pulsation velocity amplitude; $\mathrm{Re}_{re} = \bar{W}d/\nu$, reduced Reynolds number defined on the integral-mean relative flow velocity; W_0, W^*, $\bar{W}$, steady-flow, instantaneous pulsation, and integral-mean pulsation velocities, respectively; ωA, pulsation velocity amplitude; $\varphi = \omega A/W_0$, ratio of pulsation velocity amplitude to steady velocity component; $\omega = 2\pi f$, cyclic frequency; A, pulsation amplitude; k, mass-transfer coefficient; d, diameter of experimental sample; D, diffusion coefficient of benzoic acid in water; ν, kinematic viscosity coefficient; ΔG, weight loss of dissolved sample; ΔC, difference between saturation concentration and concentration in main mass of the solution; F, dissolution surface; τ, dissolution time.

LITERATURE CITED

1. G. A. Aksel'rud, Zh. Fiz. Khim., 27, No. 10, 1446 (1953).
2. V. V. Lopatin, Author's Abstract of Candidate's Dissertation, Institute of Engineering Thermophysics, Academy of Sciences of the Ukrainian SSR (1971).
3. V. E. Nakoryakov, A. P. Burdukov, A. M. Boldarev, et al., Heat and Mass Transfer in a Sound Field [in Russian], Nauka, Novosibirsk (1970), p. 253.
4. I. M. Fedotkin and V. S. Lipsman, Intensification of Heat Transfer in Food-Industrial Equipment [in Russian], Pishchevaya Prom-st', Moscow (1972), p. 240.

FREE CONVECTION IN A HETEROGENEOUSLY CATALYZED REACTION

K. V. Pribytkova, S. I. Khudyaev,
and É. A. Shtessel'

UDC 536.25

Limits have been defined for the monotonic convective instability in a horizontal layer of gas when a heterogeneous catalyzed reaction occurs at the lower boundary.

If a heterogeneous reaction is to be conducted under given conditions, it is necessary to know the precise details of the heat and mass transfer; in some instances, natural convection can accelerate the heat and mass transfer substantially, which can react back on the process. Therefore, it is important to define the conditions for free convection.

Consider an unbounded planar horizontal layer filled with a reacting liquid or gas and bounded by solid surfaces; a constant temperature and a constant reagent concentration are maintained at the upper surface. The lower surface is provided by the catalyst and is thermally insulated from the environment; the surface produces a catalytic reaction of the type

$$\nu_1 X_1 \xrightarrow{k(T)} X_2.$$

Convection can arise under such circumstances on account of the heating (cooling) at the surface and on account of the difference in molecular weight between the initial substances and the products.

The dimensionless equations are as follows in the Boussinesq approximation:

$$\frac{\partial V}{\partial \tau} + \Pr V\nabla V = -\nabla p + \Pr \Delta V + (R_1\theta + R_2 a)\,\bar{e}, \tag{1}$$

$$\frac{\partial a}{\partial \tau} + \Pr V\nabla a = \Delta a, \tag{2}$$

$$\frac{\partial \theta}{\partial \tau} + \Pr V\nabla \theta = L\Delta\theta \quad \left(L = \frac{1}{\mathrm{Le}}\right), \tag{3}$$

$$\operatorname{div} V = 0 \tag{4}$$

subject to the boundary conditions [1]

$$z = 1, \quad V = \theta = a = 0, \tag{5}$$

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 34, No. 5, pp. 818-826, May, 1978. Original article submitted April 12, 1977.

0022-0841/78/3405-0557$07.50

$$z=0,\ V=0,\quad -\frac{\partial a}{\partial z}=\gamma(1-a)\exp\theta,\quad -\frac{\partial\theta}{\partial z}=\delta(1-a)\exp\theta. \tag{6}$$

We use the following scale quantities: length h, velocity ν/h, temperature RT_0^2/E, pressure $\rho_0\nu D/h^2$, and time h^2D.

There are six dimensionless parameters in (1)-(6): the Prandtl number Pr, the Lewis number Le, the Rayleigh number R_1, the concentration analog of the Rayleigh number R_2, Frank-Kamenetskii's parameter δ for heterogeneous catalyzed reactions [1], and parameter γ, which represents the ratio of the reaction rate to the diffusion rate:

$$\mathrm{Pr}=\frac{\nu}{D},\quad \mathrm{Le}=\frac{D}{\varkappa},\quad R_1=\frac{g\varphi}{\nu D}\cdot\frac{RT_0^2}{E}h^3,\quad R_2=\frac{g\beta}{\nu D}h^3,$$

$$\delta=\frac{Q}{\lambda_1}\cdot\frac{E}{RT_0^2}hk_0\exp\left(-\frac{E}{RT_0}\right),\quad \gamma=\frac{k_0\exp\left(-\frac{E}{RT_0}\right)h}{D}.$$

The steady-state equations are solved for V = 0 to give the temperature θ_0 and the concentration a_0 at mechanical equilibrium:

$$\theta_0=A(1-z),\quad a_0=A\frac{\gamma}{\delta}(1-z),$$

where A is the temperature at the boundary z = 0 and is given by

$$\delta=A(\gamma+\exp(-A)). \tag{7}$$

We envisage equations in variations about mechanical equilibrium of the form

$$\frac{a}{\gamma}=u(z)\psi,\quad \frac{\theta}{\delta}=v(z)\psi,\quad A\,\mathrm{Pr}\,\frac{1}{\delta}w=\omega(z)\psi,$$

$$\psi=\exp(\lambda t+ik_1y+ik_2x).$$

The horizontal components of the velocity and pressure are eliminated in the usual way. Here we examine the limit to monotonic stability (we seek to define a relationship between the parameters such that $\lambda = 0$ is an eigenvalue). We put $\lambda = 0$ and introduce the symbols

$$\xi=k_1^2+k_2^2,\quad B=\gamma\cdot\exp A$$

to get the following system of equations:

$$u''-\xi u+\omega=0, \tag{8}$$

$$Lv''-L\xi v+\omega=0, \tag{9}$$

$$\omega^{\mathrm{IV}}-2\xi\omega''+\xi^2\omega-A\xi\left(\frac{\gamma}{\delta}R_2u+R_1v\right)=0. \tag{10}$$

The boundary conditions are

$$\begin{aligned}&z=0;\quad \omega=\omega'=0;\quad u'=v'=Bu-Av;\\&z=1;\quad \omega=\omega'=0;\quad u=v=0.\end{aligned} \tag{11}$$

It is complicated to define the exact limits for convection for $L \neq 1$, and very cumbersome expressions are involved; various approximate variational methods are also difficult to implement, although they are widely used in calculations on the limit to thermal gravitational convection [2-4].

Here we derive the critical Rayleigh number $R_1 = f(\gamma, \delta, L, \xi, R_2)$ by solving algebraic equations arising as difference equations on simple nets with few nodes.

Of course, this cannot be expected to give more than a qualitative result, but we shall see below that quite good quantitative results are obtained for the critical Rayleigh number.

In some simple instances, this technique amounts to approximate weighted averaging [5]; there is also a resemblance to the zero-dimensions method of [6].

We replace (10) by an algebraic equation at the point z = 1/2 on a five-point net; the four boundary conditions for ω allow us to choose the values of ω at the nodes in terms of the value at the central point z = 1/2.

The boundary condition $\omega'(0) = \omega'(1)$ is best used in integral style for a coarse net:

$$\int\limits_0^1 \omega''\,dz = 0. \tag{12}$$

We put

$$\omega_0=\omega(0);\quad \omega_1=\omega\left(\frac{1}{4}\right);\quad \omega=\omega\left(\frac{1}{2}\right);\quad \omega_3=\omega\left(\frac{3}{4}\right);\quad \omega_4=\omega(1)$$

and retain the same symbols for the derivatives of ω; we specify that (12) shall apply for the integral calculated by Simpson's method, which gives

$$\omega_0''+\omega_4''+2\omega''+4(\omega_1''+\omega_3'')=0. \tag{13}$$

The series expansions

$$\omega_1\approx\omega_0+\frac{1}{4}\omega_0'+\frac{1}{32}\omega_0'',$$

$$\omega_3\approx\omega_4-\frac{1}{4}\omega_4'+\frac{1}{32}\omega_4''$$

go with the boundary conditions $\omega_0 = \omega_4 = 0$, $\omega_0' = \omega_4'$ to give

$$\omega_0''+\omega_4''\approx 32(\omega_1+\omega_3). \tag{14}$$

A difference approximation is

$$\omega_1''\approx(\omega_0-2\omega_1+\omega)16;\quad \omega''\approx(\omega_1+\omega_3-2\omega)16;$$
$$\omega_3''\approx(\omega-2\omega_3+\omega_4)16;\quad \omega^{\mathrm{IV}}\approx(\omega_1''-2\omega''+\omega_3'')16, \tag{15}$$

which is used with (13) and (14) to give

$$\omega_1+\omega_3\approx\omega. \tag{16}$$

Equations (15) and (16) allow us to express the derivatives at point $z = 1/2$ in terms of the value of the function at that point, namely,

$$\omega''\approx-16\omega,\quad \omega^{\mathrm{IV}}\approx 512\omega. \tag{17}$$

Condition (16) is sufficient to derive (17), and ω_1 and ω_3 separately are not required. Therefore, the condition of (12) that the derivatives at the boundaries are zero is not used.

We replace (10) by an algebraic equation [$u = u(1/2)$, $v = v(1/2)$]:

$$-A\frac{\gamma}{\delta}R_2\xi u-AR_1\xi v+(512+32\xi+\xi^2)\omega=0. \tag{18}$$

Here and subsequently, it is convenient to assume that

$$\xi=8t, \tag{19}$$

and then (18) becomes

$$-A\frac{\gamma}{\delta}R_2 tu-AR_1 tv+8(t^2+4t+8)\omega=0. \tag{20}$$

Equations (8) and (9) are replaced by an algebraic equation at $z = 1/2$ by means of a three-point net.

We put

$$u_0=u(0),\quad u=u\left(\frac{1}{2}\right),\quad u_1=u(1);\quad v_0=v(0),\quad v=v\left(\frac{1}{2}\right),\quad v_1=v(1)$$

and retain the same subscripts for the derivatives of u and v; a simple approximation for the boundary conditions is

$$2u-2u_0=Bu_0-Av_0,\quad 2v-2v_0=Bu_0-Av_0$$

and this implies that

$$u_0=\frac{2-A}{2+B-A}u+\frac{A}{2+B-A}v,$$

$$v_0 = -\frac{B}{2+B-A}u + \frac{2+B}{2+B-A}v.$$

A difference approximation is

$$u'' \approx 4(u_0 - 2u + u_1), \quad v'' \approx 4(v_0 - 2v + v_1) \quad (u_1 = v_1 = 0)$$

and this is used with the values for u_0 and v_0 to get

$$u'' \approx -8\frac{1+B-\frac{A}{2}}{2+B-A}u + \frac{4A}{2+B-A}v,$$

$$v'' \approx -\frac{4B}{2+B-A}u - 8\frac{1+\frac{B}{2}-A}{2+B-A}v.$$

The difference equations corresponding to (8)-(10) take the form

$$-8b_1u + 4rv + \omega = 0, \tag{21}$$

$$-4Lqu - 8Lb_2v + \omega = 0, \tag{22}$$

$$-tA\frac{\gamma}{\delta}R_2u - tAR_1v + 8c\omega = 0, \tag{23}$$

where

$$t = \frac{\xi}{8}, \quad b_1 = t + \frac{1+B-\frac{A}{2}}{2+B-A}, \quad b_2 = t + \frac{1+\frac{B}{2}-A}{2+B-A},$$

$$c = t^2 + 4t + 8, \quad q = \frac{B}{2+B-A}, \quad r = \frac{A}{2+B-A}.$$

The determinant of (21)-(23) is equated to zero to give the following relation between the parameters:

$$R_1 = 64\frac{L}{A}\cdot\frac{(8+4t+t^2)(1+2t)\left(t+\frac{1}{2}(1+q-r)\right)}{t(q(1-L)+1+2t)} - \frac{r(1-L)+L(1+2t)}{q(1-L)+1+2t}\cdot\frac{\gamma}{\delta}R_2. \tag{24}$$

Minimization of (24) with respect to t gives the boundary to the monotonic stability as $R_1 = f(R_2, L, \gamma, \delta)$; the minimization itself represents no essential difficulty.

Formula (24) takes the following form for L = 1:

$$\mu = 64(t^2 + 4t + 8)\left(1 + \frac{\alpha}{t}\right), \tag{25}$$

where

$$\mu = \left(R_1 + \frac{\gamma}{\delta}R_2\right)\Big/A; \quad \sigma = \gamma\exp A - A; \quad \alpha = \frac{1+\sigma}{2+\sigma}. \tag{26}$$

Minimization of (25) involves solving the cubic equation

$$g(t) = 2t^3 + (\alpha + 4)t^2 - 8\alpha = 0, \tag{27}$$

whose only positive root can be determined approximately; we take t = 1 as the initial approximation and perform a single iteration in Newton's method to get

$$t_* \approx 1 - \frac{g(1)}{g'(1)} = \frac{8+9\alpha}{14+2\alpha}, \tag{28}$$

$$\mu_* \approx 64(t_*^2 + 4t_* + 8)\left(1 + \frac{\alpha}{t_*}\right). \tag{29}$$

Formula (28) is unsuitable as $\sigma \to -1$ $(\alpha \to 0)$, and in that case we have directly from (27) that

TABLE 1. Comparison of μ_* and μ_{**} Given by (29) and (35) with the μ_0 Given by Galerkin's Method

σ	μ_{**}	μ_0	μ_*	k_{**}	k_0	k_*
—0,9	932	1074	768	1,60	1,80	1,80
—0,5	1196	1215	1068	2,42	2,35	2,45
—0,2	1285	1274	1178	2,50	2,50	2,53
0	1331	1304	1230	2,53	2,55	2,58
0,2	1364	1330	1272	2,56	2,60	2,61
0,5	1405	1362	1328	2,61	2,67	2,65
1	1450	1404	1376	2,68	2,75	2,70
2	1507	1462	1455	2,73	2,84	2,76
5	1575	1550	1545	2,83	2,96	2,83
∞	1660	1708	1660	2,94	3,11	2,91

$$t_* \approx \left(\frac{2\alpha}{1 + \left(\frac{\alpha}{2} \right)^{1/2}} \right)^{1/2}$$

We see from (25) that there is no minimum in this function for $\sigma < -1$ ($\alpha < 0$) if $t > 0$, which agrees with the observation that $\sigma < -1$ means that there is an unstable steady-state solution to (1)-(4) for $V = 0$ and, therefore, $\sigma < -1$ means that convection always occurs for appropriate initial conditions. There are no critical conditions.

We denote the right side of (7) by $f(A)$, $f(A) = A(\gamma + \exp(-A))$, which gives

$$f'(A) = \gamma - (A - 1)\exp(-A). \tag{30}$$

The condition $\sigma < -1$ of (26) means that $f'(A) < 0$, so $\sigma < -1$ occurs only over the decreasing range $A_1 < A < A_2$ for $f(A)$, which itself occurs for $\gamma < e^{-2}$ [1]. In that case, (7) has three roots in the range $\delta_1 < \delta < \delta_2$, and the middle one of these falls in the decreasing range of $f(A)$ that corresponds to an unstable steady-state solution to (1)-(4) for $V = 0$.

The quantities A_1 and δ_1 and also A_2 and δ_2 correspond to the critical conditions for ignition and extinction, respectively [1]; if $\gamma \ll 1$, it follows from (7) and $f'(A) = 0$, as implied by (30), that

$$A_1 \approx 1 + e\gamma, \quad \delta_1 \approx \frac{1}{e} + \gamma, \quad \sigma = -1, \tag{31}$$

$$A_2 \approx \ln \frac{\ln \frac{1}{\gamma} - 1}{\gamma}, \quad \delta_2 \approx \gamma \ln \frac{\ln \frac{1}{\gamma} - 1}{\gamma} \left(1 + \frac{1}{\ln \frac{1}{\gamma} - 1} \right), \quad \sigma = -1. \tag{32}$$

The stable roots of (7), i.e., those occurring for $A < A_1$, $A > A_2$, imply that σ exceeds -1, and this always occurs for $\gamma > -e^{-2}$.

The same coarse net has also been used with other approximations, in particular, the following. The integral relation

$$\int_0^1 u'\,dz + u_0 = 0$$

applies by virtue of $u(1) = 0$; the following is the value of the integral given by Simpson's formula:

$$u_0' + u_1' + 4u' + 6u_0 = 0. \tag{33}$$

Boundary condition (11) gives us $u_0' = \sigma u_0$ for $L = 1$; we use (33) with the difference approximation

$$u' = u_1 - u_0, \quad u'' = 4(u_0 - 2u + u_1),$$
$$u - u_1 = -\frac{1}{2}u_1' + \frac{1}{8}u_1'' - \frac{1}{48}u_1''',$$

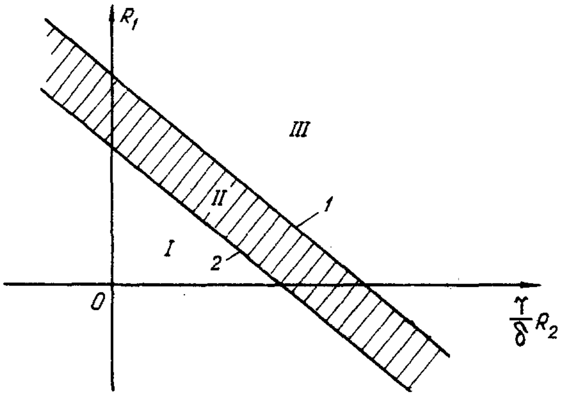

Fig. 1. Regions of convective stability: I) convective stability; II) region of stability for a reaction occurring in the kinetic mode but instability for a reaction occurring in the diffusion mode; III) region of instability.

and the equations $u_1 = 0$, $u_1'' = 0$, $u_1''' = \xi u_1'$ implied by (8) to get

$$u_0 \simeq \frac{2u}{(2+\sigma)\left(1+\frac{t}{3}\right)}, \quad u'' = -8\,\frac{3\alpha+t}{3+t}\,u.$$

This approximation resembles (28) and (29) in leading to the following results for L = 1;

$$t_{**} \simeq \frac{155+69\alpha}{262-54\alpha}, \tag{34}$$

$$\mu_{**} = 64\,(t_{**}^2 + 4t_{**} + 8)\left(1 + \frac{3\alpha + t_{**}}{t_{**}(3+t_{**})}\right). \tag{35}$$

Table 1 compares calculated values for μ_* and μ_{**} given by (28), (29), (34), and (35) with the critical number μ_0 calculated by Galerkin's method via a single basis function $w = z^2(1-z)^2$ as in [3].

Table 1 also gives for comparison the wave numbers $k = \sqrt{\xi} = \sqrt{8t}$ at which the values μ_*, μ_0, and μ_{**} are attained, respectively; if we eliminate the neighborhood of $\sigma = -1$ and consider only the range $-0.5 \leqslant \sigma < \infty$, there is only 2-3% deviation of μ_{**} from μ_0. Also, μ_* gives a good approximation, particularly for $\sigma > 0$.

A relationship between u and u_0 is

$$u - u_0 = \frac{1}{2}\,u_0' + \frac{1}{8}\,u_0'' + \frac{1}{48}\,u_0''',$$

where $u_0' = \sigma u_0$, $u_0'' = \xi u_0$, and $u_0''' = \sigma\xi u_0$; we then get a result close to that given in the table.

Therefore, a simple net gives a stable result largely independent of the method of approximation. The method is readily extended to a finer net, but the most interesting result appears to be that a very simple net can give an adequate approximation. Another interesting point is that convenient working formulas are obtained.

Of course, this net provides only the least eigenvalue; a finer net with more nodes must be used if the larger eigenvalues are required.

In conclusion, we describe the structure of the convective region for L = 1 and $\gamma < e^{-2}$, i.e., in the region of the three steady-state solutions.

Various possible modes can occur in a heterogeneous catalytic reaction, where γ and δ are the decisive factors [1]. The conditions for convection vary similarly. It follows from (7) that there will be a jump from the kinetic region to the diffusion one and back again for the critical ignition and extinction conditions if $\gamma < e^{-2}$; the catalyst temperature and the product concentration then vary sharply. There are no critical conditions if $\gamma > e^{-2}$, because (7) has a single solution, so the temperature and concentration vary smoothly. The critical ignition and extinction conditions are defined by (31) and (32) for $\gamma \ll 1$.

We consider the expression for the critical convection conditions for these modes; since $\sigma = -1$, $\alpha = 0$ near the ignition and extinction limits, as (25) shows, we have

$$R_1 + \frac{\gamma}{\delta} R_2 = \frac{1}{A_i} 64 (t^2 + 4t + 8), \ i = 1,2.$$

Here (31) and (32) define A_1 and A_2.

Figure 1 shows these relationships qualitatively in R_1, $(\gamma/\delta)R_2$ coordinates, where curve 1 corresponds to the ignition condition (i = 1) and curve 2 corresponds to the extinction condition (i = 2). The region of convective stability lies below curve 2 (region I); III corresponds to the region of convective instability; and II is the region of convective stability for the kinetic mode but of instability for the diffusion mode.

It is clear that conditions are most favorable to convection when the reaction occurs in the diffusion mode; this is physically reasonable, since then there are the largest temperature and concentration differences on account of the reaction.

Curve 1 is displaced continuously upward as we recede from the ignition limit, since the temperature rise at the catalyst and the product concentration there are reduced by the resulting convection. When the critical conditions for ignition are reached, straight line 1 for convective stability passes stepwise into region I; i.e., in region II there cannot be a single straight line that separates the regions of convective stability and instability for any δ and γ.

NOTATION

u, v, temperature variations; ω, vertical velocity variation; k_1, k_2, Fourier transform parameters (wave numbers); $\xi = k_1^2 + k_2^2$, $t = \xi/8$; μ, Rayleigh number; σ, parameter in boundary condition; $u' = \sigma u$, $\alpha = (1 + \sigma)/(2 + \sigma)$; X_1, initial substance; X_2, reaction product; ν_1, stoichiometric coefficient; k(T), rate constant; V, velocity vector; w, vertical velocity; p, pressure; a, product concentration; θ, temperature; τ, time; h, layer thickness; ν, kinematic viscosity; D, diffusion coefficient; $\varkappa$, thermal diffusivity; g, gravitational acceleration; φ, volume expansion coefficient; R, universal gas constant; E, activation energy; ρ_0, density in initial state; T_0, upper wall temperature; β, diffusion analog of the volume expansion coefficient; Q, heat of reaction; λ_1, thermal conductivity; k_0, preexponential factor; $\bar{e}$, unit vector antiparallel to g; Pr, Prandtl number; Le, Lewis number; R_1, thermal Rayleigh number; R_2, concentration Rayleigh number; δ, Frank-Kamenetskii parameter; γ, ratio of reaction rate to the diffusion rate; A, temperature at z = 0; λ, Laplace transform parameter (perturbation decrement); b_1, b_2, c, q, r, combinations of the kinetic parameters δ and γ.

LITERATURE CITED

1. D. A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetics [in Russian], Nauka, Moscow (1967).
2. K. V. Pribytkova and É. A. Shtessel', "Effects of gravitational convection on the course of a heterogeneous catalyzed reaction under isothermal conditions," Inzh.-Fiz. Zh., 30, No. 2 (1976).
3. G. Z. Gershuni and E. M. Zhukhovitskii, Convective Stability in an Incompressible Liquid [in Russian], Nauka, Moscow (1972).
4. P. Glensdorf and I. Prigogine, The Thermodynamic Theory of Structure, Stability, and Fluctuations [Russian translation], Mir, Moscow (1973).
5. A. I. Vol'pert and S. I. Khudyaev, Analysis in Classes of Discontinuous Functions and the Equations of Mathematical Physics [in Russian], Nauka, Moscow (1975).
6. L. A. Vulis, Thermal Conditions of Combustion [in Russian], Gosénergoizdat, Moscow (1954).