About control of convection intensity in chemical reacting equilibrium gas

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Abstract. The problem of the Rayleigh–Benard convection in a gas in a state of chemical equilibrium is considered in the frames of Boussinesq approximation. The method of linear analysis is used. Horizontal boundaries are assumed to be isothermal and free from shearing stresses. Thermodynamic parameters of a gas are described by the model of chemical equilibrium. Stoichiometric hydrogen-oxygen mixture is considered. It is shown that owing to recombination and dissociation processes the Rayleigh number in the gas under consideration equals to the corresponding number in chemically inert gas, multiplied with some additional factor. The critical Rayleigh number weakly depends on the pressure. Another and more effective way to control of the convection is to change temperature. The minimal value of the convection intensity is realized at very low and very high temperatures. At such temperatures the mixture under consideration can be considered as inert gas. An increase of temperature between its minimal and maximal values led to a shift of chemical equilibrium. As the result, the convection intensity pass through a local maximum.

1. Introduction

The Rayleigh–Benard convection is the classical field of fluid mechanics where a mathematical model based on the Boussinesq approximation and corresponding numerical methods were developed [1–4]. Traditionally, the major attention was paid to modeling convection in chemically inert gases and liquids. However, convective processes also occur in chemically reacting gases: combustion of gas mixtures in industrial reactors, engineering devices, and experimental facilities. Convection in a chemically equilibrium gas is fairly frequent case of convection in gases accompanied by chemical reactions, which occurs if the characteristic time of the chemical reaction is much smaller than the characteristic time of the convective process. It can be naturally expected that the qualitative and quantitative characteristics of convection are determined to a large extent by the dependence of the thermal expansion coefficient of the medium on temperature because it directly determines the buoyancy force responsible for convection.

The thermal expansion coefficient of a chemically inert gas is monotonic and inversely related to the temperature. In the case of a chemically equilibrium gas, the dependence of this coefficient on
temperature changes considerably and becomes non-monotonic with a noticeable local maximum [5-7].

Authors in [8, 9] were the first to formulate and solve numerically a two-dimensional problem for Rayleigh-Benard convection in a chemically equilibrium gas, as well as considered linear and non-linear regimes. The molar mass and thermodynamic parameters of the gas were calculated according to a high accuracy model of chemical equilibrium [5-7]. Nevertheless, the physical and mathematical model provided in [8,9] is quite complicated and inconvenient. Some development of this physical and mathematical model may be found in [10]. However, results of the linear analysis [10] need an additional improvement.

In laboratory scales, the gas compressibility can be neglected and the convection media can be considered as incompressible. Moreover, if the domain has a certain geometry and small supercriticality, convection develops as two-dimensional rolls [4], which allows us to consider two-dimensional convective flows of a viscous incompressible fluid even at the first stage of our investigation.

Following [8-10], we consider a convective two-dimensional and non-stationary flow of a viscous incompressible fluid in the horizontal layer heated from below in the Boussinesq approximation. The boundaries of the layer are assumed isothermal and free from shearing stresses. Thermodynamic parameters of a chemical equilibrium gas are calculated according to the model, presented in [5-7].

In the frames of present work the linear analysis of convective instability will be investigated and the problem of control of Rayleigh-Benard convection by means of pressure and temperature will be considered.

2. Nomenclature
The following notations will be used:

Table 1. A list of notations used in this article.

| Notation | Description |
|----------|-------------|
| \(\rho, P, T \text{ and } \mu\) | the density, pressure, absolute temperature and molar mass of the gas; |
| \(R\) | the universal gas constant; |
| \(\mu_{\text{min}}, \mu_{\text{max}}\) | the molar masses of the gas in the completely dissociated and completely recombined states; |
| \(A, K_+\) | the rate constants of dissociation and recombination of the generalized reaction products; |
| \(\theta\) | the effective excitation temperature of the vibrational degrees of freedom of the molecules; |
| \(E\) | the mean dissociation energy of the reaction products; |
| \(\beta\) | the thermal expansion coefficient of the reacting equilibrium gas; |
| \(\beta_{\text{in}} = 1/T\) | the thermal expansion coefficient of the inert ideal gas; |
| \(u, v\) | the velocities in x and y directions; |
| \(\nu, \chi\) | the kinematic and thermal diffusivity coefficients; |
| \(T_{h, c}\) | the temperatures of the lower and upper boundaries; |
| \(H\) | the thickness of the layer; |
| \(\psi\) | the stream function \((\psi_x = u \text{ and } \psi_y = -v)\); |
| \(\omega\) | the vorticity \(\omega = v_x - u_y\); |
| \(Ra = gH^3 \delta T/(T\chi v)\) | Rayleigh number defined for inert gas; |
| \(Ra_{\text{cr}}, \alpha_n\) | the critical values of Rayleigh and wave numbers; |
| \(Pr = v\chi/\nu\) | Prandtl number; |
\( \lambda, \alpha, \pi m \) - the eigenvalue and the wavenumbers of linear problem in x and y directions;

\( Q = T - T_e \) - the temperature deviation from linear equilibrium distribution.

3. Kinetic model
To describe chemical equilibrium in the gas mixture, we use a highly accurate kinetic model [5-7]. According to this approach, the density of a chemical equilibrium ideal gas can be considered as a function of the absolute temperature and pressure:

\[
\rho = \frac{p\mu}{RT}, \quad \mu(T) = \mu_{\text{max}} + 0.5 \cdot (f - \sqrt{f^2 + 4f(\mu_{\text{max}} - \mu_{\text{min}})}),
\]

\[
f = \frac{AR\mu_{\text{max}}^{2.75}}{4K_p\mu_{\text{min}}}(1 - \exp(-\Theta/T))^{1.5}\exp(-E/RT)).
\]

The molar mass of the gas can vary within the interval \( \mu_{\text{min}} \leq \mu \leq \mu_{\text{max}} \). We have \( \mu \to \mu_{\text{max}} \) with decreasing temperature and \( \mu \to \mu_{\text{min}} \) with increasing temperature.

We assume that the pressure \( P \) in the gas mixture (external pressure) is constant. Then, the gas density \( \rho \), as is seen from system (1), depends on the absolute temperature \( T \) only. Note that the molar mass and density have monotonic dependence from absolute temperature [8,9]. The more detailed description of used kinetic model may be found in [10].

The present paper refers to a stoichiometric hydrogen-oxygen mixture. The numerical values of the constants were as follow: \( E = 459.2\cdot\text{kJ/mole}, \quad \Theta = 4000\text{K}, \quad K_+ = 6\cdot10^8\text{m}^6/(\text{kmole}^2\cdot\text{sec}), \quad A = 5.1\cdot10^{10}\text{m}^3/(\text{kmole}\cdot\text{sec}^{1/4}), \quad \mu_{\text{min}} = 6\text{kg/kmole}, \quad \mu_{\text{max}} = 18\text{kg/kmole} [5-7].

Considering the expression for \( f \) at comparatively high temperatures \( T \), we have the following

\( T \to \infty, \quad f \simeq T^{0.25}(E/R \ll T), \quad \mu = \mu_{\text{min}} + (\mu_{\text{max}} - \mu_{\text{min}})^2 f / f + O(f^{-2}). \)

The thermal expansion coefficient \( \beta \) can be found dependent on the density or the molar mass as

\[
\beta = -\frac{1}{\rho} \frac{d\rho}{dT} = -\frac{d}{dT}\ln(\mu / T) = \frac{1}{T} - \frac{1}{\mu} \frac{d\mu}{dT}.
\]

Notice that the asymptotic approximation of the molar mass \( \mu \) to constants as the temperature is reduced or increased allows us to find the asymptotics for the thermal expansion coefficient as \( \beta = 1/T \).

4. Mathematical model
Convection of incompressible fluids in the Boussinesq approximation is described by the following system of equations [1,2]:

\[
\begin{align*}
\alpha_t + \frac{1}{Pr}(\psi_x, \omega_x - \psi_y, \omega_y) &= \Delta \omega + C \cdot Ra Q_x, \\
\Delta \psi &= -\omega,
\end{align*}
\]

\[
\begin{align*}
Q_t + \frac{1}{Pr} (\psi, Q_x - \psi, Q_y) &= \frac{1}{Pr} \Delta Q - \frac{1}{Pr} \psi_x, \\
C &= \frac{\beta(T)}{\beta_m(T)} = T \cdot \beta(T).
\end{align*}
\]

We choose the following reference values for the layer: \( H \) for length, \( H^2/\nu \) for time, \( \chi/H \) for velocity, \( \rho_0\gamma/\nu^2 \) for pressure, \( \rho_0 = \rho(T) \) for density, and \( \delta T = T_h - T_e \) for temperature, \( Q \) is temperature deviation from equilibrium linear distribution and \( \Delta f = f_{xx} + f_{yy} \) is the Laplace operator.

According to the buoyancy force in the first equation of system (2), we see that the convection rate is defined by \( C \cdot Ra \). The Rayleigh criterion specifies the ratio between the buoyancy force and the viscosity and depends on the temperature gradient or the degree of heating, while the dimensionless factor \( C \) depends on the recombination and dissociation processes under the temperature given.

Figures 1 - 3 were plotted with \( P = 1\text{atm}. \)
The solid curves in Figures 1 and 2 show the thermal expansion coefficient $\beta = \beta(T)$ and factor $C = C(T)$. We see there asymptotics (dashed curve 1) with close values at high temperature. The temperature interval where the thermal expansion coefficient $\beta$ and factor $C$ demonstrate an anomalous (not-monotonic) behavior with noticeable local maximum are also seen. As it is shown below, it is this anomalous behavior that causes a possibility of convective instability amplification in comparison with inert gas.

Figure 2 shows that when the temperature falls or rises, the convection intensity decreases up to convection intensity level in an ideal inert gas. Note that the value of local maximum $C$ has very weak dependency from pressure and vanishes in a practically linear way with respect to $\lg(P)$ as

$$C(P) = 3.9241 - 0.44393 \cdot \lg(P/1\text{atm}).$$

![Figure 1. The thermal expansion coefficient.](image1)

![Figure 2. The factor $C = C(T)$.](image2)

5. Linear analysis

Consider the linear analog of system (2) and seeking harmonic solution in the time exponential form [2,10], we find:

$$\lambda_{1,2} = \frac{1 + \Pr}{2\Pr} S \pm \sqrt{\left(1 - \frac{1}{2\Pr}\right) S^2 + \frac{C \cdot Ra \cdot \alpha^2}{S \Pr}},$$

where $S = \alpha^2 + m^2 \pi^2$. Here eigenvalue $\lambda$ is matched by amplitude losses and $\lambda < 0$ by amplitude rises in harmonic solutions. Formulas for an inert medium correspond to written here expressions with $C = 1$.

Assuming eigenvalue $\lambda$ in the last equation is equal to 0, one can obtain the Rayleigh number corresponding to the neutral curve:

$$Ra = \left(\frac{m^2 \pi^2 + \alpha^2}{C \cdot \alpha^2}\right)^3.$$

The critical value of the Rayleigh number (minimum of $Ra$ versus $\alpha$ with $m = 1$) can be found by the formula [1]:

$$Ra_{cr} = \frac{27}{4C} \pi^4 = \frac{657.511}{C}, \quad \alpha_{cr} = 2.221.$$

And if $C - I$ is small (for $|T - \Theta| >> 1$), one can obtain that:

$$Ra_{cr} = \frac{657.511}{C} = 657.511 \cdot (2 - C).$$

The factor 657.511 is identified here as the critical value of the Rayleigh number for the convection in a chemically inert media [1,2], and the factor $1/C$ as the function of temperature and pressure is due to recombination and dissociation processes.
Figure 3 shows the critical Rayleigh number as a function of $T$ (solid curve), its asymptotic (dashed curve 1) and $Ra_{cr} = 657.511\cdot(2-C)$ (dashed curve 2). It can be seen that in domain ($3000K \leq T \leq 5000K, T \approx \Theta = 4000K$) the chemical reactions in gas considerably decrease the critical Rayleigh number.

Taking into account at a high temperature the expression for $f$, we can obtain the far-field asymptotics for $\beta, C, Ra_{cr}$ and increment $\lambda$ as:

$$f = \frac{AR\mu_{max}^2\Theta^{1.5}}{4KP\mu_{min}}T^{0.25} \quad (T \to \infty)$$

$$\beta = \frac{1}{T}(1+C\), \quad C = 1 + C\), \quad Ra_{cr} = 657.511\cdot(1-C\),$$

$$\lambda_r = \lambda_{in} \pm \frac{Ra\alpha^2C\}{S^{0.5}\sqrt{(1-Pr)^2S^{1.5}+4Ra\alpha^2Pr}}, \quad C\ = (\mu_{max}-\mu_{min})^2\frac{K}{Pr},$$

Here $\lambda_r$ and $\lambda_{in}$ are increments for the reacting and inert gases correspondingly. The dependences given show that $\beta$ and $C$ approach asymptotics with the rise of the temperature quite slowly, which means that the corresponding boundary is fuzzy.

The convective processes intensiveness can be influenced. The critical Rayleigh number $Ra_{cr}$ is weakly depending on the pressure, the intensiveness decreases as the pressure grows, changing from the maximum values at low pressure to minimal values at high pressure. Another more cardinal way to affect the intensiveness is to change the temperature. The intensiveness of convective processes is equal to its minimal value (inert media) at high and low temperatures and its maximal value in between. Of course, it is possible to change both the pressure and the temperature.

To study the possibility to control convective processes by changing the pressure and the temperature in more details, let us consider the instability domain on $P-T$ plane in Figure 4.

A curve 1 in Figure 4 correspond to the temperatures at which the maximum convection intensiveness at given pressure is observed (maximum $C$ with respect to $T$ corresponds to curve $Ra_{cr}$). Curves 2 and curve 3 correspond to the top and low boundaries of domain where reacting-inert gas transitions are observed.

It is obvious that the highest increase in temperature occurs at the upper boundary of the reacting-inert gas transition (curve 2), whereas the other curves demonstrate a substantially smaller change of temperature.

6. Conclusion

Given recombination and dissociation processes, the Rayleigh number in the gas under consideration equals to the corresponding number in chemically inert gas, multiplied with some additional factor $C = C(T)$. Hence, all the regimes and characteristics of convective flows of a chemical equilibrium gas
can be derived from the corresponding system of equations of convection in a chemically inert gas by means of re-determination of Rayleigh number.

The neutral curve on the plane $T$-$Ra$ shows the significant decreasing of the critical Rayleigh number in the reacting gas. Note that the critical Rayleigh number (minimal value with respect to $T$) weakly depends on the pressure. Another and more effective way to control of the convection is to change temperature. The minimal value of the convection intensity is realized at very low and very high temperatures. At such temperatures the mixture under consideration can be considered as inert gas. An increase of temperature between its minimal and maximal values led to a shift of chemical equilibrium. As the result of dissociation and recombination processes, the convection intensity pass through a local maximum.

7. Discussion

In the present work the far-field high-temperature asymptotes for factor $C$, critical Rayleigh number and the increment $\lambda$ are derived. It would be of certain interest to investigate also the low-temperature asymptotic curves.

The performed linear analysis shows the existence of the anomalous (non-monotonic) behavior of the thermal expansion coefficient on temperature. It seems to be possible that such anomalous behavior must bring to the secondary instability. It would be interesting to investigate such kind of instability.

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