INVESTIGATION OF NATURALLY CONVECTIVE HEAT EXCHANGE IN THE PRESENCE OF A HETEROGENEOUS CATALYTIC REACTION

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The intensity of heat transmission because of natural convection in the presence of a heterogeneous catalytic reaction is investigated experimentally taking account of temperature and concentration factors.

The intensity of heat transmission with thermal natural convection, which is characterized by the dependence of the Nusselt number Nu on the Rayleigh number Ra, has been studied sufficiently well at present. At the same time, the appearance of a product with a molecular weight different from that of the initial substance is possible during the progress of a heterogeneous chemical reaction. This should result in a dependence of the density on the coordinates, i.e., concentration convection can appear under definite conditions. At the same time, if the product being obtained as a result of the reaction is heavier than the initial substance, then the dependence of the density on the concentration of the product will have a stabilizing effect in the presence of an external negative temperature gradient. It is hence interesting to investigate the dependence of the intensity of heat transmission on the natural convection described by two causes: thermal and concentration.

Experiments were performed on a model reaction. The reaction of oxidizing sulfur dioxide on a platinum catalyst was taken as such a reaction which is used in investigations of heat transmission because of thermal and concentration convection. The product obtained as a result of the reaction is heavier than the initial substance. It is known that the reaction of oxidizing sulfur dioxide proceeds exothermally with the thermal effect $Q = 22$ kcal per mole of SO_3 [1].

The tests were conducted with an excess of SO_2. The mixture consisted of 87% SO_2 and 13% O_2. The reaction of oxidizing SO_2 proceeds in the kinetic domain in the 300-450°C temperature range [2]. Passage into the diffusion domain occurs in the 750-800°C temperature range, where the reverse reaction yields an essential contribution at these temperatures. Hence, the tests to study heat transmission were performed at 300-450°C temperatures.

Two problems are manifest in studying the progress of the reaction under natural convection conditions: first is the origination and development of convection because of the heterogeneous catalytic reaction; the second is the investigation of the influence of the development of convection on the progress of the reaction. The influence of the reaction on the intensity of convection is evidently realized in both the kinetic and diffusion modes. The reverse influence is most substantial just in the diffusion domain.

An electrothermographic method [3] was used to investigate the heat transmission. A platinum catalyst in the form of a 50-μ-thick foil was used as measuring element – as a resistance thermometer. The foil had transverse slits to increase the initial resistance. The diagram of the measuring cell is shown in Fig. 1.

The platinum foil 1 was glued to a mica plate 2 of $\approx 100\ \mu$ thickness, which was supported on the thin porcelain rods 3. The rods were fastened to a cylindrical vessel filled with the heat insulator 4. The platinum foil plate had a 64 mm diameter, equal to the diameter of the outer vessel. Because of this construction the reaction could only proceed on the upper surface of the foil. Together with the fastened platinum element, the inner vessel was placed in the outer vessel of 130 mm height. The end face of the outer vessel was the 0.5-mm-thick glass plate 6 with 100-200-μ-diameter holes. The holes were arranged uniformly over the whole surface of the plate. The spacing between the holes was 2 mm. Such a plate has no diffusion resistance but is hydrodynamically impermeable to natural convection. Above a porous plate parallel to it the reactive mixture is

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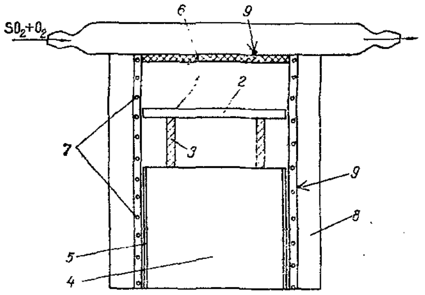

Fig. 1

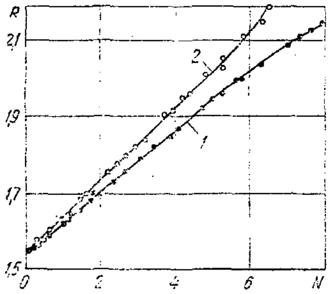

Fig. 2

Fig. 1. Diagram of the measuring cell: 1) platinum foil; 2) mica; 3) porcelain rod; 4) heat insulator; 5) inner vessel; 6) porous baffle; 7) heating spiral; 8) external heat insulation; 9) thermocouple.

Fig. 2. Dependence of the electrical resistance R (Ω) of the catalyst on the power N (cal/sec): 1) inert mixture; 2) reactive mixture.

bubbled through at a definite velocity. The outer vessel was heated by the electric spiral, which accomplished preliminary heating of the measuring cell. After the preliminary heating, the electric circuit of the platinum resistance thermometer was switched in, and the platinum catalyst was heated to the required temperature. Uniformity of the heating of the platinum element was checked by special thermocouples (≈10 μ thick). The temperature fluctuations along its surface did not exceed ±1.5°C for the maximum temperatures on the element. Therefore, convection could only occur over the platinum element. The spacing between the porous baffle and the catalyst could be varied. The temperature of the platinum catalyst was determined to no worse accuracy than 1% by its resistance. The temperature of the porous baffle and the side surface was found by the thermocouples 9. The platinum resistance thermometer was connected in the arm of the measuring bridge.

The resistance and the current flowing through the catalyst were measured in the test. The catalyst temperature and the electrical power N supplied to the catalyst were computed from these results.

A standard $SO_2 + N_2$ mixture, whose thermophysical properties are quite similar to the properties of the reacting mixture, was initially bubbled through the preheated cell during performance of the experiments.

After equilibrium had built up, the platinum plate was heated by the current. The coefficients of heat elimination through the endfaces and side surface of the vessel were determined by conducting tests with an inert mixture. Then the rate of the reaction heat evolution could be determined by bubbling through the $SO_2 + O_2$ mixture. Preliminary warming of the outer surface permitted increasing the initial resistance of the measuring element, but meanwhile decreasing the heat losses.

Since the main problem of the investigation was determination of the coefficient of heat transmission from a catalytic surface to an outer surface over which a fresh mixture is blown, then this heat flux should be extracted from the total heat losses from the element.

Let N be the electrical power extracted from the catalyst and let α be the coefficient of heat elimination from the catalyst through the upper endface surface. Then the following expression can be written in the absence of a reaction:

$$N = \alpha S (T_1 - T_0) + \varphi (T_1), \tag{1}$$

where $\varphi(T_1)$ denotes the total heat flux down through the side walls.

The expression (1) was used to determine the function $\varphi(T_1)$ when the outer surface was blown off by the mixture of sulfur dioxide and nitrogen. The platinum element was hence 4 mm from the upper surface. Convection is completely absent at this height, since the value of the Rayleigh number is less than critical for such a gap. Therefore, in this case the quantity α can be computed by means of the formula $\alpha = \bar{\lambda}/h$. By knowing α, the desired function $\varphi(T_1)$ was determined from (1) by means of the measured N and T_1.

Upon replacement of the inert gas mixture by the reacting mixture, (1) will be

$$N = \alpha S (T_1 - T_0) + \varphi (T_1) + q (T_1), \tag{2}$$

where q is the heat liberated because of the reaction. Comparing (1) and (2) at the same temperature (or, equivalently, at a constant electrical resistance), we find the rate of reaction heat liberation.

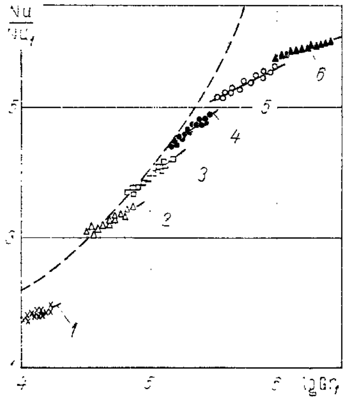

Fig. 3

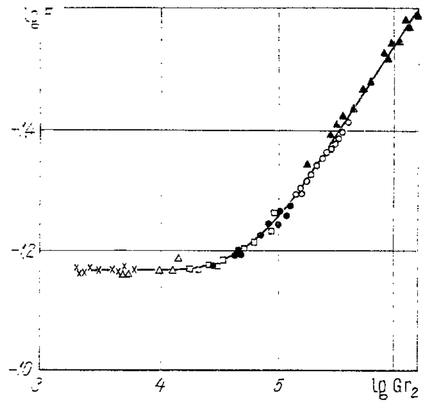

Fig. 4

Fig. 3. Dependence of Nu/Nu_1 on $\log Gr_1$ (dashed curve corresponds to an inert mixture): 1) 0.75 cm; 2) 1; 3) 1.5; 4) 2; 5) 3; 6) 4 cm.

Fig. 4. Dependence of $\log F$ on $\log Gr_2$.

The dependence of the electrical resistance of the catalyst on the electrical power is shown in Fig. 2. Curve 1 corresponds to the inert mixture and curve 2, to the reacting mixture. The reaction heating, which corresponds to the difference between curves 2 and 1 for N = const, can also be determined by means of these curves. Reaction heating is absent, in practice, at catalyst temperatures less than 280°C. Reaction heating was substantial at the 450°C temperature and equal to 73°C. It should be noted that the test reproducibility was good. It is known that the reactivity of a platinum catalyst varies if the platinum is treated in oxygen at a temperature above 850°C [2]. Hence, each test was accompanied by blowing in nitrogen at temperatures on the order of 300°C and only then was the reactive mixture passed through. Moreover, temperatures above 500°C were not achieved in the tests; hence, the reactivity of the platinum was constant, although possibly not the maximum, in all the tests.

By increasing the gap between the catalyst and the porous baffle, a certain height h_* could be reached for which the conditions for the origination of natural convection are satisfied. Tests were performed at the following bed heights: 0.75, 1, 1.5, 2, 3, and 4 cm in order to establish the heat-transmission intensity because of natural convection. Hence, the α in (2) is an unknown and depends on the convection intensity. Since the functions $\varphi(T_1)$ and $q(T_1)$ are determined in preliminary tests, $\alpha(h)$ can be determined by measuring N.

Dependences of the electrical resistance on the electrical power are located sufficiently closely to the curve corresponding to no convection for different bed heights. This latter is related to the fact that an increase in the heat flux because of developed convection is canceled by the diminution in heat flux because of heat conduction with the increase in the bed height.

From an analysis of the mathematical equations describing the natural convection process in the presence of heterogeneous catalytic reactions there follows that the intensity of heat transfer should be a function of the thermal and diffusion Rayleigh numbers (Ra_1 and Ra_2) and should also depend on the parameters of the reaction. Since we have been considering a gas, henceforth let us consider the Grashof number, which is defined as follows:

$$Gr_1 = \frac{g\beta_1(T_1 - T_0)}{\nu^2} h^3;\ Gr_2 = \frac{g\beta_2}{\nu^2} h^3;\ \beta_2 = \frac{\mu_1 - \mu}{\mu_1},$$

instead of the Rayleigh number.

The experiments should be processes as a function of the above-mentioned parameters. The dependence of Nu/Nu_1 on $\log Gr_1$ is shown in Fig. 3. The dependence $Nu/Nu_1 = f(Gr_1)$ for inert media [4] is given by the dashed curve:

$$\frac{Nu}{Nu_1} = 1 + \frac{C\,Ra^{4/3}}{A + Ra}, \tag{3}$$

where C = 0.07 and A = 3200. It follows from this figure that all the experimental points do not lie on one curve in the coordinates selected but are below the curve constructed by means of (3). Therefore, for identical numbers Gr_1 the intensity of heat transfer in the presence of a heterogeneous catalytic reaction is below that in its absence. In the case under consideration this is evidently associated with the fact that a heavier product is obtained during the reaction, which reduces the intensity of convection by accumulating on the lower catalytic surface.

It should be noted that the intensity of heat transfer should also depend on Gr_2 in the presence of a reaction. The dependence of the logarithm of the function F on $\log Gr_2$ is shown in Fig. 4. The function F has the form

$$F = \left(\frac{Nu}{Nu_1} - 1\right) Gr^{-1/3}.$$

It turns out that processing the experiments in such coordinates yields a practically universal curve. This permits describing the intensity of heat exchange by the following approximate formula:

$$\frac{Nu}{Nu_1} = 1 + \frac{Gr_1^{1/3}(1 + 0.14\,h/d)}{(3200 + 0.03Gr_2)^{1/3}}, \tag{4}$$

where h/d is the ratio of the bed height to its width (to the diameter of the outer vessel in this case).

Formula (4) is valid for the variation of the parameters within the following limits:

$$Gr_1 = 10^4 - 10^7;\ Gr_2 = 10^3 - 10^7;\ h/d = 0.06 - 0.6.$$

The heat-transmission law (4) should depend also on the reaction parameters, particularly, on the reaction rate. The dependence on the reaction rate does not enter explicitly into (4). It is taken into account in evaluating the thermal Grashof number Gr_1. The quantity $T_1 - T_0$ enters into the expression for Gr_1, where the catalyst temperature T_1 depends on the rate of the reaction heat liberation.

If there is no vertical temperature gradient (i.e., the catalyst temperature T_1 and that of the porous plate are identical and equal to T_0) at the time of admitting the reacting mixture, then the difference $T_1 - T_0$ is the reactive heating of the catalyst. In this case convection originates because of the reaction proceeding on the catalyst.

Let us introduce the dimensionless temperature of the catalyst as [5]

$$\theta = \frac{E}{\bar{R}T_0^2}(T_1 - T_0).$$

Hence, introducing the Grashof reaction number as $Gr_0 = (g\beta_1\bar{R}T_0^2/\bar{\nu}^2E)h^3$, expressed in terms of the reaction heating scale $\bar{R}T_0^2/E$, we obtain the following expression: $Gr_1 = Gr_0\theta$. Then (4) is rewritten as

$$Nu/Nu_1 = 1 + \frac{Gr_0^{1/3}\theta^{1/3}(1 + 0.14\,h/d)}{(3200 + 0.03Gr_2)^{1/3}}. \tag{5}$$

The quantity θ in (5) is unknown. However, it can be determined by using results obtained by Frank-Kamenetskii [5].

Since critical ignition and extinction conditions are possible during the progress of the reaction on the surface, then the dependence of the intensity of heat transfer because of natural convection will differ during progress of the reaction in the ignition and combustion modes.

NOTATION

α, coefficient of heat elimination; N, electrical power; S, catalyst surface; R, electrical resistance; h, height of gas layer; d, vessel diameter; $\bar{\lambda}$, coefficient of thermal conductivity of the mixture; q, heat liberated during the reaction; T_1, temperature of the platinum plate; T_0, temperature of the upper porous baffle; g, acceleration of gravity; β_1, coefficient of volume expansion; $\bar{\nu}$, mixture coefficient of kinematic viscosity; μ_1, molecular weight of the product (SO_3); μ, molecular weight of the initial mixture; Gr_1, thermal Grashof number; Gr_2, concentration Grashof number; Nu, Nusselt number; Nu_1, Nusselt number for heat conduction; $\bar{R}$, universal gas constant; E, activation energy.

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DETACHMENT SIZE OF BUBBLES DURING QUASISTATIC GROWTH ON HEATER

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The critical bubble dimensions for detachment from a smooth surface and from the edge of a recess are calculated. The boundary of the quasistatic regime is estimated on the basis of the pressure.

One of the most important problems in the physics of boiling is that of determining the size of vapor bubbles as they detach from the heater. The detachment size and the nature of the detachment depend on the magnitude of the inertial forces in comparison with the forces due to gravity and surface tension. The inertial forces are governed primarily by the rate of growth of the bubble surface area and are proportional to β^4 [1]. Since β in turn is proportional to the m-th power of the Jacobi number ($0.5 \leq m \leq 1$) [2], and the Jacobi number is inversely proportional to ρ'', at high pressures the rapid increase in ρ'' causes β^4 to become extremely small. Under these conditions we can neglect the influence of inertial forces on the bubble detachment. The bubble growth is assumed to be quasistatic, and the detachment is assumed to begin at the instant the equilibrium free surface of the liquid becomes unstable.

Despite the importance of the problem of the detachment of bubbles during boiling, it has received little study, even in the case of quasistatic bubble growth. The average detachment radius $r_d = (3v_d/4\pi)^{1/3}$ is usually estimated from the equation [3]

$$r_d \cong 0.01 \sqrt{\frac{\sigma}{(\rho-\rho'')g}}\,\theta \quad (r_d \cong 0.01\, b^{-1/2}\theta;\ b = (\rho-\rho'')\,g/\sigma). \tag{1}$$

This equation was derived by Fritz [4] for a bubble sitting on a smooth horizontal plate; Fritz determined v_d as the maximum bubble volume (for a given value of θ) and used the tables of Bashforth and Adams [5] to construct the function $V_d(\theta)$ for $\theta \geq 59°$ ($V_d = v_d b^{3/2}$). We note that Eq. (1) becomes unacceptably inaccurate at $\theta > 125°$, according to the results of [4]. Furthermore, the applicability of (1) for $\theta < 59°$ has yet to be proved.

Nesis and Komarov [6] proposed an approximate analytic solution of this problem for small θ on the basis of a study of the behavior of the base radius X as a function of the bubble height h. They asserted that for $\theta < 70°$ the condition $dX/dh = -\infty$ becomes satisfied upon the appearance of an inflection point of the generatrix of the bubble surface at the base; this condition was adopted as the stability threshold. Analytic and numerical calculations in [10] showed that the inflection point does not coincide with the point at which we have $dX/dh = -\infty$. Furthermore, the satisfaction of the condition $dX/dh = -\infty$ cannot be judged a rigorous criterion for the loss of stability; as follows from a numerical solution of the variational problem, the instability occurs upon the appearance of an inflection point on the profile, but before the time at which the condition $dX/dh = -\infty$ becomes satisfied [10, 14].

For liquids with very small wetting angles (e.g., for cryogenic liquids, for which $\theta \approx 0°$), Eq. (1) predicts values of r_d which are far too low. It is reasonable to assume that the vapor bubble does not detach from the smooth wall of the heater but from the edge of a microscopic recess [1]. The most likely place for the nucleation of a bubble is at the bottom of a microscopic recess. As the bubble grows, the base of the bubble

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