Journal of Engineering Physics and Thermophysics, Vol. 70, No. 1, 1997

DETERMINATION OF KINETIC PARAMETERS OF REACTIONS IN GAS–LIQUID SYSTEMS BY ELECTRICAL MEASUREMENTS

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UDC 541.12.013.6:543.25.253.3

Diffusion is one of the processes that determines the physicochemical properties of gas–liquid systems and is accompanied by an increase in the conductivity of the liquid phase of the system. It is proposed that electrodynamic methods be used to determine the parameters of liquid–gas interaction.

It is well known that one of the consequencies of industrial man's activities is deterioration of the ecological situation. In particular, acid rain is caused by the presence of such gases as SO_2, NO_2, CH_2O, $ClONO_2$, etc. in the atmosphere. The latter are industrial and automobile exhaust gases [1-6]. The acidity of precipitates falling onto the Earth's surface is determined by regularities of the chemical reactions proceeding in gas–liquid systems.

As water exists in aerosol form in the atmosphere, modeling of the interaction of a droplet with its surrounding gas makes it possible to establish regularities and quantitative characteristics that allow forecasting of the formation of acidic precipitates.

Modeling of the physicochemical processes accompaning the motion of a water droplet in a gas was carried out in [7-12]. In so doing, quantitative characteristics of droplet–gas interaction (here, the processes involve gas diffusion into a droplet volume and its dissolution there) were determined by measuring the conductivity of the solution obtained after passage through the gas-filled working volume by a droplet as well as from spectroscopic results for gas sampled from the working volume (Fig. 1). These methods of analysis of a substance allow successful concentration measurement of a gas dissolved in the droplet for the time of its residence in the gas but they are inapplicable for direct recording of fragments of the process of gas penetration into the droplet volume. Below we propose a procedure for recording the kinetic parameters of processes in the liquid–gas system by electrical measurements.

Conductometric Measurements of Diffusion Front. As gas dissolution in a liquid is accompanied by changes in conductivity, a change in the gas concentration on the liquid surface can be determined from measurements of the conductivity profile of a diffusion wave. In the latter, three regions with substantially different conductivities can be distinguished (Fig. 2): 1) a gas-free liquid region (in front of the diffusion wave) with conductivity σ_1; 2) the front of the diffusion wave with conductivity $\bar{\sigma}_2$ ($\bar{\sigma}_2 = (\int_{\Delta l} \sigma_2 dx)/\Delta l$); 3) a gas-saturated region with conductivity σ_3. Here $\sigma_1 \ll \sigma_2 < \sigma_3$ (Fig. 2).

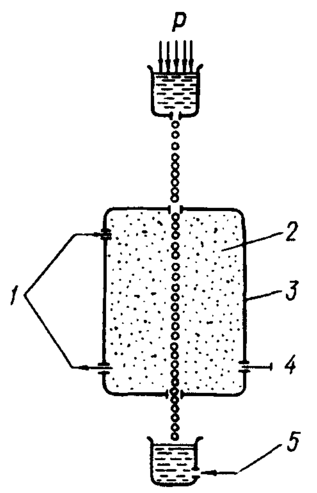
The region of the medium occupied by the front of the diffusion wave can be connected by contacts to an electric circuit (Fig. 2). Then, any change in the resistivity of the front is recorded by measuring the volt–ampere characteristic of the circuit.

Assume that the wave front is series-connected to a circuit with load resistance R and an e.m.f. source U_0. Here, the voltage U across the load resistance R is

$$U = IR = \frac{R}{R_1 + R_2 + R_3 + R} U_0 , \tag{1}$$

from which the total resistance of the medium is

Academic Scientific Complex "A. V. Luikov Heat and Mass Transfer Institute of the Academy of Sciences of Belarus," Minsk, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 70, No. 1, pp. 68-72, January-February, 1997. Original article submitted October 14, 1994.



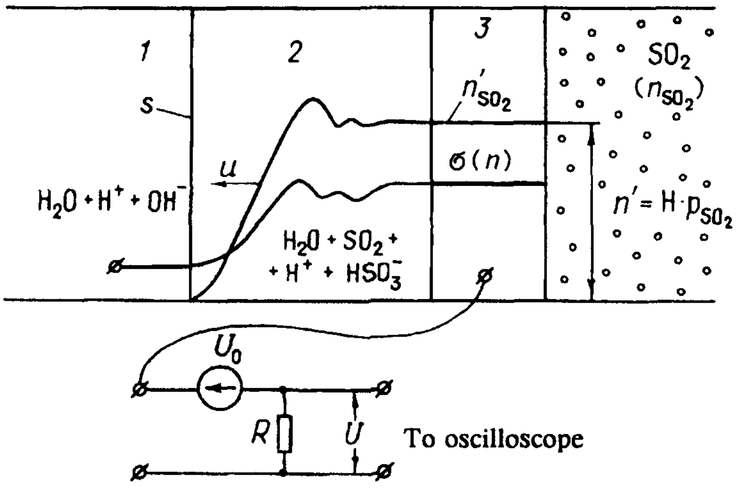


Fig. 1. Schematic of the installation used in [7-12] for determination of the kinetic parameters of interaction of gas–liquid systems: 1) to pump; 2) tested gas; 3) working chamber; 4) to spectrometer; 5) pH measurement.

Fig. 2. Block-diagram of measurements of the kinetic parameters of the chemical reactions proceeding in gas–liquid systems at the phase boundary.

$$R_\Sigma = R_1 + R_2 + R_3 = R\left(\frac{U_0}{U} - 1\right). \tag{2}$$

Having performed time differentiation of (2), we arrive at

$$\dot{R}_1 + \dot{R}_2 + \dot{R}_3 = A\,, \tag{3}$$

where $A = -R(U_0/U^2)\dot{U}$.

As in the course of motion of the wave front regions 1, 2, and 3 are successively connected to the circuit, five stages of the front can be distinguished: 1) $R_\Sigma = R_1$, the region between the contacts is filled with gas-free water; 2) $R_\Sigma = R_1 + R_2$, smooth connection of the front to the electric circuit; 3) $R_\Sigma = R_1 + R_2 + R_3$, region 3 is brought into the circuit, where R_2 = const; 4) $R_\Sigma = R_2 + R_3$, smooth disconnection of the front from the electric circuit; 5) $R_\Sigma = R_3$, the region between the contacts is fully occupied by gas-saturated water

To determine σ_2, it is possible, as follows from (3), to use the volt–ampere characteristics of the electric circuit recorded at stages 2 and 4. However, since $\sigma_3 >> \sigma_1$, it is more convenient to use only stage 4 ($\bar{\sigma}_2 \sim \sigma_3$, i.e., $R_2 \sim R_3$) to measure the conductivity distribution of the front. In this case, considering that $\dot{R}_3 = u/\sigma_3 s$ and $\dot{R}_2 = -u/\sigma_2 s$, we have from (3) that

$$\sigma_2 = \frac{\sigma_3}{1 + \sigma_3 R \dfrac{s}{u} \dfrac{U_0}{U^2} \dot{U}}\,.$$

As in the course of gas-diffusion into a droplet volume the conductivity of the gas-saturated region of the volume changes, the parameters of the process of reaching an equilibrium gas concentration in the droplet volume can be recorded by an electromagnetic method.

2. Electromagnetic Method. The method is based on measuring the perturbation of an electromagnetic field caused by a droplet (a finitely conducting sphere in a magnetic field [13]) with a conducting envelope of thickness Δ with outer radius b and inner radius a when it passes through the magnetic field of a source (e.g., an energized coil).

Now we determine the distribution of the magnetic field which emerges around a spherical droplet with a conducting envelope.

A system of equations describing the diffusion of a magnetic field into a motionless conducting sphere is:

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \quad \nabla \times \mathbf{H} = \mathbf{j}, \quad \nabla \mathbf{H} = 0, \quad \nabla \mathbf{E} = 0. \tag{4}$$

Here, the boundary conditions (index "i" stands for the parameters inside the sphere, index "e," for those outside the sphere, and the coordinate system used is r, φ, Θ) are: 1) $r \to \infty$, $\mathbf{H} = \mathbf{H}_0 \cdot e^{-i\omega t}$, $-\infty < t < +\infty$; 2) $r = b$, $\mathbf{H}^{(i)} = \mathbf{H}^{(e)}$; $r = a$, $\nabla \mathbf{A}^{(i)} = 0$ (considering that $\sigma = 0$, if $0 < r < a$; $\sigma \not\equiv 0$, if $a \le r \le b$, here σ is the conductivity of water saturated with gas).

In choosing system (4) for describing diffusion into a moving spherical droplet, it was implicitly assumed that motion of the medium does not exert a pronounced influence on the diffusion process, i.e., $|\mathbf{v} \times \mathbf{B}| << \omega B b$, where v is the droplet velocity.

1. External problem of magnetic field determination ($r > b$). Here the condition $\nabla \times \mathbf{H} = 0$ is fulfilled; therefore, the magnetic field has a scalar potential ψ

$$\mathbf{H} = -\nabla \psi, \tag{5}$$

but at $r \to \infty$

$$\psi \to -Hr \cos \Theta. \tag{6}$$

Provided boundary condition (6) is fulfilled, the solution of (5) for region $r \in [a, \infty]$ is

$$\psi = \left(\frac{C}{r^2} - Hr\right) \cos \Theta. \tag{7}$$

2. Internal problem ($a \le r \le b$). To solve it, we use the vector potential $\mathbf{A}$ [13]:

$$\mathbf{H} = \nabla \times \mathbf{A},$$

here $\nabla \mathbf{A} = 0$ (the condition of a zero space charge).

Combining the equations of system (4), we arrive at the Helmholtz vector equation

$$\nabla \mathbf{A}^{(i)} + k^2 \mathbf{A}^{(i)} = 0, \tag{8}$$

where $k = (1 + i)/(a/\delta)$. The boundary condition for A on a droplet surface S is $\mathbf{A}^{(i)}|_S = \mathbf{A}^{(e)}|_S$.

Since the vector potential of the source ($\mathbf{A}_0 = 1/2\mathbf{H}_0 \times \mathbf{r} \cdot e^{-i\omega t}$) is $0 \cdot \mathbf{e}_r + 1/2rH_0 \sin \Theta e^{-i\omega t} \mathbf{e}_\varphi + 0 \cdot \mathbf{e}_\Theta$, in order to satisfy the boundary condition at $r \to \infty$, it is necessary to seek $\mathbf{A}^{(i)}$ in the form

$$\mathbf{A}^{(i)} = DA_1(r) \sin \Theta \, e^{-i\omega t} \mathbf{e}_\varphi. \tag{9}$$

Then Eq. (8) is reduced to the scalar form

$$\frac{\partial^2 A_1}{\partial x^2} + \frac{2}{r}\frac{\partial A_1}{\partial x} + \left(A_1 - \frac{2A_1}{x^2}\right) = 0, \tag{10}$$

where $x = kr$.

Substituting $A_1 = A_2/\sqrt{x}$, we obtain a Bessel equation from (10):

$$\frac{\partial^2 A_2}{\partial x^2} + \frac{1}{x}\frac{\partial A}{\partial x} + \left(1 - \frac{9/4}{x^2}\right) A_2 = 0,$$

a solution of which is $A_2 = C_1 J_{3/2}(x) + D_1 N_{3/2}(x)$. Hence, $A_1 = C_2 J_{3/2}(x)/\sqrt{x} + D_2 N_{3/2}(x)/\sqrt{x}$.

The necessity of fulfilment of the boundary conditions gives a system of equations for determination of C, C_2, and D_2:

$$C_2 = \frac{J_{3/2}}{\sqrt{y}} + D_2 \frac{N_{3/2}}{\sqrt{y}} = 0 \,, \quad \frac{2k}{x} \left(C_2 \frac{J_{3/2}}{\sqrt{x}} + D_2 \frac{N_{3/2}}{\sqrt{x}} \right) = \frac{2C}{b^3} + H_0 \,,$$

$$\frac{k}{x} \left(C_2 \left(\frac{J_{3/2}}{2\sqrt{x}} + \sqrt{x}\, J'_{3/2} \right) + D_2 \left(\frac{N_{3/2}}{2\sqrt{x}} + \sqrt{x}\, N'_{3/2} \right) \right) = \frac{C}{b^3} - H_0 \,.$$

If the frequency of the magnetic field of the source is such that a strong skin-effect (x, $y << 1$) occurs [13], the amplitude of the magnetic field of the reaction recorded by an electromagnetic probe [14] is at its maximum and practically equal to the field amplitude of the source [13], which is optimal from the viewpoint of the problem of recording the parameters of the field of the reaction. It is interesting to consider below just this regime of magnetic-field variation.

Using asymptotic expressions for the Bessel functions [15], we obtain a system for determination of the constant coefficients D_2, C_2, and C:

$$D_2 \sin y - C_2 \cos y = 0 \,,$$

$$\frac{k}{x} \sqrt{\left(\frac{2}{\pi}\right)} \left(D_2 \frac{2 \sin x}{x} - C_2 \frac{2 \cos x}{x} \right) = \frac{2C}{b^3} + H_0 \,,$$

$$\frac{k}{x} \sqrt{\left(\frac{2}{\pi}\right)} \left(D_2 \left(\cos x - \frac{3 \cos x + 2 \sin x}{x} \right) + \right.$$

$$\left. + C_2 \left(\sin x + \frac{2 \cos x - 3 \sin x}{x} \right) \right) = \frac{C}{b^3} - H_0 \,,$$

where

$$D_2 = -2 \sqrt{\left(\frac{\pi}{2}\right)} \frac{x}{k} \frac{\cos y}{\cos x \cos y + \sin y \cos x} H_0 \,,$$

$$C_2 = -2 \sqrt{\left(\frac{\pi}{2}\right)} \frac{x}{k} \frac{\sin y}{\cos x \cos y + \sin y \sin x} H_0 \,,$$

from which we obtain

$$H_r = -H_0 \left(\frac{b}{r}\right)^3 \left(\left(1 - \frac{3}{4} \frac{\delta}{b} + \right.\right.$$

$$\left. + \frac{\delta}{b} \frac{e^{\frac{4(b-a)}{\delta}} + 2e^{\frac{2(b-a)}{\delta}} \sin \frac{2(b-a)}{\delta} - 1}{e^{\frac{4(b-a)}{\delta}} - 2e^{\frac{2(b-a)}{\delta}} \cos \frac{2(b-a)}{\delta} + \cos \frac{2(b-a)}{\delta}} \right) \cos \omega t -$$

$$\left. - \frac{\delta}{b} \left(\frac{3}{4} + \frac{e^{\frac{4(b-a)}{\delta}} + 2e^{\frac{2(b-a)}{\delta}} \sin \frac{2(b-a)}{\delta} - 1}{e^{\frac{4(b-a)}{\delta}} - 2e^{\frac{2(b-a)}{\delta}} \cos \frac{2(b-a)}{\delta} + \cos \frac{2(b-a)}{\delta}} \right) \sin \omega t \right) . \qquad (11)$$

In the limiting cases, depending on Δ and δ expression (11) acquires a form that is "transparent" for analysis:

1. $\Delta/\delta \gg 1$, then

$$H_r = -H_0 \left(\frac{b}{r}\right)^3 \left(\left(1 + \frac{1}{4}\frac{\delta}{b}\right)\cos\omega t + \frac{7}{4}\frac{\delta}{b}\sin\omega t\right),$$

here H_r is independent of Δ/δ (we restrict ourselves to an accuracy not higher than δ/b), i.e., the initial stage of diffusion is not recorded.

2. $\Delta/\delta \ll 1$ (the developed stage of diffusion), then

$$H_{r_p} = -H_0 \left(\frac{b}{r}\right)^3 \left(\left(1 - \frac{3}{4}\frac{\delta}{b} + 4\frac{\Delta}{b}\right)\cos\omega t + \frac{3}{4}\frac{\delta}{b}\sin\omega t\right).$$

In this case, the magnitude of the field of the reaction depends on Δ/b, which allows Δ to be determined. Consequently, the parameters of the process of establishing an equilibrium concentration of a gas dissolved in a droplet volume can be recorded.

NOTATION

σ, conductivity; Δl, front width; R, load resistance; U_0, e.m.f. source; U, voltage; R_1, total resistance of region 1; R_2, total resistance of region 2 of the front; R_3, total resistance of region 3; ψ, scalar potential; v, droplet velocity; **A**, vector potential; **j**, current density; $\mathbf{H}^{(i)}$, $\mathbf{H}^{(e)}$, intensities of the magnetic field; **E**, intensity of electric field; ω, frequency of magnetic field; **B**, magnetic-field induction; s, electrode area; u, velocity of diffusion-wave front; C, C_1, C_2, D, D_1, D_2, arbitrary constants; i, e, indices; δ, skin-layer thickness.

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