

## THE EFFECT OF UNIFORM MAGNETIC FIELD ON THE STABILITY OF RAYLEIGH–BENARD CONVECTION IN THE ELECTROCHEMICAL SYSTEM

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**Introduction.** When a current is passed through a stagnant solution between two horizontal electrodes, two states of the system can be observed: (1) The solution remains stagnant in spite of the variation in its density  $\rho$  near the electrodes. The buoyancy forces are balanced by the viscosity forces. (2) The buoyancy force initiates convective instability, the initially stagnant solution starts to flow: a solution with a higher density, which forms near the upper electrode, flows downward, and a solution with a lower density, which forms near the lower electrode, flows upward. For the limiting-current mode, to the approximation of solution electroneutrality, the problem of Rayleigh-Benard instability for a binary electrolyte is equivalent to the problem of heat convection that has been much studied [1, 2, 3, 4, 5]. In this case, only a monotonic convective instability can arise [6]. In a solution with a more complex composition, an oscillatory instability can arise along with the monotonic one. Several works were devoted to the study of monotonic and oscillatory instabilities in electrochemical systems with three types of ions [7, 8]. In these works, approximate solutions of the problem for the cathodic deposition (anodic dissolution) of metal were obtained. Systems with redox reactions were not considered in the literature. Moreover, the Rayleigh numbers, which were used in these studies, differ from the commonly accepted values. The problem of Rayleigh-Benard for heat convection in the magnetic field was studied by Chandrasekhar [1]. In this work, we will theoretically analyze the conditions of the onset of monotonic and oscillatory free-convective instabilities in the solution with three types of ions with concentrations  $c_1$ ,  $c_2$ , and  $c_3$ , diffusion coefficients  $D_1$ ,  $D_2$  and  $D_3$ , and charges  $z_1$ ,  $z_2$  and  $z_3$ , which is placed in the space between two plane horizontal electrodes, taking into account the migration transfer of a supporting electrolyte. The effect of applied magnetic field on the onset of free convective instability is discussed.

**1. Mathematical model.** Within the theory of dilute electrolytes, in the Boussinesq approximation, taking into account the electroneutrality of the solution, the equations of incompressible viscous liquid flow and the ionic transfer in the electrolyte layer between two horizontal electrodes can be written as follows

$$\begin{aligned} \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} &= -\frac{1}{\rho_b} \nabla p + \nu \Delta \mathbf{v} + \frac{1}{\rho_b} \mathbf{i} \times \mathbf{b} + \frac{\mathbf{g}}{\rho_b} (\rho - \rho_b), \quad \text{div}(\mathbf{v}) = 0, \\ \frac{\partial c_1}{\partial t} &= D_1 \Delta c_1 - \mathbf{v} \cdot \nabla c_1, \quad \frac{\partial c_2}{\partial t} = D_2 \Delta c_2 + \nabla \cdot \left[ \frac{F z_2 D_2 c_2}{RT} \nabla \varphi \right] - \mathbf{v} \cdot \nabla c_2, \\ \frac{\partial c_3}{\partial t} &= D_3 \Delta c_3 + \nabla \cdot \left[ \frac{F z_3 D_3 c_3}{RT} \nabla \varphi \right] - \mathbf{v} \cdot \nabla c_3, \quad z_1 c_1 + z_2 c_2 + z_3 c_3 = 0, \end{aligned} \quad (1)$$

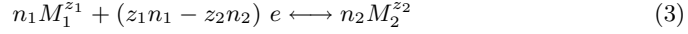
where  $\mathbf{b}$  is the magnetic flux density vector,  $\mathbf{g}$  is the gravity acceleration vector.

In the set of equations (1), the migration term in the transfer equation for electroactive component ( $c_1$ ) is omitted; this is allowed at a high concentration of the supporting electrolyte, i.e., at  $c_2 \gg c_1$ .

For a solution containing three types of ions, which is produced of two source substances (for example,  $\text{CuSO}_4$  and  $\text{H}_2\text{SO}_4$ ), the electrolyte density can be expressed in terms of concentrations of two types of ions, because the concentration of ions of the third type is uniquely determined by the electroneutrality condition. For the sake of definiteness, assume that the electrolyte density is expressed as follows:

$$\rho - \rho_b = \frac{\partial \rho}{\partial c_1} (c_1 - c_{1b}) + \frac{\partial \rho}{\partial c_2} (c_2 - c_{2b}) \quad (2)$$

Assume that the following reaction proceeds on the electrodes:



Equation (3) describes both the redox reactions ( $n_2 \neq 0$ ) and the reactions of cathodic deposition (anodic dissolution) of metal ( $n_2 = 0$ ).

Minding the fact that the concentration of electroactive ions is relatively low, we can eliminate the term with the gradient of electric potential from the transfer equations. To do this, in accordance with [6, 7, 8], we introduce a hypothetical concentration  $c_4$ :

$$c_4 = \frac{n_2 D_1}{n_1 D_2} c_1 + c_2 + c_3. \quad (4)$$

Thus the set of equations (1) can be presented in the dimensionless form:

$$\begin{aligned} \frac{\partial \mathbf{V}}{\partial t} + \frac{1}{\text{Sc}_1} (\mathbf{V} \cdot \nabla) &= -\nabla P + \Delta \mathbf{V} + \text{Ha}^2 \mathbf{I} \times \mathbf{B} + \gamma \text{Ra}_1 (C_1 - 0.5 + C_4 - C_{4b}) \\ \text{div}(\mathbf{V}) &= 0; \quad \text{Sc}_1 \frac{\partial C_1}{\partial t} = \Delta C_1 - \mathbf{V} \nabla C_1; \quad \text{Sc}_1 \frac{\partial C_4}{\partial t} = \bar{D}_4 \Delta C_4 - \mathbf{V} \nabla C_4 + \bar{D}^* \Delta C_1 \end{aligned} \quad (5)$$

$$\mathbf{V} \Big|_{Z=0, Z=1} = 0, \quad C_1 \Big|_{Z=0} = 0, \quad C_1 \Big|_{Z=1} = 1, \quad \frac{\partial C_4}{\partial Z} \Big|_{Z=0, Z=1} = 0 \quad (6)$$

where  $\text{Ha} = bH \sqrt{\frac{\chi_b}{\rho_b \nu}}$  is the Hartmann number;  $\chi_b$  is the conductivity before the current is switched on.  $H$  is the interelectrode distance,  $\text{Ra} = \frac{2gH^3 c_{1b} \alpha}{\rho_b \nu D_1}$  is the Rayleigh number. When we passed to the dimensionless variables, the following relations were used:

$$\begin{aligned} X &= \frac{x}{H}, \quad Y = \frac{y}{H}, \quad Z = \frac{z}{H}, \quad T = \frac{\nu}{H^2} t, \quad \bar{D}_4 = \frac{D_4}{D_1}, \quad \bar{D}^* = \frac{z_3 D^*}{\alpha D_1 (z_3 - z_2)} \frac{\partial \rho}{\partial c_2} \\ C_1 &= \frac{c_1}{2C_{1b}}, \quad C_4 = \frac{z_3 c_4}{2\alpha C_{1b} (z_3 - z_2)} \frac{\partial \rho}{\partial c_2}, \quad P = \frac{H^2}{\rho_b \nu D_1} p, \\ \mathbf{V} &= \frac{H}{D_1} \mathbf{v}, \quad \mathbf{I} = \frac{H}{D_1 \chi_b b} \mathbf{i}, \quad \mathbf{B} = \frac{\mathbf{b}}{b}, \quad b = |\mathbf{b}|, \end{aligned} \quad (7)$$

where

$$D_4 = \frac{D_2 D_3 (z_3 - z_2)}{z_3 D_3 - z_2 D_2}, \quad D^* = \frac{D_1}{D_2} \left[ \frac{n_2}{n_1} D_1 - \frac{D_3 (z_3 - z_2) + (D_3 - D_2) z_1}{z_3 D_3 - z_2 D_2} D_2 - \frac{n_2 - n_1}{n_1} D_4 \right].$$

The lower electrode is placed in the  $x$ - $y$  plane, the  $z$ -axis is directed upwards.

To investigate the stability of the set of equations (5), it is necessary to obtain a steady-state solution for a stagnant electrolyte and a set of equations for small perturbations. The character of behavior of perturbations, which are always present in the electrochemical systems, enables one to determine whether the steady state is stable or not. If small perturbations damp with time, the system is stable; this is attributed to the absence of convection. Otherwise, the system is unstable and, hence, electrolyte flow will arise.

**2. Steady-state solution for the stagnant electrolyte.** We will examine the stability of the steady-state solution of (5). To do this, the behavior of the system under the action of small perturbations  $\tilde{C}_1$ ,  $\tilde{C}_4$ ,  $\tilde{\mathbf{V}}$ ,  $\tilde{P}$ . Taking into account only the terms, which are linear in the perturbations, we obtain the following set of equations for the disturbed state:

$$\begin{aligned} \frac{\partial \tilde{\mathbf{V}}}{\partial T} &= -\nabla \tilde{P} + \Delta \tilde{\mathbf{V}} + \text{Ha}^2 \tilde{\mathbf{I}} \times \mathbf{B} + \gamma \text{Ra}_1 (\tilde{C}_1 + \tilde{C}_4), \quad \text{div}(\mathbf{V}) = 0 \\ \text{Sc}_1 \frac{\partial \tilde{C}_1}{\partial T} &= \Delta \tilde{C}_1 - \tilde{V}_z, \quad \text{Sc}_1 \frac{\partial \tilde{C}_4}{\partial T} = \bar{D}_4 \Delta \tilde{C}_4 + \bar{D}^* \Delta \tilde{C}_1 \end{aligned} \quad (8)$$

A solution for the set of equations (8) is sought in the form of normal perturbations:

$$\begin{aligned} \tilde{V}_z(X, Y, Z, T) &= w(Z) e^{\lambda T + i(k_X X + k_Y Y)} \\ \tilde{C}_1(X, Y, Z, T) &= e_1(Z) e^{\lambda T + i(k_X X + k_Y Y)} \\ \tilde{C}_4(X, Y, Z, T) &= e_4(Z) e^{\lambda T + i(k_X X + k_Y Y)} \end{aligned} \quad (9)$$

To eliminate the pressure from flow equations (8), we apply rot rot to (8) and project the equations thus obtained onto the  $z$ -axis. Substituting perturbations (9) into thus transformed (8), we obtain:

$$\begin{aligned} \lambda(w'' - k^2 w) &= w'' - 2k^2 w'' + k^4 w - \\ &\quad - \text{Ha}^2 (w'' \sin^2 \alpha + 2ik_1 w' \sin \alpha \cos \alpha - k_1^2 w \cos^2 \alpha) k^2 \text{Ra}_1 (e_1 + e_4) \\ \lambda \text{Sc}_1 e_1 &= e_1'' - k^2 e_1 - w \\ \lambda \text{Sc}_1 e_4 &= \bar{D}_4 (e_4'' - k^2 e_4) + \bar{D}^* (e_1'' - k^2 e_1), \end{aligned} \quad (10)$$

where quantities differentiated with respect to  $z$  are primed,  $\alpha$  is an angle between the magnetic field and the electrodes. The boundary conditions for amplitudes of perturbations of concentrations and vertical component of hydrodynamic velocity are expressed as follows:

$$e_1(0) = e_1(1) = 0, \quad e_4'(0) = e_4'(1) = 0, \quad w(0) = w(1) = 0, \quad w'(0) = w'(1) = 0. \quad (11)$$

To solve the set of amplitude equations (11) with boundary conditions (12), the approximate analytical Galerkin method is used.

**3. Approximate analytical solution by the Galerkin method.** The set of equations (10) will be solved using the Galerkin method [3]. For the functions  $w(Z)$ ,  $e_1(Z)$ ,  $e_4(Z)$ , the following approximations satisfying the boundary conditions will be used:

$$w(z) = Z^2(1-Z)^2 w_0, \quad e_1(z) = Z(1-Z) e_{10}, \quad e_4(z) = Z^2(1-z)^2 e_{40}. \quad (12)$$

Here  $e_{10}$ ,  $e_{40}$ , and  $w_0$  are the amplitudes of perturbations of concentrations and hydrodynamic velocity that are independent of coordinates and time.

As a result of application of the Galerkin method with approximating functions (12), the following set of equations for the perturbation amplitudes is obtained:

$$\begin{aligned} &\left[ \lambda(k^2 + 12) + k^4 + 24k^2 + 504 + \text{Ha}^2 (12 \sin^2 \alpha + \bar{k}_1^2 \cos^2 \alpha) \right] w_0 + \\ &+ \frac{9k^2 \text{Ra}_1}{2} \left( e_{10} + \frac{2}{9} e_{40} \right) = 0 \\ (\lambda \text{Sc}_1 + k^2 + 10) e_{10} + \frac{3}{14} w_0 &= 0, \quad e_{40} = - \frac{3\bar{D}^* (3k^2 + 28)}{2 [\text{Sc}_1 \lambda + \bar{D}_4 (k^2 + 12)]} e_{10} \end{aligned} \quad (13)$$

The monotonic instability corresponds to  $\lambda = 0$ . Then, from the condition of zero determinant of homogeneous set of equations (14), we obtain the following

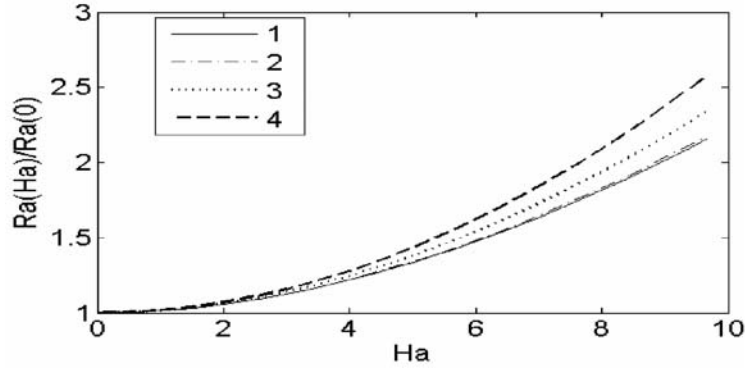


Fig. 1. The effect of magnetic field on the critical Rayleigh number for the onset of oscillatory (1, 2) and monotonic (3, 4) instabilities (1)  $D_4 = 1$ ,  $D^* = 1$ ,  $Ra(0) = 3676$ ; (2)  $D_4 = 1$ ,  $D^* = 0.1$ ,  $Ra(0) = 1942$ ; (3)  $D_4 = 1$ ,  $D^* = 0.8$ ,  $Ra(0) = 5783$ ; (4)  $D_4 = 1$ ,  $D^* = 1$ ,  $Ra(0) = 12763$ .

equation for the Rayleigh number:

$$Ra_1 = \frac{28(k^4 + 24k^2 + 504 + Ha^2(12\sin^2\alpha + \bar{k}_1^2\cos^2\alpha))(k^2 + 10)}{27k^2} \cdot \frac{1}{1 - \frac{3k^2 + 28}{3k^2 + 36} \frac{D^*}{D_4}} \quad (14)$$

The oscillatory instability corresponds to  $\text{Re}(\lambda) = 0$ ,  $\text{Im}(\lambda)^2 = \omega^2 > 0$ .

Using the same condition of zero determinant of homogeneous set of equations (13), the equation for the Rayleigh number for oscillatory perturbations can be obtained. Then, using the fact that the Schmidt numbers are high for electrochemical systems, we obtain an approximate equation for the critical Rayleigh number for oscillatory perturbations:

$$Ra_1 = \frac{28(k^4 + 24k^2 + 504 + Ha^2(12\sin^2\alpha + \bar{k}_1^2\cos^2\alpha))[\bar{D}_4(k^2 + 12) + k^2 + 10]}{27k^2} \quad (15)$$

provided that  $\bar{\omega}^2 = \frac{\bar{D}^*(3k^2 + 28)[\bar{D}_4(k^2 + 12) + k^2 + 10] - 3\bar{D}_4^2(k^2 + 12)^2}{3} > 0$ .

The Rayleigh numbers for the monotonic (14) and oscillatory (15) instabilities depend on the wavenumber  $k$ .

The critical Rayleigh numbers are defined by minimizing the right-hand sides of equations (14) and (15) with respect to  $k$ .

Fig. 1 shows the effect of magnetic field on the critical Rayleigh number for the onset of oscillatory (1, 2) and monotonic (3, 4) instabilities.

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