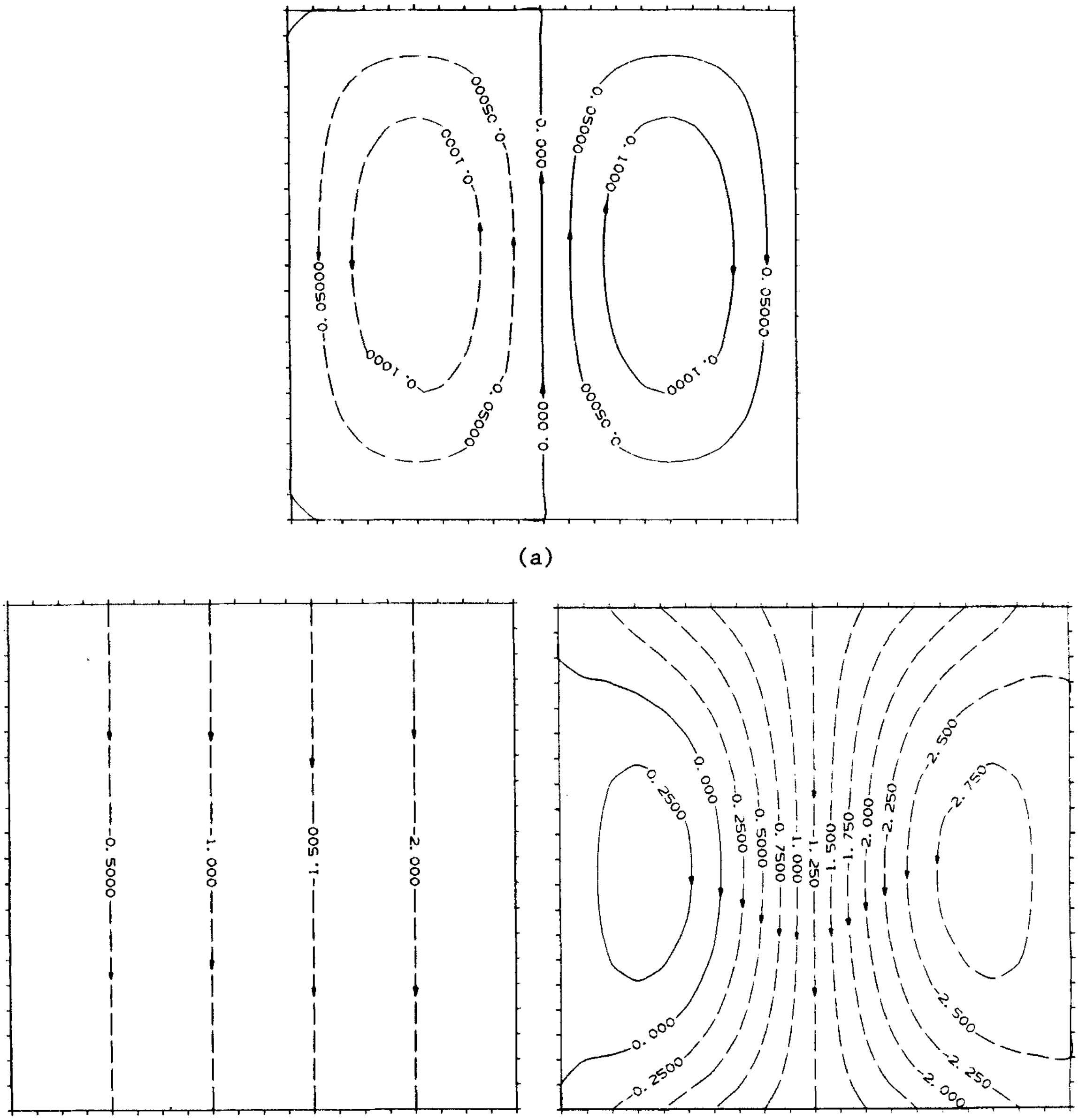
For the sake of simplicity, the situation of $Le = 1$ will be analyzed in this work. For this particular case the solutions (y_o, θ_o, ψ_o) of Eqs. 8 and 9 satisfy the relation $y_o = \theta_o/B$, and Eq. 16 is reduced to the simpler expression:

$$Ra_c^o = \frac{[\bar{Pe} + C - FK(E_1^* + E_2^*/B)]}{(-\bar{D}_1)}$$

where the global Rayleigh number, Ra_c^o, stands for the linear relation defined by

$$Ra_c^o = Ra_{1c}^o + Ra_2/B. \tag{17}$$

For the computation of the integrals in the dispersion relation—namely, Pe^*, D_1^*, D_2^*, E_1^*, and E_2^*—the basic state is calculated by numerical solution of Eqs. 8 and 9 for $Ra_1 = Ra_2 = 0$.



(a)

(b)

(c)

Figure 5a. Flow fields for kinetic regime in region II ($\alpha = 2.5$).

(a) $Ra = 75$, $Pe = 0$; (b) Basic solution $Pe = 1$; (c) $Ra = 135$, $Pe = 1$

To compute the neutral stability curve the Petrov-Galerkin approach with $v = 1$ and the Galerkin approach are used.

Below we are going to analyze the effect of free convection on the behavior of kinetic and diffusion regimes. For basic solutions in the kinetic regime, the analysis showed to be insensitive to the weight function chosen. On the other hand, basic solutions in the diffusion regime are characterized by the existence of boundary layers caused by the chemical reaction; that is, the major conversion and temperature variations are confined to a thin layer adjacent to one of the boundaries. Stability predictions are strongly dependent on the kind of weighting function used. In the latter situation, the problem becomes independent on the length of the system and it should be rescaled.

Values of the Parameters

In this section some typical values of system parameters are presented and bounds of reliability of the analysis are established.

The reaction parameters, namely, adiabatic temperature rise, activation energy, and Damköhler number, do not depend on the system geometry or flow characteristics. Typical values for fluid-solid reaction systems are

$$10 \leq \gamma \leq 50$$

$$2 \leq B \leq 50$$

$$0.001 \leq Da \leq 0.1$$

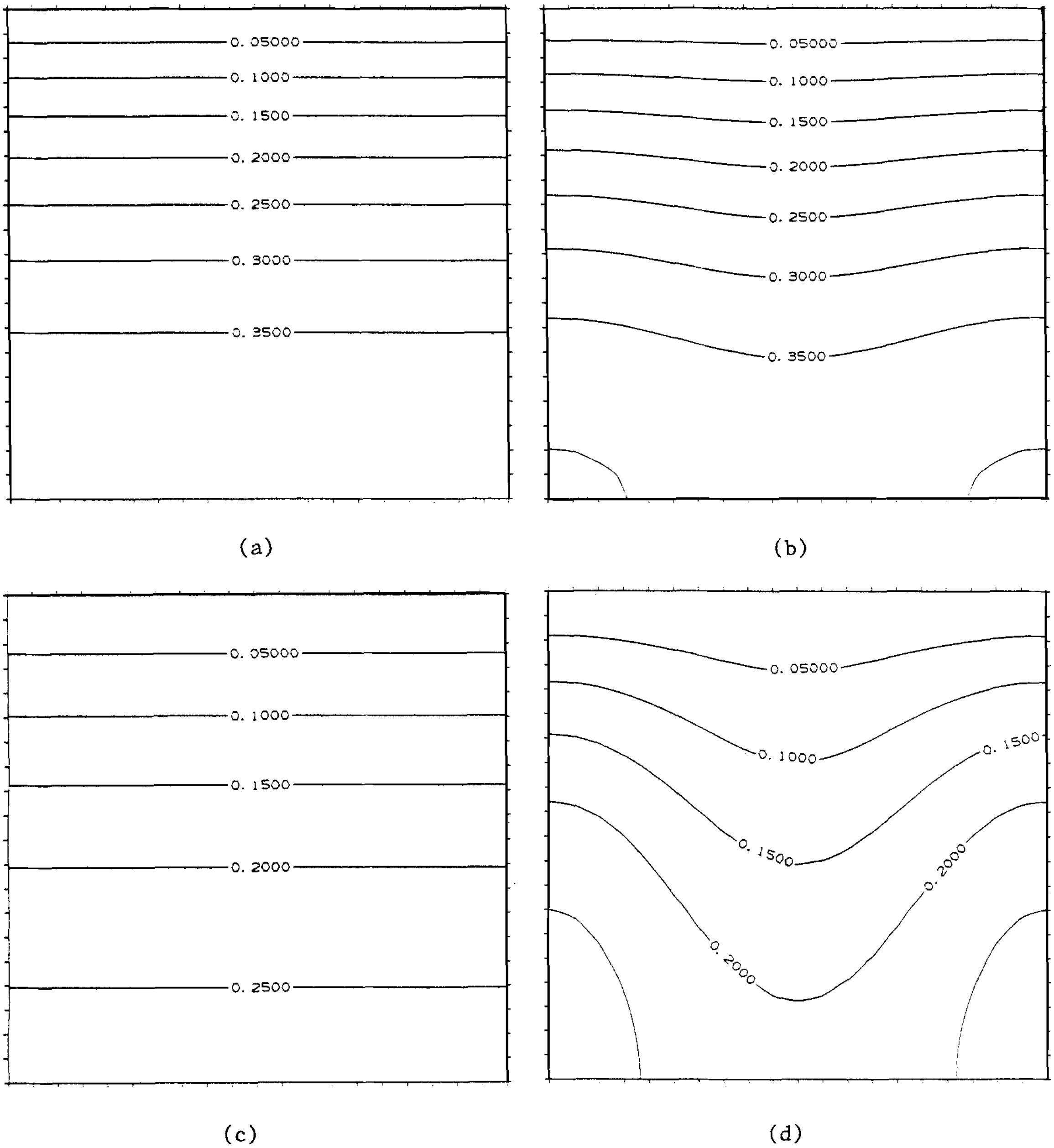


Figure 5b. Temperature fields for kinetic regime in region II ($\alpha = 2.5$).

(a) Basic solution $Pe = 0$; (b) $Ra = 75$, $Pe = 0$
(c) Basic solution $Pe = 1$; (d) $Ra = 135$, $Pe = 1$

It is well known that the pressure drop in a porous medium can be approximated as a linear combination of the Carman-Kozeny and Burke-Plummer equations (Ergun, 1952).

$$\text{Friction forces} = \frac{150(1-\epsilon)^2}{\epsilon^3 D_p^2} \cdot \frac{k_e}{L} \frac{\mu_f}{\rho_f C_{pf}} \cdot Pe + \frac{1.75(1-\epsilon)}{D_p \epsilon^3} \left(\frac{k_e}{L}\right)^2 \frac{1}{\rho_f C_{pf}^2} \cdot Pe^2$$

However, for a certain range of fluid velocities, just the linear dependence of the pressure drop on the fluid velocity (namely, the Carman-Kozeny equation) provides a reliable description. The range of linear dependence depends on fluid and packing characteristics. Consider a packed bed of 0.5 m depth filled with glass beads of 0.01 m dia. If the fluid is a gas (e.g., air) at room temperature and atmospheric pressure, the bound is $Pe \leq 0.015$. For a liquid (e.g., water) at the same conditions, the limit of reliability is expanded to $Pe \leq 1$.

As explained above, the validity of Darcy's law (linear dependence between pressure drop and fluid velocity) allows estimation of the Rayleigh number through the Carman-Kozeny relation. Thus the Rayleigh number defined as

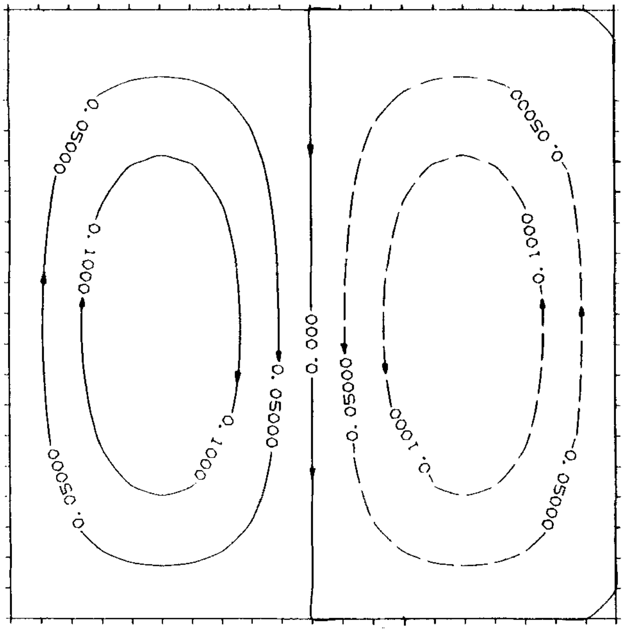
$$Ra_1 = \beta_1 \cdot g \left(\frac{\rho C_p}{\nu}\right)_f \frac{\kappa}{k_e} \cdot L \cdot \frac{T_o}{\gamma}$$

becomes

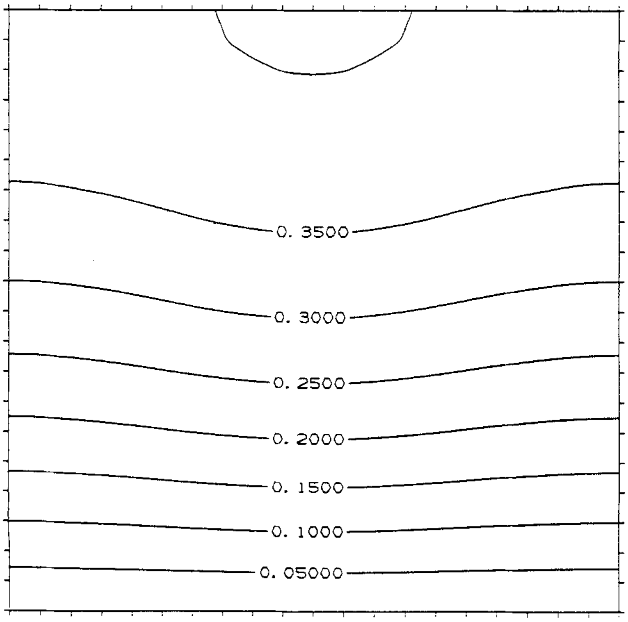
$$Ra_1 = \beta_1 \cdot g \cdot \left(\frac{\rho C_p}{\nu}\right) \frac{D_p^2 \epsilon^3}{150(1-\epsilon)^2} \frac{L}{k_e} \frac{T_o}{\gamma}$$

For the example presented above, a typical value of the Rayleigh number for air is $Ra_1 = 0.4(T_o/\gamma)$, and for a liquid $Ra_1 = 93.6(T_o/\gamma)$. Typical values for the driving force (T_o/γ) can be estimated as $10 \leq T_o/\gamma \leq 50$, K.

The thermal Rayleigh number Ra_1 is usually positive (an exception is water between 0 and 4°C). The concentration Rayleigh number Ra_2 can attain negative values if a heavy product is formed during the course of the reaction. Shtessel et al. (1978) showed that for both gases and liquids, $|Ra_2| > Ra_1$. Evidently, Ra—as defined by Eq. 17—can be negative.



(a) Flow Field



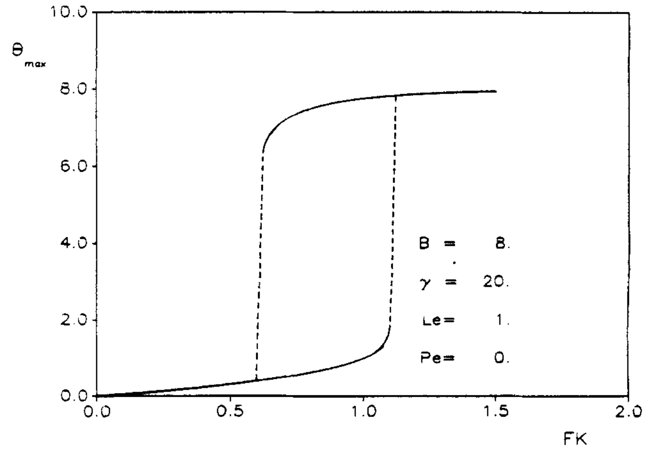
(b) Temperature Field

Figure 6. Perturbed solutions in kinetic regime for negative values of Rayleigh number.

$\alpha = 2.5$; $Ra_1 = 75$; $Ra_2 = -1{,}200$; $Pe = 0$

Discussion of Results

It has been shown above that Eq. 16 represents the condition for neutral stability. In Figure 3, neutral stability curves are displayed for a typical set of system parameters. The solid lines in Figure 3 indicate the minima of the set of curves presented. The region above a solid line will be referred to in terms of the k value of the solid line. For example, region I refers to values of Ra_1 slightly larger than those indicated by the solid part of the $k = 1$ line. When two k lines have the same minimum, two possibilities exist. This question, however, cannot be elucidated from



(a)

Figure 7. Multiplicity of solutions for basic state.

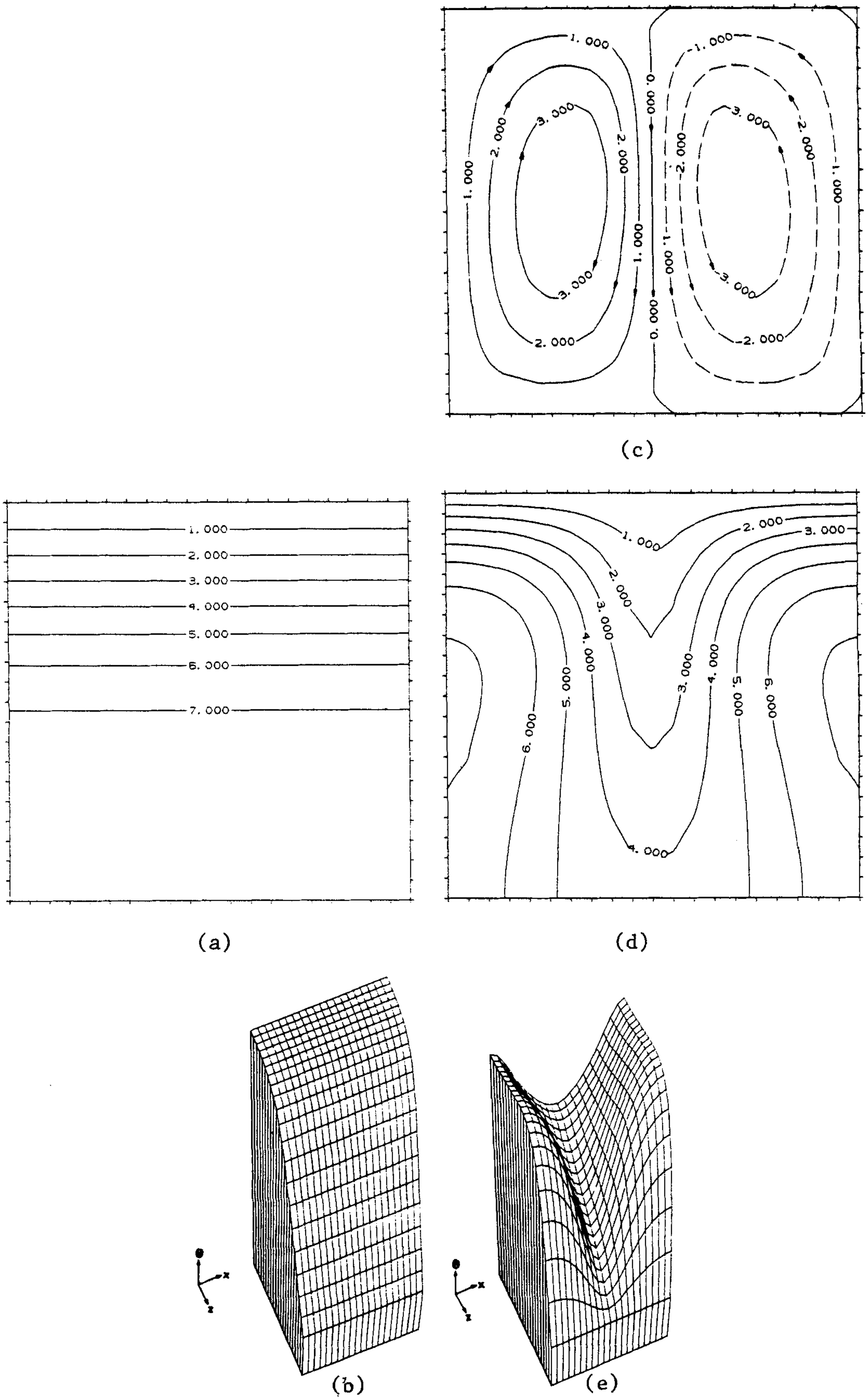


Figure 8. Influence of natural convection in diffusion regime ($\alpha = 2$, $Pe = 0$).

(a), (b) Basic temperature field; (c) Flow field for $Ra = 10$; (d), (e) Temperature field for $Ra = 10$

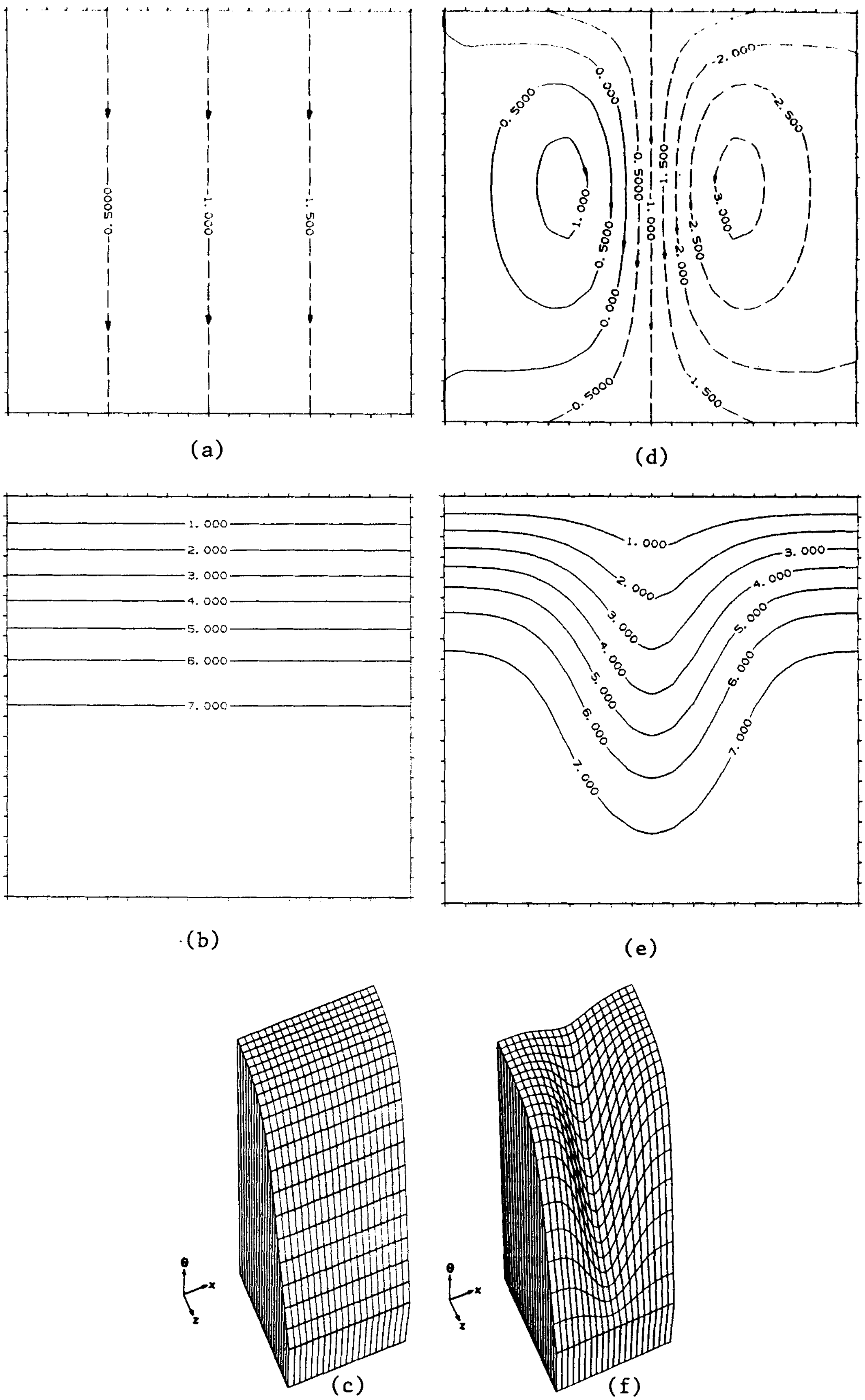


Figure 9. Influence of natural convection in diffusion regime ($\alpha = 2$, $Pe = 1$).
(a) Basic flow field; (b), (c) Basic temperature field; (d) Flow field for $Ra = 6$; (e), (f) Temperature field for $Ra = 6$

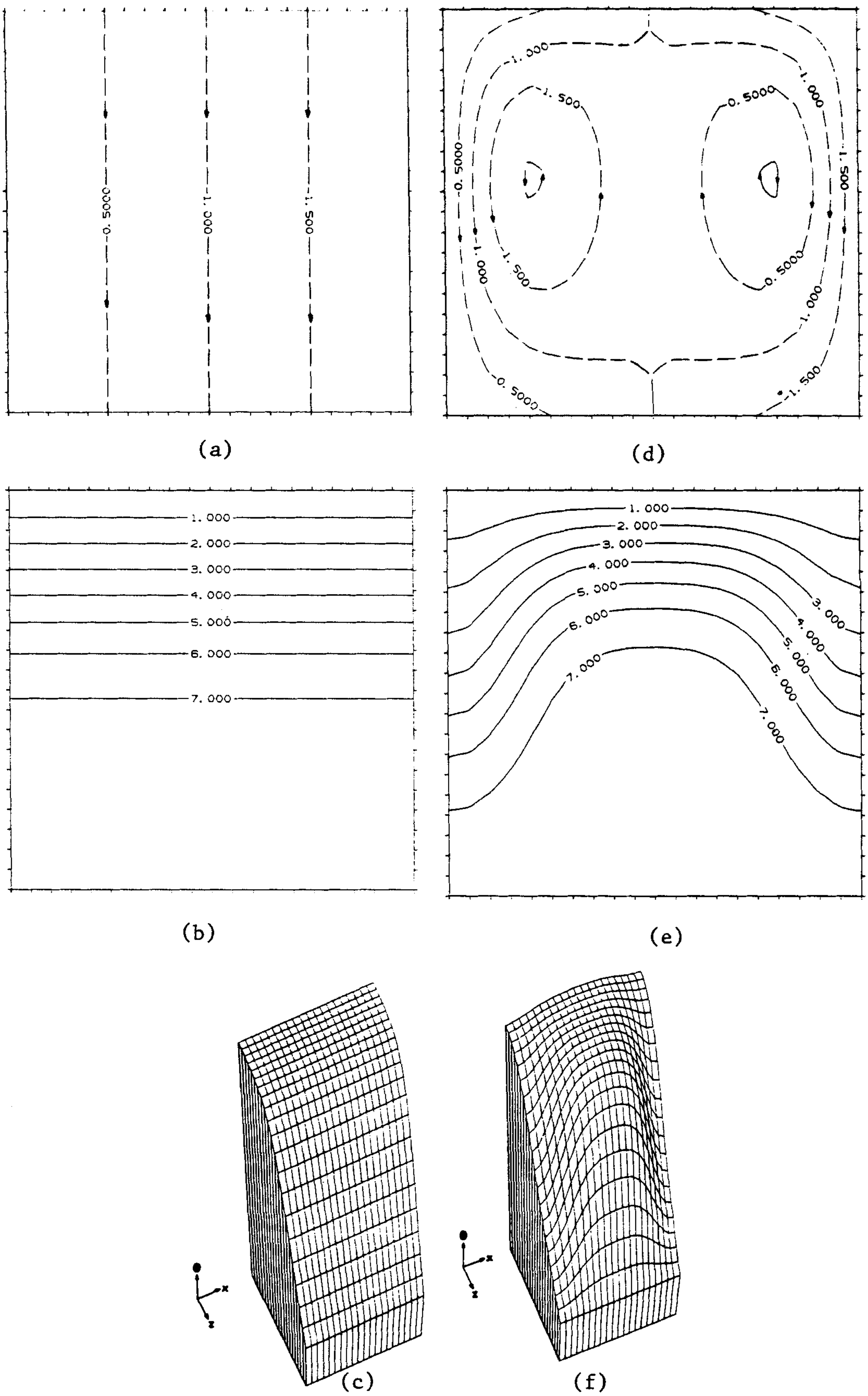


Figure 10. Different rotation direction for recirculation cells ($\alpha = 2$, $Pe = 1$).

(a) Basic flow field; (b), (c) Basic temperature field; (d) Flow field for $Ra = 6$; (e), (f) Temperature field for $Ra = 6$

the linear stability analysis and pattern interaction must be considered.

It can be shown (Viljoen, unpublished results) that the linear stability analysis is second-order accurate. Thus, the solution can be predicted for system parameters slightly away from the lines in regions where there is no overlapping.

From Figure 3, as well as from the dispersion relation, Eq. 16, it follows that the forced flow constitutes a stabilizing factor. As the Peclet number increases, the neutral stability curves are shifted toward the region of higher values of the Rayleigh number.

From Figure 3 we can infer the minimum and maximum size of a cell. This is apparent from a comparison of Figures 4 and 5, where both the basic and perturbed solutions are shown. These drawings differ in the aspect ratios. A change in the size (width) of the system can change the number of stable cells. In terms of the neutral stability curves, this is equivalent to moving parallel to the abcissa axis, from region I to region II or vice versa.

For open systems, the influence of the natural convection can be assessed from Figures 4 and 5. Natural convection generates cells which, in the case of open systems, create stagnant regions (recirculation cells) and preferential paths (channeling) for the flow. Obviously, the stronger the forced convection, the smaller the size of free convection cells.

An interesting result was observed for the closed system ($Pe = 0$) when $\beta = 3\pi/2$. Natural convection is stabilized by sufficiently large negative values of the global Rayleigh number Ra_c^o. Owing to Ra_2, this number can be negative and natural convection is stabilized. In Figure 6, where this situation is illustrated, the combination of mass and thermal Rayleigh numbers provides a negative value for the global Rayleigh number.

It is well known that the chemical reaction system addressed in this work can exhibit multiplicity of solutions when natural convection is neglected, Figure 7. The analysis presented here has shown that for operation in the diffusion regime (upper branch), the critical values for the onset of convection can be more than one order of magnitude smaller than those in the kinetic regime. It was shown above, in discussing typical values of the parameters, that Ra_1 can attain values ranging from 4 to 20 for a gas. Even for these low values of Ra_1, natural convection is likely to develop for reaction systems operating in the diffusion regime, Figure 3.

Figures 8 and 9 present a comparison of basic and perturbed solutions. These figures reveal that the effect of natural convection is more prominent in the diffusion regime. In this regime, the basic solution is usually characterized by the existence of boundary layers close to the inlet of the system. The natural convection creates recirculation flow (cells) inside the system; this flow is divided upward or downward and the system is cooled or heated depending on the flow direction. The boundary layers expand where the flow effectively cools the system; conversely, they are compressed where the flow brings warmer fluid to regions of higher reactant concentration. The wrinkling of the boundary layers also depends on the number of convection cells present. Thus, even though the maximum temperature is still equal to the adiabatic value and complete conversion is achieved, the natural convection is responsible for nonuniform temperature and concentration fields.

As a final remark, it should be pointed out that different rotations correspond to different temperature and flow fields. For instance, Figures 9 and 10 display different flow patterns for the same governing parameters. The channels occur either at the center or adjacent to the lateral walls. However, the linear stability analysis does not provide any information on the stability of opposite rotating modes and the subject needs further investigation.

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Notation

C = concentration, kmol · m_f^{-3}
C_p = specific heat, kJ · kg^{-1} · K^{-1}
D_e = effective mass diffusivity, m_f^3 · m^{-1} · s^{-1}
D_p = equivalent catalyst pellet diameter, m
D_t = tube diameter or width of system, m
E = activation energy, kJ · $kmol^{-1}$
g = gravity acceleration, m · s^{-2}
k_e = effective thermal conductivity, kJ · m^{-1} · s^{-1} · K^{-1}
k_o = preexponential factor, s^{-1}
L = length or height of system, m
n_l = order of reaction
p' = pressure, Pa
p = dimensionless pressure, $p = p' \kappa \cdot \epsilon/(\mu_f \alpha')$
R = universal gas constant, kJ · $kmol^{-1}$ · K^{-1}
t' = time, s
t = dimensionless time, $t = t' \cdot u_o/L$
T = temperature, K
$\underline{u}'$ = fluid superficial velocity vector (u'_x, u'_z), m · s^{-1}
$\underline{u}$ = dimensionless fluid velocity vector $(u'_x/u_o, u'_z/u_o)$
u_o = characteristic velocity $(u_o = \alpha'/L)$, m · s^{-1}
x' = horizontal coordinate, m
x = dimensionless horizontal coordinate, $x = 2x'/D_t$
y = conversion, $y = 1 - C/C_o$
z' = vertical coordinate, m
z = dimensionless vertical coordinate, z/L

Dimensionless groups

B = adiabatic temperature rise, $B = (T_a - T_o)\gamma/T_o$
Da = Damköhler number, $Da = k_o e^{-\gamma} L^2 C_o^{n-1}/(\epsilon\alpha')$
FK = Frank-Kamenetskii parameter, $FK = B.Da$
Le = Lewis number, $Le = D_e/\alpha'$
Pe = Peclet number, $Pe = u'_z L/\alpha'$
Pr_p = Prandlt number for porous media (Darcy number), $Pr_p = \nu_f \epsilon^2 L^2/(\kappa \cdot \alpha')$
Ra_1 = thermal Rayleigh number, $Ra_1 = \beta_1 g \cdot \kappa \cdot L/(\nu_f \alpha')(T_o/\gamma)$
Ra_2 = concentration Rayleigh number, $Ra_2 = \beta_2 g \kappa L/(\nu_f \alpha')C_o$

Greek letters

α = aspect ratio, $\alpha = D_t/2L$
α' = thermal diffusivity, m^2 · s^{-1}
β = tilt angle, rad
β_1 = coefficient of volumetric expansion (thermal), K^{-1}
β_2 = coefficient of volumetric expansion (mass), m^3 · $kmol^{-1}$
γ^1 = dimensionles activation energy, $\gamma = E/RT_o$
ϵ = void fraction, m_f^3 · m^3
θ = dimensionless temperature, $\theta = (T - T_o)\gamma/T_o$
ρ = density, kg · m^{-3}
κ = permeability, m^2
μ = dynamic viscosity, Pa · s
ν = kinematic viscosity, m^2 · s^{-1}
σ = heat capacities ratio, $\sigma = 1 + \rho_s C_{ps} \cdot (1 - \epsilon)/(\rho_f \cdot C_{pf} \epsilon)$
ψ' = stream function, m^2 · s^{-1}
ψ = dimensionless stream function, $\psi = \psi'/\alpha'$

Subscripts

a = adiabatic
c = critical
f = fluid phase
s = solid phase
o = at $z' = L$

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