

2. Galkin, V. S., Kogan, M. N. and Fridlender, O. G., On free convection in gas in the absence of external forces, *Izv. Akad. Nauk SSSR, MZhG*, № 3, 1971.
3. Galkin, V. S., Fridlender, O. G. and Tsar'kova, G. E., Examples of thermal-stress convection. *Uch. Zap. TsAGI*, № 5, 1972.
4. Galkin, V. S., Kogan, M. N. and Fridlender, O. G., Flow past a strongly heated sphere by a gas with low Reynolds numbers. *PMM Vol. 36*, № 5, 1972.
5. Chapman, S. and Cowling, T. G., *Mathematical Theory of Nonuniform Gases*, Camb. Univ. Press, 1960.
6. Maxwell, J. C., On stresses in rarefied gases arising from inequalities of temperature. *Phil. Trans. Roy. Soc.*, Vol. 170, 1879.
7. Epstein, P. S., Zur Theorie des Radiometers. *Z. Für Physik*, Vol. 54, p. 537, 1929.
8. Stratton, J., *Theory of Electromagnetism*, Gostekhizdat, Moscow, 1948.
9. Sone, Y., Flow induced by thermal stresses in rarefied gas. *Phys. Fluids*, № 8, 1972.
10. Dwyer, H. A., Thirteen-moment theory of the thermal force on a spherical particle. *Phys. Fluids*, № 5, 1967.
11. Kochin, N. E., Kibel', I. A. and Roze, N. V., *Theoretical Hydromechanics, pt. 2*, Gostekhizdat, Moscow-Leningrad, 1948.
12. Galkin, V. S., Kogan, M. N. and Fridlender, O. G., On concentration stress convection and certain properties of slow flows of gas mixtures. *Izv. Akad. Nauk SSSR, MZhG*, № 2, 1972.
13. Shavaliyev, M. Sh., The Barnett approximation in multiconstituent gas mixtures. *Collection: Kinetic Theory of Gases and Plasma*, SO Akad. Nauk SSSR, Novosibirsk, 1971.
14. Waldmann, L., Transport phenomena in gases at average pressure. *Collection: Thermodynamics of Gases, Mashinostroenie*, Moscow, 1970.

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CONVECTION IN CHEMICALLY ACTIVE MEDIA

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We consider the stability of a horizontal layer of a dissociating liquid or gas subject to a given vertical temperature gradient. We determine conditions for the appearance of stationary and oscillating convection corresponding to an arbitrary time for the establishment of local chemical equilibrium.

Two problems concerning the appearance of convection in a layer of dissociating fluid with an arbitrary dissociation time were investigated in [1]. In the first of these problems it was assumed erroneously that unlike the temperature the degree of dissociation does not depend on the height, although there is

"chemical equilibrium". In the second problem convection was considered in a fluid chemically not in equilibrium. In contrast to [1], we study convection when the initial degree of dissociation depends on the height, although chemical equilibrium is present. We also take into account the compressibility of the gas.

1. Description of the model. Consider a horizontal layer of a liquid or a gas whose molecules or atoms react according to the scheme $A \rightleftharpoons B + C$, the molecular (or atomic) weights of the components B and C being identical. This type of reaction is realized, for example, in the dissociation of a diatomic gas ($A_2 \rightleftharpoons A + A$).

The equation for energy conservation can be written in the form

$$\rho \frac{dU}{dt} + p \nabla \mathbf{v} = - \nabla \mathbf{q} \quad (1.1)$$

Here ρ is the mass density of the reacting mixture, p is the pressure, \mathbf{v} is the momentum per unit volume, U is the internal energy per unit mass, and \mathbf{q} is the heat flow. The internal energy depends linearly on the temperature T and on α , the relative concentration of the component B (or C)

$$U = c_0 T + c_1 \alpha$$

(c_0 is the specific heat capacity for $\alpha = \text{const}$, and c_1 is the specific heat capacity for $T = \text{const}$). When the heat diffusion and the barodiffusion are inconsequential the heat flow is given by

$$\mathbf{q} = -\lambda \nabla T - \rho D_{12} c_1 \nabla \alpha$$

Throughout the sequel we assume that the coefficients of thermal conductivity λ and of diffusion D_{12} are constant.

For small departures from chemical equilibrium the equation for the relative concentration assumes the form

$$\frac{d\alpha}{dt} + \frac{\alpha - \alpha_e(T)}{\tau} = \frac{D_{12}}{\rho} \nabla (\rho \nabla \alpha) \quad (1.2)$$

Here τ is a characteristic time for the establishment of chemical equilibrium and $\alpha_e(T)$ is the equilibrium value of the relative concentration α at the temperature which the gas or liquid has in a given volume element. In problems dealing with convective stability it is necessary to distinguish this temperature from the initial equilibrium temperature. For small temperature drops we can write (ϕ is a coefficient independent of the temperature and the pressure)

$$\alpha_e(T) = \alpha_m + \phi (T_0 + T') \quad (1.3)$$

Here and in the sequel an arbitrary quantity f is written in the form

$$f(x, y, z; t) = f_m + f_0(z) + f'(x, y, z; t)$$

The subscript m means that the value of f is taken (for definiteness) at the lower boundary of the layer; the coordinate z is reckoned vertically upwards from the median layer; and x, y are horizontal coordinates.

Let us assume that the temperature on each boundary remains constant and d is the layer thickness, we have

$$T\left(z = \pm \frac{d}{2}\right) = T_m$$

We can choose the chemical composition on the boundaries $z = \pm d/2$ to be in equi-

librium and, by virtue of Eq. (1.3), we can assume it to be constant; for simplicity we choose the boundaries to be "free" [2]

$$v_z = \partial^2 v_z / \partial z^2 = 0 \quad \text{for } z = \pm d/2$$

For the equilibrium state ($d/dt = 0 = v$, $\alpha = \alpha_e$) it follows from Eqs. (1.1) and (1.2) and from the conditions of mechanical equilibrium ($\mathbf{g} = (0, 0, -g)$ is the free-fall acceleration) that

$$\frac{d}{dz} \left[(\rho_m + \rho_n) \frac{dx_0}{dz} \right] = 0, \quad \frac{dp_0}{dz} = -g(\rho_m + \rho_n) \quad (1.4)$$

$$T_0 = \gamma(z + d/2) \quad (\gamma = \text{const})$$

It is evident from (1.3) that the thermochemical equilibrium value must conform to the linear law

$$\alpha_0 = \phi\gamma(z + d/2) \quad (1.5)$$

If we assume that the characteristic scale of variation of all the quantities is considerably larger than the thickness d of the layer, it becomes convenient to introduce the small parameter $\varepsilon = d / D_{\min}$, where D_{\min} is the smallest of the quantities

$$D_f = \left| \frac{f_m}{\partial f_0 / \partial z} \right|$$

Upon retaining terms of order ε^0 and ε^1 , we see that the relation (1.5) satisfies the first of the equations (1.4).

In what follows we can use an equation of state written in the linearized form ($\beta_{1,2}$ are the thermal and concentration contraction coefficients, and β_3 is the compressibility coefficient)

$$\frac{\rho' + \rho_0}{\rho_m} = \beta_1(T - T_m) + \beta_2(\alpha - \alpha_m) + \beta_3(p - p_m)$$

2. Dispersion relation. If we use the Boussinesq approximation in the momentum conservation equation we can retain only one term of order ε , the term corresponding to the buoyancy force [3] (ν is the coefficient of kinematic viscosity)

$$\left(\frac{\partial}{\partial t} - \Delta \nu \right) \mathbf{v} = \mathbf{g}(\beta_1 T' + \beta_2 \alpha') - \frac{\nabla p'}{\rho_m} \quad (2.1)$$

From Eq. (1.1) we obtain

$$\frac{\partial}{\partial t} (c_p T' + c_1' \alpha') + v_z \gamma (c_p + \phi c_1') - g v_z = \frac{\lambda}{\rho_m} \Delta T' + D_{12} c_1 \Delta \alpha' \quad (2.2)$$

$$c_p = c_0 - \frac{p_m \beta_1}{\rho_m}$$

In the sequel we assume that $c_1' \approx c_1$. Small changes in the relative concentration conform to the equation

$$\frac{\partial \alpha'}{\partial t} + \phi \gamma v_z + \frac{\alpha' - \phi T'}{\tau} = D_{12} \Delta \alpha' \quad (2.3)$$

by virtue of the relations (1.2) and (1.3). Equations (2.1) - (2.3), together with the incompressibility condition, form a closed system with the boundary conditions described above. The horizontal homogeneity of the medium and the linearity of the equations makes it possible to seek dynamic perturbations in the form

$$f' = F(z) \exp(ikr + \omega t)$$

where \mathbf{r} and \mathbf{k} are, respectively, the radius vector and the wave vector in the horizontal plane. The resulting linear equations for the amplitudes F reduce to a system containing the operators d^n / dz^n for even n only; on the boundaries these derivatives are equal to zero, therefore

$$F \propto \sin [m\pi (z / d + 1/2)] \quad m = 1, 2, 3, \dots$$

Using this relation, we can obtain the dispersion equation

$$\Lambda \sigma^3 + a \Lambda \sigma^2 + \left[b + \frac{l^2}{P} \left(R \frac{\beta_1 + \beta_2 \phi}{\beta_1} - R_* \right) \right] \sigma + \tag{2.4}$$

$$\frac{l^2}{P} \left\{ R \left[\frac{c_T}{c_p} q + \Lambda \phi \left(\frac{c_1}{S c_p} - \frac{\beta_2}{\beta_1 P} \right) \right] - q R_* \right\} + \Lambda^3 \left[\frac{c_T}{c_p \xi} P_*^{-1} - \frac{\Lambda}{SP} \right] = 0$$

where

$$a = c_T / (c_p \xi) - \Lambda (1 + S^{-1} + P^{-1}), \quad \Lambda = \pi^2 + l^2$$

$$b = \Lambda^3 (P^{-1} + P^{-1} S^{-1} + S^{-1}) - \Lambda^2 c_T (1 + P_*^{-1}) / (c_p \xi)$$

$$q = (\beta_1 + \beta_2 \phi) / (\beta_1 \xi) - \Lambda / S, \quad \kappa = \lambda / (\rho_m c_p)$$

$$R_* = g^2 \beta_1 d^4 / (v \kappa c_p), \quad P_* = v / \kappa_0, \quad \kappa_0 = (\lambda + \rho_m D_{12} c_1 \phi) / (\rho_m c_T)$$

$$R = \gamma \beta_1 g d^4 / (v \kappa), \quad P = v / \kappa, \quad S = v / D_{12}$$

(σ, l, ξ are, respectively, the dimensionless frequency, wave number, and dissociation time; R, P, S are, respectively, the Rayleigh, Prandtl, and Schmidt numbers).

3. Conditions for the rise of convection. We clarify, first of all, whether it is possible to have oscillating convection in the system. Let $\sigma = \sigma_r + i\sigma_i$. According to (2.4) a departure from the neutral state ($\sigma_r = 0$) can be accompanied by oscillations if the equations

$$-\Lambda \sigma_i^2 = b + \frac{l^2}{P} \left[R \left(1 + \frac{\beta_2 \phi}{\beta_1} \right) - R_* \right] \tag{3.1}$$

$$\Lambda a \sigma_i^2 = \frac{l^2}{P} (R \Sigma - q R_*) + \Lambda^3 \left(\frac{c_T}{c_p} \frac{1}{\xi P_*} - \frac{\Lambda}{SP} \right) \tag{3.2}$$

$$\left(\Sigma = \frac{c_T}{c_p} \frac{\beta_1 + \beta_2 \phi}{\beta_1 \xi} - \frac{\Lambda}{S} - \frac{\Lambda \phi \beta_2}{\beta_1 P} \right)$$

are satisfied by real values of σ_i and R .

It is known that stationary convection does not arise if $R < R_0^{(st)}$, where $R_0^{(st)}$ is the minimum of the function $R^{(st)}(l^2)$, equal, according to the dispersion relation, to

$$R^{(st)} = \left[\frac{\Lambda^3}{l^2} \left(\frac{\Lambda}{S} - \frac{P}{P_*} x \right) + R_* \left(\mu x \frac{c_p}{c_T} - \frac{\Lambda}{S} \right) \right] \left[\mu x - \frac{\Lambda}{S} - (\mu - 1) \frac{\Lambda}{P} \right]^{-1} \tag{3.3}$$

$$\mu \equiv 1 + \frac{\beta_2 \phi}{\beta_1}, \quad x \equiv \frac{c_T}{c_p \xi}$$

The convection can only be oscillating if $R > R_0^{(0)}$, where $R_0^{(0)}$ is the minimum of the function $R^{(0)}(l^2)$, obtained by solving the system (3.1) and (3.2) for R

$$R^{(0)} = \{ -\Lambda (1 + P_*^{-1}) x^2 + [1 + M + (S^{-1} + P^{-1})(P_*^{-1} + 1)] \times \tag{3.4}$$

$$\Lambda^2 x - \Lambda^3 (S^{-1} + P^{-1}) (1 + M) + [(R_* / \Lambda) (\mu c_p / c_T - 1) x +$$

$$\Lambda (P^{-1} + 1)] l^2 P^{-1} \} l^{-2} P [P^{-1} + \mu + (\mu - 1) S^{-1}]^{-1}$$

$$M = P^{-1} + P^{-1} S^{-1} + S^{-1}$$

The frequency σ_i of the oscillations in the neutral state is given by

$$\sigma_i = \left\{ \frac{l^2 R_*}{P \Lambda} (\mu - 1) (P^{-1} - S^{-1}) - \Lambda^2 \left[\frac{P^{-1} + 1}{S^2} + (\mu - 1) \frac{S^{-1} + 1}{P^2} \right] + \right. \quad (3.5)$$

$$x \left[\mu (\mu - 1) \frac{l^2 R_*}{P \Lambda^2} - \Lambda \mu (P_*^{-1} - M) + \Lambda (P_*^{-1} + 1) \left(S^{-1} + \frac{\mu - 1}{P} \right) \right] -$$

$$\left. (1 + P_*^{-1}) \mu x^2 \right\}^{1/2} \left(\mu + P^{-1} + \frac{\mu - 1}{S} \right)^{-1/2}$$

and satisfies the relation

$$\sigma_i^2 a / \Sigma = R^{(st)} - R^{(0)} \quad (3.6)$$

4. Results. **4.1. Convection for instantaneous establishment of chemical equilibrium.** Letting $\tau \rightarrow 0$ in Eqs. (3.3) and (3.5) shows that oscillating convection cannot develop, and the condition for the rise of stationary convection assumes the form

$$\frac{g (\beta_1 + \beta_2 \phi) d^4}{\nu \kappa_0} \left(\gamma - \frac{g}{c_T} \right) \geq \frac{27\pi^4}{4}$$

This relationship is entirely analogous to the ordinary criterion for the convective stability of a gas since $\beta_1 + \beta_2 \phi$, g / c_T and κ_0 are, respectively, the effective coefficients of contraction, adiabatic temperature gradient, and thermal diffusivity in a quasi-equilibrium state of the dissociating gas.

4.2. Binary mixture ($\tau \rightarrow \infty$). In this case the sign of the parameter ϕ determines the sign of the concentration gradient: $\gamma_2 = \phi \gamma_1$. The stability conditions are the same as the conditions obtained in [4] for the case of two free boundaries, except that R must be replaced by $R - R_*$.

4.3. Convection in an incompressible fluid. When the density of the fluid varies in the same way both during an increase in the temperature and with an increase in the monomer concentration, then no oscillation in the convection is possible: the right side of Eq. (3.5) is imaginary when $\mu \geq 1$ and $\tau \rightarrow \infty$, and $\partial \sigma_i / \partial x < 0$ for $x > 0$. It should then be expected that in chemically unstable fluids with the properties enumerated in Sect. 1 the convection is stationary. If, as is usually the case, $\beta_1 < 0$, then there is a loss of stability only at sufficient heating from below.

In [5] a conclusion was derived concerning the loss of stability when a layer of a weakly dissociating fluid with a small rise time for equilibrium dissociation is heated from above. This statement is apparently incorrect since it was obtained from the analysis of a system of equations in which the relation $\delta \alpha = \phi \delta T$ was used everywhere except in the momentum conservation equation and in the term $(\alpha - \alpha_0) / \tau$ in the equation for the relative monomer concentration (analogous to Eq. (1.2) of the present paper).

From Eqs. (3.3) - (3.6), which are also valid for $\mu < 1$, it follows that convection is also possible when a layer of a liquid with a finite rise time to chemical equilibrium is heated from above. According to (3.3), the function $R^{(st)}(l^2)$ has the vertical asymptote

$$l_a^2 = -\pi^2 - \frac{\mu x P S}{P + (\mu - 1) S}$$

subject to the condition that either $S > P$ and

$$\frac{\pi^2}{\pi^2 + P x} < \frac{\mu S}{S - P} < 1 \quad (3.7)$$

or $P > S$ and

$$1 > \frac{\mu S}{S - P} > \frac{\pi^2}{\pi^2 + Px} \quad (3.8)$$

Suppose that the conditions (3.7) are satisfied. We can then conclude that for heating from above, only stationary convection occurs (according to Eq. (3.4) the necessary condition for the onset of oscillating convection with heating from above is

$$\mu < (P - S) P^{-1} (S + 1)^{-1}$$

In the case (3.8) similar reasoning shows that with heating from below, only stationary convection is possible for $l > l_a$. For $l < l_a$ oscillating convection competes with stationary convection in both cases, depending on the way the parameters are related.

4.4. Dissociating gas. In considering convection in a gas we can use the notion of an ideal dissociating gas suggested by Lighthill [6]. It is not difficult to show that in this case convection commences only with heating from below: the functions $R^{(st)}$ and $R^{(0)}$ are positive and attain their minima only once for the various l . It is evident from (3.6) that if $\sigma_i^2 > 0$, then $R^{(0)} < R^{(st)}$. When $l \rightarrow 0$ and $l \rightarrow \infty$, we have $R^{(0)} > R^{(st)}$ for arbitrary x . By Descartes' rule the number of positive roots of the equation $\sigma_i(l^2)$ is limited to two roots. This equation has no positive roots if $\tau < \tau_*$; we can obtain a rough estimate for the critical value of the relaxation time by setting $P \approx S$

$$\tau_* = \frac{g^2 d^2}{\pi^2 \kappa} \frac{\phi}{c_T}$$

It follows from this that oscillating convection is only possible in sufficiently thick layers of gas (D is the dissociation energy)

$$d > 2 \cdot 10^{-15} \frac{T^{5/4} N V \bar{z}}{g} \left[1 + \left(\frac{D}{kT} \right)^2 \frac{\alpha}{8} \right]^{1/2}$$

For nitrogen, heated to 6000°K at a pressure of 1 atm ($\alpha \approx 0.1$, $\tau \approx 2 \times 10^{-5}$ sec, $P \approx 0.7$; $S \approx 0.5$) oscillating convection is not possible in a layer less than 20 km thick (in the model considered the thickness of the layer must be much less than the height of the "homogeneous atmosphere"). The result obtained here may prove useful in studying convective stability of the high temperature planetary atmospheres.

REFERENCES

1. Bdzil, J. and Frish, H. L. Chemical instabilities. VI. Hydrodynamic stability of the dissociating fluid $A_2 \rightleftharpoons A + A$. Phys. Fluids, Vol. 14, № 9, 1971.
2. Chandrasekhar, S., Hydrodynamic and hydromagnetic stability. Oxford Univ. Press, Oxford, 1961.
3. Spiegel, E. A. and Veronis, G., On the Boussinesq approximation for a compressible fluid. Astrophys. J., Vol. 131, № 2, 1960.
4. Nield, D. A., The thermohaline Rayleigh-Jeffreys problem. J. Fluid Mech., Vol. 29, № 3, 1967.
5. Wollkind, D. J. and Frish, H. L., Chemical instabilities 1. A heated horizontal layer of a dissociating fluid. Phys. Fluids, Vol. 14, № 1, 1971.
6. Lighthill, M. J., Dynamics of a dissociating gas. J. Fluid. Mech., Vol. 8, Part 2, 1960.

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