In the case of $KPr < 5$ the heat transfer should be calculated from Eq. (2) with allowance for the corrections for the variability of the thermophysical properties of the condensate, convective transfer, and inertial forces in the condensate film [3].

NOTATION

L, Length of the heat-exchange surface; l, coordinate of the development of wave instability; x, current coordinate; $l_\sigma = \sqrt{\sigma/\rho_1 g}$, capillary constant; $l_\nu = (\nu_1^2/g)^{1/3}$, viscosity constant; σ, surface tension coefficient; ν, kinematic viscosity; ρ, density; $g = 9.81(1 - \rho_2/\rho_1)$ reduced acceleration of gravity; $K = r/C_p\Delta T$, Kutateladze number; Pr, Prandtl number, $Ka = (l_\sigma/l_\nu)^6$, Kapitza number; $We = (l_\sigma/L)^2$, Weber number; $Re = \bar{\alpha}_N \Delta TL/\nu_1\rho_1 r = (4L/KPr l_\nu)^{3/4}/3$, Reynolds number; $\overline{Nu} = \bar{\alpha} l_\nu/\lambda_1$, averaged Nusselt number; $\bar{\alpha}$, average coefficient of heat transfer; r, latent heat of vaporization; C_p, specific heat; ΔT, temperature head. Indices: 1, 2, liquid and vapor, respectively; N, calculated from the Nusselt equation.

LITERATURE CITED

1. V. P. Isachenko, Heat Exchange with Condensation [in Russian], Moscow (1977).
2. P. L. Kapitsa, Zh. Éksp. Teor. Fiz., 18, No. 1, 1-28 (1948).
3. D. A. Labuntsov, Teploénergetika, No. 7, 72-79 (1957).
4. G. V. Ratiani and I. G. Shekriladze, Teploénergetika, No. 3, 78-80 (1964).
5. I. I. Gogonin, A. R. Dorokhov, and V. I. Sosunov, "Heat exchange during film condensation of a stationary vapor," Preprint No. 48-80, Inst. Teplofiz., Sib. Otd. Akad. Nauk SSSR, Novosibirsk (1980).
6. I. A. Shemagin, V. M. Budov, and V. A. Sokolov, Izv. Akad. Nauk SSSR, Énerg. Transp., No. 3, 160-162 (1983).
7. V. M. Budov, I. A. Shemagin, and V. A. Kir'yanov, Izv. Vyssh. Uchebn. Zaved., Énerg., No. 11, 56-62 (1983).
8. V. M. Budov, V. A. Kir'yanov, and I. A. Shemagin, Inzh.-Fiz. Zh., 48, No. 6, 958-962 (1985).

HEAT-MASS TRANSPORT IN "CHEMICAL" LIQUID BOILING

V. A. Kirillov, V. A. Kuz'min, N. A. Kuzin,
A. S. Umbetov, and V. M. Khanaev

UDC 66.015.23

Using the reaction of zinc with hydrochloric acid as an example, an experimental and theoretical study is performed of transport phenomena. The coefficients obtained are compared to data on liquid boiling.

Chemical reactions with phase transitions related to liberation of a poorly soluble gas into a liquid occur quite widely in chemical technology. Their external appearance has much in common with liquid boiling on a heating surface, which has led to introduction of the term "chemical" boiling [1, 2]. Although there have been many studies of transport phenomena during metal solution in acids [3, 4], electrolysis [5], and catalytic decomposition of hydrogen peroxide [6] such questions require further clarification. Remaining specially unclear are results involving the heat and mass transport mechanism in "chemical" boiling, regions in which the reaction occurs, and hydrodynamic and thermal regimes.

Experimental Study of Transport Processes. The simplest chemical reaction which takes place with liberation of a gaseous phase is solution of metals in acids. Zinc and hydrochloric acid were chosen for study. The experiments to determine heat-mass transport principles for this reaction were performed under static conditions on zinc specimens in the form of 10 mm diameter spheres at an HCl concentration $C_{21}^0 = 0.2$, liquid temperature $T_0 = 10\text{-}110$°C, and pressure P = 0.01-0.1 MPa.

Catalysis Institute, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk.
Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 52, No. 6, pp. 910-916, June, 1987. Original article submitted April 15, 1986.

0022-0841/87/5206-0649 $12.50

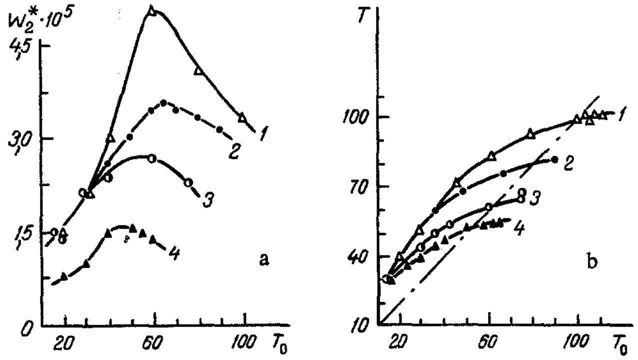

Fig. 1. Effect of temperature of liquid phase volume on gas liberation rate (a) and temperature of metal specimen (b). Pressure: 1) 0.1 MPa; 2) 0.052; 3) 0.029; 4) 0.014. W_2^*, kg/m²·C; T, °C.

In the experiments the amounts of zinc dissolved and gas liberated were measured together with the specimen temperature. The results obtained are shown in Fig. 1. A unique feature of these data is the presence of an extremal dependence of the observed gas liberation rate W_2^* on temperature of the volume T_0. The temperature change of the reacting particle is also "nonclassical." Thus with increase in temperature of the volume the specimen temperature T first increases quite intensely, and then as T_0 increases the rate of change slows and T stabilizes in some temperature range dependent on system pressure. It is characteristic that for further increase in T_0 the particle's temperature head decreases to zero, and then, despite the occurrence of an exothermal reaction, becomes negative. We will note that this result is not erroneous, since it was repeated several times, including use of other systems. Rather, it is a result of interaction between the chemical reactions. It should be noted that the existence of a limit for the gas liberation rate was noted previously in [4]; however, the negative temperature head of the reacting surface relative to the liquid volume has apparently been reported for the first time here.

Physical Interpretation of the Results. We will consider the processes occurring on the surface of the dissolving metal. We note that from an energetics viewpoint similar reactions should occur through the stage of formation of a liquid solution supersaturated with gas at the metal surface. It is known from fluctuation theory [7] that development of nuclei of a new phase occurs when a certain degree of supersaturation is attained, which is dependent on the structure and properties of the surface. In growing the nuclei significantly turbulize the diffusion boundary layer which develops at the solid surface, encouraging intensification of mass transport. It follows from general considerations that if the number of such nuclei is sufficiently small, then transport of matter to the surface is accomplished mainly by the diffusion mechanism. The region in which the action occurs is then determined by the relationship between the rate and the reagent diffusion coefficient. This situation occurs in dilute liquid solutions.

Increase in the reaction rate, for example by increasing the concentration or temperature of the volume, simultaneously encourages intensification of transport processes because the number of new phase nuclei increases and these nuclei begin to merge together, forming large bubbles.

The mass transport coefficient for formation of bubble nuclei can be estimated with the expression $\beta \sim D/r$, where r is the radius of the nucleus, equal to $2\delta/\Delta P$. With a saturation of 10-100 MPa (100 MPa being the liquid breakup pressure) the mass transport coefficient is of the order of 0.1-1 m/sec.

The gas bubbles liberated in the reaction are saturated by vapors of the components of the surrounding liquid, so that the total phase transition rate is determined by the sum of fluxes due to gas liberation and evaporation, i.e.,

$$W_\Phi = \nu_2 W_2 + W_{11} + W_{12}. \tag{1}$$

We can also write $y_{1i} = W_{1i}/W_\Phi$ for i = 1, 2, and $y_{14} = \nu_2 W_2/W_\Phi$, whence we find $W_{1i} = \nu_2 W_2 y_{1i}/y_{14}$, and $W_0 = \nu_2 W_2/y_{14}$. We obtain expressions for y_{1i}/y_{14} from Dalton's law

$$\frac{y_{11}}{y_{14}} = \frac{M_{11}}{M_{12}} \frac{C_{21}}{A} \frac{P^0_{11}}{P}; \quad \frac{y_{12}}{y_{14}} = \frac{M_{11}}{M_{14}} \frac{C_{22}}{A} \frac{P^0_{12}}{P};$$

$$A = \frac{M_{11}}{M_{12}} C_{22}\left(1 - \frac{P^0_{12}}{P}\right) + C_{21}\left(1 - \frac{P^0_{11}}{P}\right). \tag{2}$$

With increase in temperature a change in the rate of both chemical reaction and evaporation occurs. Then with approach of the temperature to the value at which $A \to 0$, $W_{1i} \to \infty$, i.e., the rate of increase of the evaporation rate exceeds the rate of increase of the chemical reaction rate.

The above statement refers to the case where the conditions for removal of gas—vapor bubbles from the reaction surface have no significant effect on the total phase transition rate. If such an effect does exist, then according to results obtained with boiling, some critical flux of vapor—gas is established from the surface into the volume, determined by the work of surface tension forces and the kinetic energy of the flux [8]. Such a situation can be seen in Fig. 1 for the temperature range T_0 = 50-70°C. Further increase in temperature of the volume leads to a reduction in the gas liberation rate. This may be related to enrichment of the surface layer by reaction products or development of critical conditions for vapor—gas removal. In fact, in the latter case for approximately constant W_Φ increase in T_0 and correspondingly T, as follows from Eq. (2), encourages increase in W_{1i}, and thus, decrease in W_2. Since with increase in T the true chemical reaction rate always increases, it can be proposed that the reduction in the observed gas liberation rate is related to a reduction in the fraction of reacting wetted surface.

Mathematical Model for Transport Processes. This model is based on the assumption that bubbles growing and breaking away create intense mixing of liquid at the reacting surface with some rate U_2', proportional to the bubble removal rate U_1, i.e., $U_2' = \gamma U_1$. Moreover, there is a flux of liquid directed to the surface from the volume at a rate U_2, which develops because of breakaway of bubbles, and transports the original reagent into the reaction zone. With consideration of these physical assumptions the equations of material and thermal balance for the Zn—HCl reaction will have the form:

$$\begin{gathered} U_2\rho_2 C^0_{21} S_2 = K_2\rho_2 C_{21} S_2 + U_1\rho_1 S_1 y_{11} + U_1\gamma\rho_2 C_{21} S_1, \\ U_2\rho_2 C^0_{22} S_2 = U_1\rho_1 S_1 y_{12} + U_1\gamma\rho_2 C_{22} S_1, \\ U_2\rho_2 C^0_{23} S_2 = -\nu_1 K_2\rho_2 C_{21} S_2 + U_1\gamma\rho_2 C_{23} S_1, \\ U_1\rho_1 y_{14} S_1 = -\nu_2 K_2\rho_2 C_{21} S_2. \end{gathered} \tag{3}$$

Furthermore,

$$\begin{gathered} U_2\rho_2 S_2 = U_1\rho_1 S_1 + U_1\rho_2\gamma S_1, \\ U_2\rho_2 S_2 \sum_{i=1}^{3} i^0_{2i} C^0_{2i} = -K_2 C_{21}\rho_2 Q_2 S_2 + U_1\rho_1 S_1 \sum_{i=1}^{4} i_{1i} y_{1i} + U_1\rho_2 S_1\gamma \sum_{i=1}^{4} i_{2i} C_{2i}. \end{gathered}$$

For the conditions $y_{13} = 0$, $C_{24} = 0$, $h_{24} = 0$, $C_{p2} \approx C_{p2i}$, from these equations we obtain the following expressions for calculation of concentrations and temperature in the reaction zone

$$C^0_{21}\left(1 + \frac{\rho_2}{\rho_1}\gamma\right) = y_{11} + \frac{y_{14}}{\nu_2} + C_{21}\gamma\frac{\rho_2}{\rho_1}, \tag{4}$$

$$C^0_{22}\left(1 + \frac{\rho_2}{\rho_1}\gamma\right) = y_{12} + C_{22}\gamma\frac{\rho_2}{\rho_1}, \tag{5}$$

$$C^0_{23}\left(1 + \frac{\rho_2}{\rho_1}\gamma\right) = \frac{\nu_1}{\nu_2} y_{14} + C_{23}\gamma\frac{\rho_2}{\rho_1}, \tag{6}$$

$$C_{p_2}\left(1+\frac{\rho_2}{\rho_1}\gamma\right)(T_0-T)=-\frac{y_{14}}{\nu_2}Q_2+\sum_{i=1}^{2}h_{2i}y_{1i}. \tag{7}$$

System (4)-(7) must be complemented by thermodynamic relationships of the form of Eq. (2).

We will now analyze these equations. If $T_0 = T$, then transcendental equation (7) will define the temperature which in the future we will call "isothermal" (T^*). In this case convective heat transport is absent, and all chemical reaction heat is expended in liquid evaporation. Calculation of the bubble composition with Eq. (2) shows that upon approach to T^* a significant enrichment of the vapor—gas phase by water vapor occurs. Then, assuming a two-component composition ($H_2 + H_2O$) from Eq. (7) with consideration of Eq. (2) we obtain the following expression for temperature:

$$\frac{1}{T^*}=\left[\frac{1}{T'}+\ln C_{22}^{M}\left(1+\frac{h_{22}}{Q_2}\nu_2\frac{M_{11}}{M_{13}}\right)\right]-\frac{R}{h_{22}}\ln\frac{P}{P'}, \tag{8}$$

where T' is the reference temperatre at which the vapor pressure P' is defined. The expression in square brackets changes insignificantly with T^*. If we construct the graph of $\ln P/P'$ va $1/T^*$, then from the slope of the straight line obtained we can find the heat h_{22}. Coincidence of this value with the tabular value will indicate the presence of concentration equilibrium between the liquid and vapor—gas phases.

From this model we have expressions for the convective and evaporative transport of heat and matter:

$$W_2Q_2=q_{\text{con}}+q_{\text{ev}} \quad \text{or} \quad W_2Q_2=\frac{\nu_2W_2}{y_{14}}\sum_{i=1}^{2}h_{2i}y_{1i}+\frac{\nu_2W_2}{y_{14}}C_{p_2}\left(1+\frac{\rho_2}{\rho_1}\gamma\right)(T-T_0),$$

whence we obtain

$$q_{\text{con}}=W_2Q_2\frac{C_{p_2}\left(1+\frac{\rho_2}{\rho_1}\gamma\right)(T-T_0)}{C_{p_2}\left(1+\frac{\rho_2}{\rho_1}\gamma\right)(T-T_0)+\sum_{i=1}^{2}h_{2i}y_{1i}}, \tag{9}$$

$$q_{\text{ev}}=W_2Q_2\frac{\sum_{i=1}^{2}h_{2i}y_{1i}}{C_{p_2}\left(1+\frac{\rho_2}{\rho_1}\gamma\right)(T-T_0)+\sum_{i=1}^{2}h_{2i}y_{1i}}. \tag{10}$$

Similar expressions can be obtained for convective and evaporative mass transport.

Determination of Heat—Mass Transport Coefficients. The equations of the model (4)-(7) contain two unknown parameters γ and C_{21}. For a known reactive surface temperature and in the presence of equilibrium (which makes it possible to use relationships of the form of Eq. (2)) these parameters can be defined from Eqs. (4)-(7).

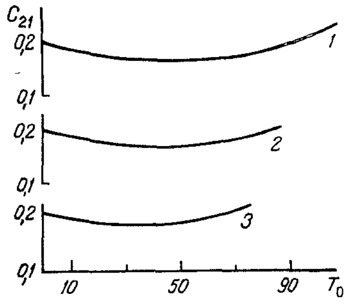

Fig. 2. Effect of temperature T_0 on HCl concentration at reacting metal surface. Pressure: 1) 0.7 MPa; 2) 0.052; 3) 0.029.

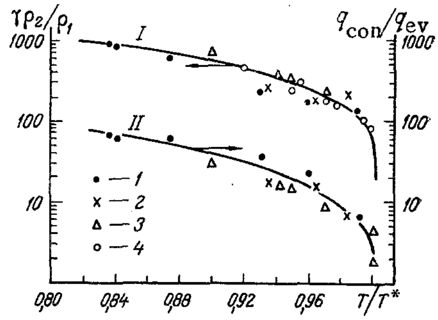

Fig. 3

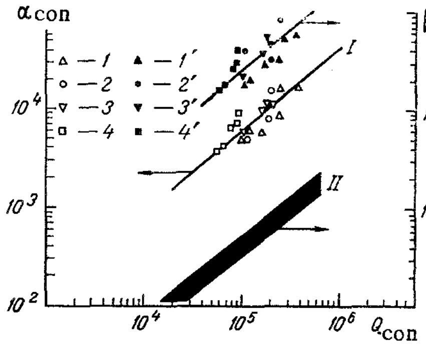

Fig. 4

Fig. 3. Processing of experimental data on effect of T/T* on $\gamma\rho_2/\rho_1$ (I) and q_{con}/q_{ev} (II). Pressure: 1) P = 0.1 MPa; 2) 0.052; 3) 0.029; 4) 0.014 MPa.

Fig. 4. Comparison of head—mass transport coefficients with data of [9]: I) $\alpha \sim Q_{con}^{0.7}$ from data of [9]; II) range of mass exchange coefficients obtained by electrochemical method for solution boiling [9]; 1, 1') P = 0.1 MPa; 2, 2') 0.052; 3, 3') 0.029; 4, 4') 0.014 MPa; 1-4) heat-exchange coefficients; 1'-4') mass exchange. α_{con}, $W/m^2\cdot{}^\circ K$; Q_{con}, W/m^2, β, m/sec.

To prove the equilibrium state of the phase composition from experimental data Eq. (8) was used to determine the heat of evaporation of water. The value obtained was 10.7 kcal/mole, close to the tabular value.

Figure 2 shows calculations for the HCl concentration in the reaction zone. It is evident from the graph that C_{21} differs only insignificantly from C_{21}^0. In the temperature range approaching T* because of intense water evaporation the reaction agent concentrates to values greater than C_{21}^0. Thus the given reaction occurs without significant braking by the reacting substance. It can be shown that for other metals and acids in the region close to critical as regards gas liberation rate the chemical reaction is also not braked by mass transport of the reactant to the surface. This conclusion does not agree with the propositions of [3, 4], where without justification an external diffusion region was assumed for the chemical reaction.

Figure 3 shows the experimental data obtained. It can be seen that in the coordinates selected the experimental results for various pressures group satisfactorily about approximating lines. It is characteristic that as $T \to T^*$ $\gamma\rho_2/\rho_1$ decreases abruptly and changes sign in the region of negative temperature heads. The same figure shows the dependence of q_{con}/q_{ev}, calculated with Eqs. (9), (10) on T/T*. This graph shows the significant increase in the contribution of evaporation to overall heat transport, especially upon approach to the "isothermal" point. This may be the explanation of the experimentally observed phenomenon of negative reaction surface temperature head. Comparison with other experimental data, for example, those obtained for boiling [9], indicates the significant contribution of evaporation process to total heat transport in our experiments. Therefore further comparison of exchange coefficients was done for the convective components. Such data are shown in Fig. 4. For comparison the solid lines and shaded region show results of [9]. The agreement of the heat-exchange coefficients with the boiling data is quite satisfactory. For the mass transport coefficients the situation is somewhat different. The shaded region in the figure corresponds to the results of [9], while the points are measurements of the present study. For the latter the mass transport coefficients referred to the entire geometric surface were found from the formal balance relationship $W_2 = \beta(C_{21}^0 - C_{21})$ for the range $T_0 \leqslant 60°C$. These data indicate that the mass exchange coefficients defined under chemical reaction conditions are some 30-40 times as large as values obtained for liquid boiling in the region of similar pressures and thermal fluxes.

To explain the cause of this divergence we offer the following analysis. It is known that for convective exchange there exists a relationship between the coefficients α and β, characterized by the Lewis number $\alpha/(\beta C_{p_2}\rho_2) = Le^{2/3}$, which defines the relationship between the thermal and diffusion boundary layers. Under our experimental conditions the value of Le was close to unity. This indicates more intense turbulization of the diffusion, rather than the thermal boundary layer. Qualitatively such a conclusion also follows from comparison of the features of bubble breakaway from the surface in chemical reaction and boiling. Thus, as cine photography results reveal, when a chemical reaction occurs on the surface of a metal, two forms of bubble can be distinguished. One of these is nuclei of micron size, which develop due to supersaturation of the surface layer of liquid transforming to gas. The size of such bubbles does not exceed the thickness of the concentration boundary layer. As these bubbles grow they turbulize the liquid layer at the metal surface, and merge together to form bubbles of larger diameter. These latter have dimensions of the order of the thickness of the thermal boundary layer, and, as in liquid boiling, they provide the major heat transport between the liquid volume and the metal surface. From such a mechanism follows the absence of similarity of heat and mass exchange during chemical reactions with a phase transition, as was observed in our experiments.

NOTATION

C, component concentration in liquid phase, mass fraction; y, component concentration in vapor—gas phase, mass fraction; T, temperature; P, pressure, MPa; W_2, chemical reaction rate, kg/m^2·sec; W_2, observed gas liberation rate, kg/m^2·sec; W_2^*, observed gas liberation rate, kg/m^2·sec; W_{1i}, evaporation rate of component i, kg/m^2·sec; M, molecular weight; ρ, density, kg/m^3; S, surface occupied by phase, m^2; U, phase flow velocity, m/sec; K, reaction rate constant, m/sec; ν, stoichiometric coefficient ($\nu_1 = 1.89$; $\nu_2 = 0.028$); Q_2, thermal effect of reaction, J/kg; i_{2i}, i_{1i}, component enthalpies in liquid and vapor phases, J/kg; h_{2i}, heat of phase transition, j/kg; C_{p2}, specific heat of liquid, J/kg·K; R, gas constant; q, thermal flux, W/m^2; α, heat-exchange coefficient, W/m^2·K; β, mass-exchange coefficient, m/sec; D, molecular diffusion coefficient in liquid phase, m^2/sec. Double subscripts — first subscript is number of phase, second, number of component: 1) vapor—gas; 2) liquid; 1) HCl; 2) H_2O; 3) $ZnCl_2$; 4) H_2. Single subscripts: 1) vapor phase; 2) liquid; 0) phase volume; M) molar; ev) evaporation; con) convection.

LITERATURE CITED

1. V. A. Kirillov and V. P. Patskov, Inzh.-Fiz. Zh., 40, No. 3, 529 (1981).
2. E. I. Nesis, Liquid Boiling [in Russian], Moscow (1973).
3. S. P. Novikov and O. I. Savina, Heat Transport and Applied Hydrodynamics [in Russian], Kiev (1983), pp. 66-70.
4. G. A. Aksel'rud and A. D. Molchanov, Solution of Solids [in Russian], Moscow (1977).
5. Yu. A. Chizmadzhev, V. S. Markin, M. V. Tarasevich, and Yu. G. Chirkov, Macrokinetics of Processes in Porous Media [in Russian], Moscow (1971).
6. H. J. Baumgartner, G. C. Hood, and J. M. Monger, J. Catalysis, 2, 405-414, 415-420 (1963).
7. Ya. I. Frenkel', Kinetic Theory of Liquids, Collected Works, Vol. 3 [in Russian], Moscow (1959).
8. S. S. Kutateladze and M. A. Styrikovich, Hydrodynamics of Gas—Liquid Systems [in Russian], Moscow (1976).
9. G. G. Kuvshinov, "Study of boiling in a large volume using the electrodiffusion method," Candidate's Dissertation, Novosibirsk (1978).