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HEAT TRANSFER DURING CHEMICAL BOILING IN THE PRESENCE OF FREE CONVECTION

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UDC 66.015.23:536.24

Heat and mass transfer between a solid body and a liquid reagent in the presence of gas liberation is studied experimentally. The experimental results are generalized by a criterional dependence.

The term "chemical boiling" refers to the process of heterogeneous chemical interaction between a solid body and a liquid reagent, accompanied by the liberation of gas. Examples of such an interaction are reactions of metals with acids, as a result of which hydrogen is liberated in the form of bubbles. The bubbles forming on the surface of a solid body in the course of their growth and detachment make the boundary diffusion layer of the liquid turbulent, thereby intensifying mass transfer.

There is a qualitative and quantitative analogy between the processes under study and heat transfer accompanying boiling [1]. It is evident from the curves of the coefficient of mass transfer k versus the concentration of the reagent c_R, obtained for the interaction of magnesium with hydrochloric acid in the presence of free convection and presented in Fig. 1 (curves 1 and 2), that as the motive force (concentration) increases, the coefficient of mass transfer increases, reaches a maximum, and then decreases. The analog of concentration in a mass transfer process is the temperature difference in heat transfer, and the coefficient of mass transfer k is the analog of the coefficient of heat transfer α.

The analogy is confirmed experimentally for other characteristics of chemical boiling also. In particular, the rate of growth of the bubbles, the number of gas-formation centers, and the detachment diameters of the bubbles obey analogous laws of heat transfer accompanying boiling. For example, the investigation of the detachment diameter of CO_2 bubbles showed that its value is independent of the reagent concentration and is determined by the surface tension force (quasistatic regime). In the case of the detachment of H_2 bubbles the inertia from the side of the surrounding liquid plays the main role (dynamic regime), while the detachment diameter d_0, as in the case of heat transfer accompanying boiling, is proportional to $d_0 \sim Ja^{2/3}$.

The kinetic laws in the process of chemical boiling in the presence of forced convection are analogous. At low concentrations the transport of the reagent into the reaction zone plays the main role, while at high concentrations gas formation plays the main role [2].

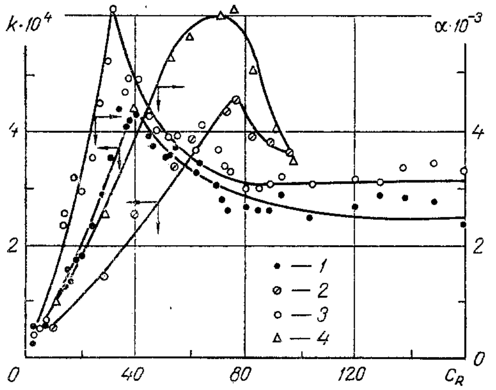

Fig. 1. Coefficients of mass transfer k (m/sec) and heat transfer α (W/(m·K)) versus the reagent concentration c_R (kg/m³) (1, 3: the initial temperature of the solution is equal to 40°C; 2, 4: the initial temperature of the solution is equal to 20°C).

Lenin Komsomol Lvov Polytechnic Institute. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 50, No. 4, pp. 645-650, April, 1986. Original article submitted February 12, 1985.

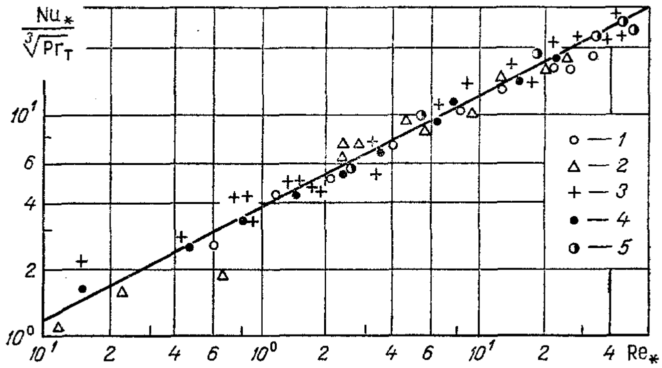

Fig. 2. $Nu_*/\sqrt[3]{Pr_T}$ versus Reynolds number Re_* with heat transfer in the presence of chemical boiling in the region of the bubble regime (1, 2, 4, 5: the system Mg + HCl; 3: Mg + HNO_3; 1, 3: the initial temperature is equal to 20°C; 2: 40; 4: 12; 5: 60°C).

Aside from analogies, significant differences between the processes under comparison were revealed. In chemical boiling the film regime is impossible, in contrast to boiling during which heat is transferred through the vapor film. During boiling the directions of natural convection of the liquid and the moving bubbles coincide, while in the case of mass transfer with gas formation they are oppositely directed. During heat transfer the solid surface, after detachment of the bubbles, comes into contact with the cold liquid, and during mass transfer the solid surface comes into contact with the rich reagent. During mass transfer new centers of gas formation appear as a result of the chemical reaction, which does not occur during heat transfer.

Each chemical interaction is accompanied by a definite thermal effect, and in addition the source of heat is located on the interphase surface, where the temperatures will be maximum. The heat liberated is expended on heating the solid body and the reagent.

If the thermal effect is ignored, then it is impossible to calculate the mass transfer process, since the physical constants (density, coefficient of viscosity, diffusion, etc.) are temperature dependent. The solution of the heat and mass transfer problems and finding the temperature in the interaction zone involve the determination of the kinetic coefficients k and α. In this investigation the coefficient α is determined for the interaction of magnesium with nitric and hydrochloric acids in the presence of natural convection.

The following experimental procedure was used. A vessel with a solution of acid with a definite concentration was placed into a thermostat. A dead-end opening was drilled into the spherical particle of magnesium and a thermocouple was inserted into it flush against the bottom of the opening. Because of the high thermal conductivity of magnesium and the short distances between the interaction surface and the end of the thermocouple (2-3 mm), we used the indications of a second device — a potentiometer — as the temperature of the surface T_s. The temperature of the solution T was recorded with a mercury thermometer. Since the volume of the solution was large, its temperature increased insignificantly. We determined the coefficient of heat transfer α from the relation

$$\alpha = \frac{Q}{F(T_s - T)\tau}. \tag{1}$$

The quantity Q is equal to the difference between the total amount of heat liberated and the amount of heat expended on heating the particle. The calculations show that the amount of heat going into heating the particle is insignificant compared with the total amount of heat. In the worst case it does not exceed 2.5% of the heat liberated and corresponds to the region of low concentrations, where it must be taken into account.

From the graph (Fig. 1) it is evident that the nature of the change in the coefficient of heat transfer α versus the reagent concentration is entirely analogous to the nature of the change in the coefficient of mass transfer k.

Indeed, as the reagent concentration increases, the kinetic coefficients k and α increase, reach maximum (critical) values, and then begin to decrease. In heat-transfer

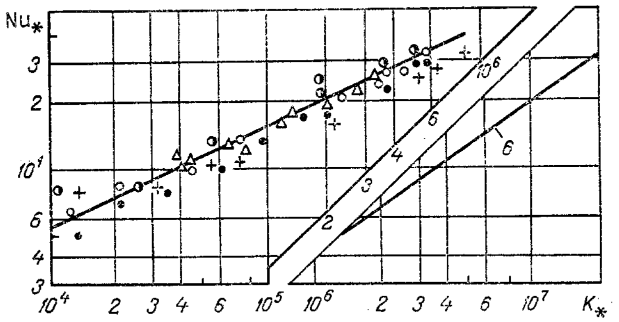

Fig. 3. Curve $Nu_* = f(K_*)$ with heat transfer in the presence of chemical boiling and for bubbling of the liquid with gas (the points correspond to the values in Fig. 2, the line 6 was constructed from the data of [7]).

processes accompanying boiling two regimes are distinguished: the bubble and film regimes, which were first interpreted theoretically by S. S. Kutateladze [3]. By analogy, in mass transfer with gas formation the first region in which k and α increase with c_R can be called the region of the bubble regime. Since during mass transfer with liberation of gas the film regime cannot be realized, because liquid reagent cannot pass through the gas film (here lies, as mentioned above, one of the differences between heat transfer accompanying boiling and mass transfer accompanying gas liberation), the latter region is called supercritical.

In the practice of mass transfer processes the region of low concentrations, for which, as is evident from Fig. 1, a significant change in the kinetic coefficients is observed, is of great interest.

An attempt was made to generalize quantitatively the experimental results on heat transfer in the region of the bubble regime. The main role here is played by the hydrodynamic environment around the spherical particle, which is determined by the mixing of the liquid by the gas bubbles and which will be the same for heat and mass transfer. As is well known, the hydrodynamics of the system is determined by the Reynolds number, into which enters the velocity of the liquid w. For heat transfer in the presence of boiling this velocity is estimated as the ratio of the quantity of heat fed into the system to the specific heat of vaporization. For chemical boiling the velocity w can be estimated from the ratio of the amount of gas liberated to its density ρ'':

$$w \sim \frac{j_g}{\rho''} \sim \frac{nkc_R}{\rho''}. \qquad (2)$$

We write Reynolds number with consideration of (2):

$$\mathrm{Re}_* = \frac{nkc_R d}{\rho'' \nu},$$

in which the quantity d is the linear scale of the capillary gravitational interaction (see [7]).

The experimental results are generalized by the dependence

$$\mathrm{Nu}_* = f(\mathrm{Re}_*, \mathrm{Pr}). \qquad (3)$$

Prandtl's number varied insignificantly in the experiments. For example, for the interaction of magnesium with hydrochloric acid Prandtl's thermal number falls in the range from 8.1 for $c_R = 3.8$ kg/m³ to 5.7 for $c_R = 78.77$ kg/m³ for one and the same initial temperature. Its variation is associated primarily with the decrease in the viscosity in the zone of interaction owing to the liberation of heat.

The effect of Prandtl's number cannot be neglected. The diameter of the magnesium particles participating in the heat and mass transfer fell into the range 22-28 mm. Taking into account the fact that in the case of mass transfer processes [1] and for heat transfer in the presence of boiling liquids [4, 5]

$$\mathrm{Nu}_* \sim \sqrt[3]{\mathrm{Pr}_T}, \qquad (4)$$

we use the same relation in generalizing the experimental results.

It is evident from Fig. 2 that in a logarithmic system of coordinates the dependence $Nu_*/\sqrt[3]{Pr_T} = f(Re_*)$ is a straight line corresponding to the equation

$$\mathrm{Nu}_* = 3{,}8\,\mathrm{Re}_*^{0.5}\mathrm{Pr}_T^{0.33}. \qquad (5)$$

S. S. Kutateladze and I. G. Malenkov confirmed the analogy between heat transfer in the presence of boiling and in the presence of bubbling of an inert gas through a layer of liquid [6]. Taking into account the fact that the effect of the increase in the coefficient of heat transfer is associated with the capillary-acoustic interactions in gas–liquid flows, in [7] the experimental data on heat transfer in the presence of developed bubble boiling were generalized by the dependence

$$\mathrm{Nu}_* \sim K_*^{2/3}, \qquad (6)$$

shown in Fig. 3 by the straight line. The dots in the figure show our data on heat transfer in the presence of chemical boiling. There is only a qualitative analogy between the chemical boiling and bubbling under conditions of the bubble regime. It is evident that as the temperature of the solution rises the values of the number Nu_* increase, and on the whole the dependence has a flatter character than that of (6). Since heat transfer accompanies mass transfer, for which in the case of chemical boiling $\mathrm{Nu} = 24\sqrt{\mathrm{Re}_*}\sqrt[3]{\mathrm{Pr}}$ [8], the same hydrodynamic environment for the processes occurring leads to the fact that the exponents in the number Re_* have the same value.

The results obtained qualitatively extend the analogy not only to mass transfer with gas formation, but also heat transfer in the presence of chemical boiling. In the presence of bubbing of gas the analogy is confirmed only in the region of the bubble regime, whereas in the presence of chemical boiling the analogy is much deeper. The critical values of k and α as well as the drop in these values in the region of large motive forces are observed.

NOTATION

Q, amount of heat delivered to the surface of the sphere by the liquid, J; F, surface area of the sphere, m²; τ, time, sec; j_g, mass flux density of the gas, kg/(m²·sec); n, a stoichiometric coefficient; $d = [\sigma/g(\rho'-\rho'')]^{1/2}$; ρ', ρ", density of the liquid and of the gas, respectively; ν, coefficient of kinematic viscosity; $\mathrm{Nu}_* = \alpha d/\lambda$, thermal Nusselt number; $\mathrm{Pr}_T = \nu/a$, Prandtl thermal number; $\mathrm{Ja} = nc_R/\rho''$, Jacob's diffusion number, and K_*, dynamic criterion of heat transfer [7].

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