CONVECTIVE INSTABILITY OF EQUILIBRIUM OF A CHEMICALLY ACTIVE LIQUID IN A HORIZONTAL BED OF A POROUS MEDIUM

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This article gives the results of an investigation of the convective equilibrium of a reactive liquid saturating a horizontal porous bed, bounded by isothermal planes which have identical tempeatures. As the result of a chemical reaction of zero order, heat is evolved in the whole volume of the liquid; the amount of the heat evolution depends exponentially on the temperature. It is well known that [1], in such a system, in some interval of values of the Frank–Kamenetskii parameter δ, there are two possible sets of steady-state of heat-conducting conditions, corresponding to the mechanical equilibrium of the medium. One of these sets of conditions, corresponding to lower heatings, is stable; the second, characterized by higher equilibrium temperature conditions, is unstable. Since the heat-evolving medium is movable, there arises the question of the stability of these steady-state heat-evolving conditions with respect to the appearance of convection. In this work, the limits of the stability of both the lower and upper equilibrium states are determined. It is shown that the critical Rayleigh number, determining the threshold of convection, depends strongly on the rate of the chemical reaction. With all values of the parameters, the instability has a monotonic character.

An infinite horizontal bed of a porous medium with a thickness d is bounded by ideally heat-conducting impermeable planes. In the bed, saturated by a chemically active liquid, a homogeneous, exothermic decomposition reaction is going forward. The heat effect of the reaction is assumed to be high, which makes it possible to leave burn-up of the reagent out of consideration; i.e., a model of a reaction of zero order is used. The rate of the chemical process is described by the Arrhenius law. The bed boundaries are maintained at a constant temperature T_0. The z axis is directed vertically upward, and the xy plane coincides with the lower bed boundaries.

The kinetics of the reaction described differ considerably from those discussed in [2], in which an investigation was made of the development of concentrational convection in a porous medium, in the case of an isothermal reaction of the first order. The convective stability of a horizontal bed of an ordinary chemically active liquid with a reaction of zero order has been studied in [3, 4].

The equations of thermal convection of a reactive liquid in a porous medium differ from the equations of convective filtration [5] by the presence of a term describing the heat sources and have the form

$$\frac{1}{\rho_l}\nabla p+\frac{\nu}{K}\mathbf{v}-g\beta\Theta\boldsymbol{\gamma}=0,$$

$$(\rho c_p)_s\frac{\partial\Theta}{\partial t}+(\rho c_p)_l\mathbf{v}\nabla\Theta=\varkappa_s\Delta\Theta+Qk_0\exp\left(-\frac{E}{RT}\right),\quad \operatorname{div}\mathbf{v}=0. \qquad (1)$$

The filtration rate, as a rule, is small, which allows us to neglect the inertial terms in the equation of motion.

The following notation is introduced in system (1): $\mathbf{v}$ is the filtration rate; p is the convective addition to the pressure; Θ is the temperature, reckoned from the temperature of the boundaries of the bed: $\Theta = T - T_0$, where T and T_0 are the absolute temperatures, respectively, inside the bed and at its boundaries; ρ is the density; ν is the kinematic viscosity; β is the coefficient of volumetric expansion of the liquid; K is the permeability; c_p is the heat capacity at constant pressure; $\varkappa$ is the coefficient of thermal conductivity; g is the acceleration due to gravity; γ is a unit vector, directed vertically upward; Q is the heat

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effect of the reaction; k_0 is the preexponential factor; E is the activation energy; R is the universal gas constant. The subscripts l and s denote quantities relating, respectively, to the liquid and to the porous medium, saturated by the liquid.

We rewrite (1) in dimensionless form, retaining the previous notation and selecting the following units of measurement: the distance d, the time $d^2\chi$, the velocity χ/d, the temperature RT_0^2/E, the pressure $\rho_l \nu\chi/K$, where $\chi = \varkappa_s/(\rho c_p)_l$:

$$\nabla p + \mathbf{v} - \mathrm{Ra}\Theta\gamma = 0,$$

$$b\partial\Theta/\partial t + \mathbf{v}\nabla\Theta = \Delta\Theta + \delta \exp(\Theta/1 + \beta\Theta), \ \mathrm{div}\,\mathbf{v} = 0. \quad (2)$$

The dimensionless parameters of the problem: $\mathrm{Ra} = g\beta RT_0^2 Kd/E\nu\chi$ is the filtration analog of the Rayleigh number; $\delta = Qk_0 d^2 E \exp(-E/RT_0)/\varkappa_s RT_0^2$ is the Frank-Kamenetskii parameter; $\beta = RT_0/E$ is a small parameter, whose values do not exceed 0.1; $b = (\rho c_p)_s/(\rho c_p)_l$; the values of b are usually close to unity and, in what follows, we assume $b = 1$.

The mechanical equilibrium of the liquid, with which $\mathbf{v}_0 = 0$ and $\partial/\partial t = 0$, is described by the equations

$$\nabla p_0 = \mathrm{Ra}\Theta_0\gamma, \ \Delta\Theta_0 = -\delta \exp(\Theta_0/(1 + \beta\Theta_0)). \quad (3)$$

At the boundaries $z = 0, 1, \Theta_0 = 0$.

The first equation of system (3) shows that a necessary condition of equilibrium is a vertical tempeature gradient, which, in the presence of internal heat sources, depends on z.

The solution of the nonlinear differential equation of thermal conductivity from (3) is given in [1]. It is shown that steady states of the system with $\beta = 0$ are possible only with values of δ from 0 to 3.514. The upper boundary of this interval δ_{cr} determines the threshold of thermal explosion. The equilibrium distributions of the temperature are symmetrical with respect to the middle of the bed (see [1, 4]), where the temperature attains a maximum Θ_{0m}. Figure 1 gives the dependence of Θ_{0m} on δ for $\beta = 0$ and $\beta = 0.1$. In the region $\delta < \delta_{cr}$, there exist two sets of steady-state conditions, the upper of which is unstable [1].

Let us investigate the convective stability of the above-described equilibrium states. For this purpose, we consider small perturbations of the velocity, the temperature, and the pressure (for the perturbations, we retain the previous notation for $\mathbf{v}$, Θ, p). After linearization taking account of (3), the system of equations for the perturbations assumes the form

$$\nabla p + \mathbf{v} - \mathrm{Ra}\,\Theta\gamma = 0,$$

$$\frac{\partial\Theta}{\partial t} + \mathbf{v}\nabla\Theta_0 = \Delta\Theta + \delta\frac{\exp(\Theta_0/(1+\beta\Theta_0))}{(1+\beta\Theta_0)^2}\Theta, \ \mathrm{div}\,\mathbf{v} = 0. \quad (4)$$

At the walls of the bed, the normal component of the filtration rate and the perturbations of the temperature revert to zero

$$v_z = 0, \ \Theta = 0 \text{ with } z = 0;\ 1. \quad (5)$$

Let us consider normal perturbations, depending on the horizontal coordinates and the time in accordance with the law $\exp[-\lambda t + i(k_1 x + k_2 y)]$, where k_1 and k_2 are real wave numbers; λ is the decrement of the perturbations.

Eliminating the pressure from the equation of motion, from (4), (5) we obtain a boundary-value problem for the amplitudes of the perturbations of the velocity w(z) and the temperature $\theta(z)$

$$(w'' - k^2 w) = -k^2\mathrm{Ra}\theta,$$

$$-\lambda\theta = (\theta'' - k^2\theta) - w\Theta_0' + \delta\frac{\exp(\Theta_0/(1+\beta\Theta_0))}{(1+\beta\Theta_0)^2}\theta, \quad (6)$$

$$w = 0, \ \theta = 0 \text{ with } z = 0;\ 1,$$

where $k^2 = k_1^2 + k_2^2$; a prime denotes differentiation with respect to z.

The boundary-value problem was solved using the Runge–Kutta–Merson method [6], which makes it possible to automatically select a spacing of the integration which will assure a given accuracy of the calculations. The numerical calculations were made in an electronic computer. The use of this method for solution of problems of convective stability is dis-

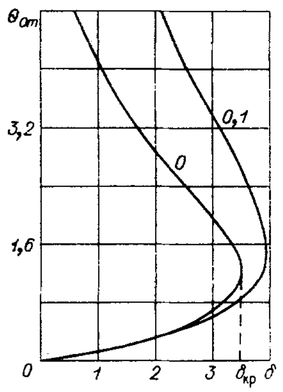

Fig. 1

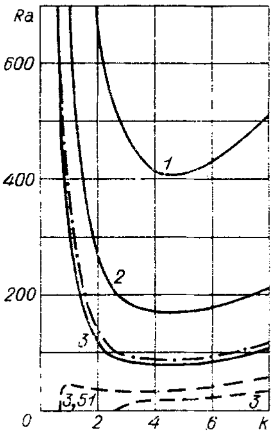

Fig. 2

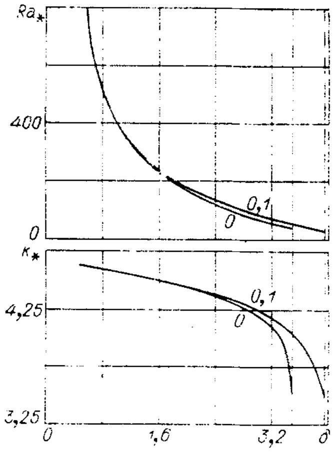

Fig. 3

cussed in [7]. In accordance with [7], the equations of the boundary-value problem were represented in the form of a system of ordinary differential equations of the first order, and, using the method described, two linearly independent partial solutions of the problem were constructed, satisfying the boundary conditions at the start of the integration interval $z = 0$. From the requirement of the existence of a nontrivial solution of the problem, satisfying the conditions at the end point of the integration $z = 1$, there follows a characteristic relationship from which the eigenvalues of the problem are determined. The eigenvalues of the problem are the decrements of the normal perturbations λ, depending on three parameters: the Rayleigh number, the Frank-Kamenetskii parameter, and the wave number. In the general case, the decrements are complex: $\lambda = \lambda_r + i\lambda_i$. Stable states correspond to $\lambda_r > 0$, unstable states to $\lambda_r < 0$; at the limit of stability, $\lambda_r = 0$.

In distinction from the usual problem of the convective stability of a horizontal bed of liquid without internal heat sources, for the problem under discussion, it is not possible to prove the principle of monotonicity; however, calculations show that all the decrements are real ($\lambda_i = 0$) and there are no vibrational conditions in the system.

In the limiting case Ra = 0, which is realized, for example, in the absence of a lifting force, problem (6) reduces to a boundary-value problem, determining the stability of equilibrium solutions in a liquid at rest. Its solution gives the spectrum of the decrements $\lambda(\delta)$. From the form of the spectrum of $\lambda(\delta)$ it follows that, with Ra = 0, steady-state equilibrium heat-conducting conditions, corresponding to small heatings, are stable, and conditions corresponding to large heatings, are unstable; here, perturbations with a plane-parallel structure ($k = 0$) are found to be the most dangerous.

Let us consider the general case, where the Rayleigh number differs from zero. As a result of an exothermic chemical reaction, the liquid inside the bed is heated and, in the upper half, there arises an unstable stratification, leading, with certain values of the parameters, to a crisis of the equilibrium of the system and to the development of convection. The threshold for the appearance of instability for a fixed value of δ is characterized by a neutral curve of Ra(k). In Fig. 2, the solid lines show a family of neutral curves of the convective stability of lower steady-state thermal conditions with different values of the Frank-Kamenetskii (δ = 1, 2, 3). The unstable region ($\lambda < 0$) is situated above the curves. Figure 2 exhibits a considerable lowering of the stability with a rise in δ. The destabilization is connected with the fact that, with an increase in the Frank-Kamenetskii parameter for this solution there is an increase in the equilibrium temperature at the center of the bed (see Fig. 1); i.e., there is a rise in the gradient of the density in its unstably stratified part.

The effect of the small parameter β is insignificant, and leads to a small increase in the convective instability of the system. A neutral curve, corresponding to δ = 3 and β = 0.1 is shown in Fig. 2 by the dot-dash line. The dashed curves of the neutral perturbations in Fig. 2 relate to the second equilibrium solution (δ = 3.51, 3). A stable state of the liquid corresponds to the region below the limits of stability. With a change in the heat-conducting conditions for values of δ close to δ_{cr}, there is deformation of the neutral curves, and long-wave perturbations lead to absolute instability of the upper steady state.

The decrease in δ, accompanying an increase in $\Theta_{\circ m}$ for the second solution, broadens the region of absolute instability. Thus, a rise in the Rayleigh number does not lead to stabilization of the second equilibrium state of the system, unstable under conditions of pure thermal conductivity.

We note that the picture obtained for convective instability in a bed of a porous medium is qualitatively similar to the known picture for a viscous chemically active liquid [3, 4].

Dependences of the minimal critical Rayleigh number Ra_* and the corresponding critical wave number k_* on δ for the lower equilibrium conditions are shown in Fig. 3. The curves are plotted with limiting values of β, i.e.. 0 and 0.1. With $\delta = \delta_{cr}$, Ra_* has a finite value.

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