MEASUREMENT OF THERMAL ACTIVITY IN ELECTRICALLY CONDUCTING SOLUTIONS

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The article describes a method for the determination of thermal activity of electrically conducting solutions based on pulsed heating of a thin dielectric film in contact with the solution.

Nonsteady-state methods of measuring the thermophysical characteristics of materials based on the use of electronic techniques and, particularly the pulse method for measuring thermal activity [1] have a number of indisputable advantages, principal amongst which are the simplicity of the measurement cell, the short measurement time, the slight depth of penetration of the temperature field into the material, and the satisfactory reliability of the results.

However, the pulsed method for determining thermal activity is inapplicable in the case of electrically conducting solutions because the solution in contact with the metal film of the probe acts as a shunt. The existence of a double electric layer at the solution–metal boundary gives rise to significant distortion of the recorded signal during the transmission of a rectangular current pulse through a metal film.

In order to eliminate the latter, it is necessary to consider the problem involving an insulating wall between the metal film and solution. We consider the one-dimensional thermal problem of heating a plate of thickness l which is in contact with a semiinfinite volume of solution on one side and is thermally insulated on the other. At the initial time, the temperatures of the plate and of the medium are identical at all points. From the time $\tau = 0$, a constant flux, $q_0 = \text{const}$, acts at the point $x = 0$. For this problem, the equations of thermal conductivity are

$$\frac{\partial t_1}{\partial \tau} = a_1 \frac{\partial^2 t_1}{\partial x^2}, \quad 0 \leqslant x \leqslant l,$$
$$\frac{\partial t_2}{\partial \tau} = a_2 \frac{\partial^2 t_2}{\partial x^2}, \quad l < x < \infty. \tag{1}$$

We write the initial and boundary conditions as

$$t_1(x,\ 0) = t_2(x,\ 0) = 0, \quad t_1(l,\ \tau) = t_2(l,\ \tau),$$
$$\frac{\lambda_2}{\lambda_1} \frac{\partial t_2(l,\ \tau)}{\partial x} = \frac{\partial t_1(l,\ \tau)}{\partial x}, \tag{2}$$
$$t_2(\infty,\ \tau) = 0, \quad \frac{\partial t_2(\infty,\ \tau)}{\partial x} = 0, \quad \lambda_1 \frac{\partial t_1(0,\ \tau)}{\partial x} + q_0 = 0.$$

The solution of this system has the following form

$$t_1 = \frac{2q_0 \sqrt{\tau}}{\varepsilon_1} \left[\operatorname{ierfc} \frac{x}{2\sqrt{a_1 \tau}} - h \sum_{n=1}^{\infty} (-h)^{n-1} \left(\operatorname{ierfc} \frac{2nl - x}{2\sqrt{a_1\tau}} + \operatorname{ierfc} \frac{2nl + x}{2\sqrt{a_1\tau}} \right) \right.,$$
$$t_2 = \frac{2q_0 \sqrt{\tau}}{\varepsilon_1} (1 - h) \sum_{n=1}^{\infty} (-h)^{n-1} \operatorname{ierfc} \frac{(2n-1)\, l + K_a^{1/2} (x - l)}{2\sqrt{a_1\tau}}, \tag{3}$$

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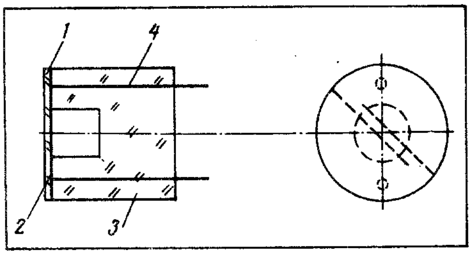

Fig.1

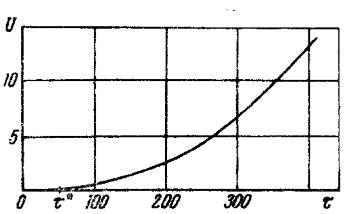

Fig.2

Fig.1. Probe construction: 1) polymer film; 2) metal film; 3) backing; 4) leads in contact with metal film.

Fig.2. Typical signal trace. U, mV; τ, μsec.

where

$$h = \frac{1 - K_\varepsilon}{1 + K_\varepsilon}; \quad K_\varepsilon = \sqrt{\frac{\lambda_1 c_1 \gamma_1}{\lambda_2 c_2 \gamma_2}} = \frac{\varepsilon_1}{\varepsilon_2}; \quad K_a = \frac{a_1}{a_2}.$$

The usually accepted notation is used [2]. For the free surface of the plate ($x = 0$), we have

$$t = \frac{2q_0 \sqrt{\tau}}{\varepsilon_1} \left[\frac{1}{\sqrt{\pi}} - 2h \sum_{n=1}^{\infty} (-h)^{n-1} \operatorname{ierfc} \frac{n}{\sqrt{\mathrm{Fo}_1}} \right]. \tag{4}$$

Equation (4) is the theoretical basis for the proposed method of pulsed measurement of thermal activity of solutions. The thermal problem discussed above was realized experimentally by means of the probe shown in Fig.1.

A strip of polyethylene terephthalate film metallized on one side was fastened to the face of a cylindrical cone with a blind opening along the axis. The metal coating of the film (aluminum) was cut beforehand along two parallel lines in order to delineate a portion of known ohmic resistance ($R_g \simeq 10$) above the opening. Conductive adhesive provided contact between the metal coating and two conductors mounted in the body of the probe. To avoid solution leakage, the polyethylene terephthalate film 4 μ thick was sealed around the edges with epoxy resin. The probe was connected in an arm of a bridge. When a rectangular voltage pulse was fed in at the neutral point of the bridge, thermal power which was active during the pulse was deposited in the resistance R_g. For a pulse length $\tau_p = 400$ μsec and metal coating thickness $l_m < 0.1$ μ, Eq.(4) describes the law of temperature variation of the free surface of the film with sufficient accuracy for the case where the probe is submerged in the solution. Errors resulting from the neglect of the heat transfer into air and of the thermal capacity of the metal coating are small and can be neglected. For the given dimensions of the portion of the film giving rise to the thermal flux (5 × 0.5 mm), the error arising from the deviation of the actual model from one-dimensional is also small and was not taken into account.

The temperature of the free surface of the film was monitored by measurement of the resistance R_g which produced imbalance of the bridge. The signal U taken from the reference point of the bridge was recorded with an S1-19 oscilloscope which was triggered in synchronization with the rectangular voltage pulse. Under the given experimental conditions, the magnitude of the signal U is proportional to the change in temperature of the free surface, which can be represented in the form

$$U = U_1 + U_2, \tag{5}$$

where

$$U_1 = k \frac{2q_0 \sqrt{\tau}}{\varepsilon_1} \cdot \frac{1}{\sqrt{\pi}};$$

$$U_2 = -k \frac{2q_0 \sqrt{\tau}}{\varepsilon_1} 2h \sum_{n=1}^{\infty} (-h)^{n-1} \operatorname{ierfc} \frac{n}{\sqrt{\mathrm{Fo}_1}};$$

k is a constant of proportionality.

Use of a complex bridge circuit similar to that in [3] made it possible to record the signal U_2 directly (Fig.2). In the interval $0 - \tau^*$, the polyethylene terephthalate film can be considered a semiinfinite medium. Obviously, the recorded signal $U = U_1$ for pulse durations $\tau_1 < \tau^*$.

TABLE 1. Experimental Values of ε for a Number of Fluids

Fluid	ε, J/m^2·deg ·sec$^{1/2}$	Fluid	ε, J/m^2·deg ·sec$^{1/2}$
Water	1530	Glycerine	890
95% Ethyl alcohol	600	Benzene	440
95% Acetic acid	650	Aqueous solution of NaCl (saturated)	1490
50% Aqueous solution of sulfuric acid	1150		

To find h and therefore ε_2 we use the following formula:

$$\frac{U_2(\tau_2)}{U_1(\tau_1)} = -\frac{\sqrt{\tau_2}}{\sqrt{\tau_1}}\, 2\sqrt{\pi}\, h \sum_{n=1}^{\infty} (-h)^{n-1} \operatorname{ierfc} \frac{n}{\sqrt{\mathrm{Fo}_1}}, \tag{6}$$

where $\tau_i < \tau^*$; $\tau_2 > \tau^*$.

An analysis of the possible errors shows that the measurement accuracy is practically determined by the accuracy of signal measurement.

In this work, the errors in the measurement of ε_2 were 2-6% for a signal measurement accuracy of 2%. The error grows with an increase in the difference $\varepsilon_2 - \varepsilon_1$. The data obtained are in agreement with other well-known data [4], within experimental error.

The determination of the thermal activity in solutions gives quantitative information about nonsteady-state concentrations in binary solutions when periodically sequential pulses are used for the measurements. Periodic rectangular electrical pulses give rise to periodic heating of the thin film in contact with the solution. A change in solution concentration changes the conditions for heat exchange with the fluid, which had an effect on the temperature of the free surface of the film recorded experimentally.

The method discussed is an extension of that presented in [3], but this method can be applied also to electrically conducting solutions.

In this case, we record the signal U_2, the value of which is determined by the thermal activity of the solution and consequently depends on its concentration. Since the pulse frequency can reach 100 Hz, the method presented offers an opportunity to follow changes in the solution concentration during quite rapid processes (chemical reactions, diffusion processes, etc.). The measurements are made in a very thin boundary layer a few microns thick.

NOTATION

ε is the thermal activity coefficient;
τ is the time;
U is the potential difference;
Fo is the Fourier number;
λ is the thermal conductivity;
a is the thermal diffusivity;
l is the film thickness;
R is the ohmic resistance;
t is the temperature;
q_0 is the heat flux.

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