METHOD OF MEASURING THE HEAT OF UNSTEADY-STATE PROCESSES

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The heat released with the passage of an electric current through an electrode-solution interface can be measured with a calorimeter in the case of a steady-state oxidation-reduction reaction at the electrode [1]. Up to the present time there exists no method permitting a direct evaluation of the heat of unsteady-state electrochemical processes, such as adsorption with a determined change in the potential. Unsteady-state conditions are also important in investigation of the heat of reactions, since they would permit finding the heat effects of individual stages taking place at different rates.

In the method described, through the boundary between a solid electrode and a solution there is passed an alternating current with the required frequency and, at the same frequency, recordings are made of the mechanical vibrations of the electrode, due to the periodic component of the thermal deformation. For absolute measurements of the heat effect, use is made of an electrode in the form of a thin layer of metal on a dielectric plate. After the main experiment, a short-circuited alternating current with a frequency twice less than the frequency of the measurement is passed along the layer of metal. The variable component of the Joule heating of the layer, arising in this case, exactly reproduces the action of the heat of reaction and, with identical amplitudes of the mechanical fluctuations of the electrode, it remains only to equate the two heats.

Results of measurements in the system $K_3Fe(CN)_6/K_4Fe(CN)_6$ at different concentrations are given in Fig. 1. The electrode was a Pt.foil with a thickness $\delta = 10\ \mu$, a length $l = 1.26$ cm, and a width $b = 0.36$ cm, welded from below to a vitreous material fused in a layer 0.2 mm thick onto a Pt plate 0.35 mm thick (Fig. 1). This same plate serves as the current lead. To this plate, and to another such plate, arranged vertically, the foil is welded by its own ends. The relatively low resistance of the current leads and their geometrical arrangement, practically, with an accuracy of better than 1%, exclude their effect on the bending vibrations of the plate, due to heating of the foil. A uniform distribution of the reaction current is attained by a parallel arrangement of the main and auxiliary electrodes, with a gap of 3 mm. The measurements were made at resonance frequencies of the electrode-piezoelement system of 660 and 3780 Hz. For example, for 0.20 M $K_3Fe(CN)_6$ + 0.20 M $K_4Fe(CN)_6$, the passage of a reaction current with a frequency of 660 Hz and an amplitude $|\Delta I_r| = 5.35 \cdot 10^{-2}$ A through the electrode-solution boundary leads to an amplitude of the voltage $|\Delta v_r| = 142\ \mu V$ in the plates of the piezoelement, clamped to the electrode. With the passage of a short-circuited current with an amplitude $|\Delta I_h| = 1.07$ A and a frequency of 330 Hz through the foil, the amplitude of the voltage in the piezoelement, recorded previously at 660 Hz, is $|\Delta v_h| = 164$ V. For 3780 Hz: $|\Delta I_r| = 2.67 \cdot 10^{-2}$ A, $|\Delta v_r| = 270\ \mu V$, $|\Delta I_h| = 0.486$ A (1890 Hz), $|\Delta v_h| = 132\ \mu V$. The heat of the electrochemical reaction is calculated by the formula:

$$W = {}^1\!/_2 (l\rho \,/\, b\delta)\,(|\Delta I_h|^2 \,/\, |\Delta I_r|)\,(|\Delta v_r| \,/\, |\Delta v_h|), \tag{1}$$

where ρ is the specific resistance of the electrode (for Pt at 20°C, $\rho = 1.07 \cdot 10^{-5}\ \Omega$-cm). Hence, at 660 Hz, W = 0.348 V = 8.02 kcal/F; at 3780 Hz, W = 0.340 V = 7.84 kcal/F. The mean value, at 0.2 and 0.3 M, 660 and 3780 Hz, is W = 0.34 V = 7.8 kcal/F, with a deviation of ± 3%.

The form of the vibrations of the electrode-piezoelement system is considerably different at different resonance frequencies. Therefore, the closeness in the values of W, found at 660 and 3780 Hz, points to the absence of distortions from the side of the instrument. The premises of the method are confirmed also by the practically complete coincidence of the resonance curves obtained with excitation of the vibrations by the reaction current (Fig. 2, a) and by the short-circuited current (Fig. 2, b). This agreement shows that the forces arising in both cases are located at exactly the same point of the system. Thanks to the small thickness of the foil in comparison to the thickness of the plate, and to the high rate of heat propagation (in the range of 1-5 kHz, it penetrates into the platinum to a depth on the order of 100 μ), the difference consists in the fact that, with reaction, the heat is evolved at the

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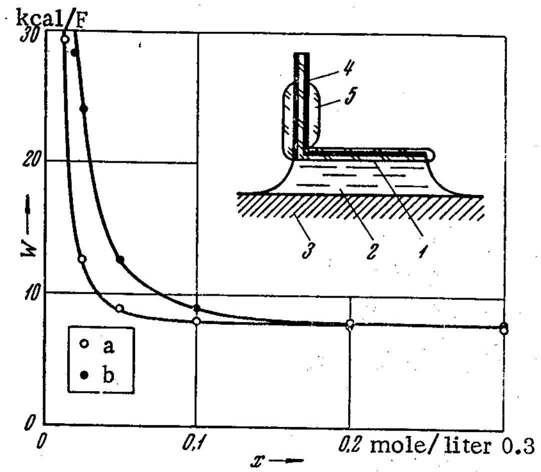

Fig. 1. Dependence of the amplitude of the fluctuations of the electrode, expressed in terms of the equivalent heat of reaction, W, on the concentration, x, for the system $xK_3Fe(CN)_6 + xK_4Fe\cdot(CN)_6$ at an equilibrium and at frequencies of the current of 600 Hz(a), 3780 Hz (b), 20°C. From above: 1) foil; 2) solution; 3) secondary electrode; 4) current leads; vitreous material.

surface of the foil, while, with a short-circuited current, it is evolved inside it to only an insignificant degree. With respect to the escape of heat into the depths of the plate (the vitreous layer inhibits this process) and into the depths of the solution (about 1%, due to the low heat conductivity of the solution), both heatings are under the same conditions. The escape of the short-circuited current is small (1%) due to the relatively high resistance of even concentrated solutions; the heat effect of the reaction due to escape of the current has a frequency twice less than the frequency of the measurement, and is not recorded. Calibration using the short-circuited current may be carried out by replacing the solution with water. The effect of Joule heating by the reaction current is completely excluded with a mean current equal to zero, since the frequency of this heating, proportional to the square of the current, is twice as great as the frequency of the measurement. In irreversible systems, in which the mean current is different from zero, the effect of Joule heating is negligibly small, since the layer of solution embraced by the oscillations of the heat flux is very small (10 μ at a frequency of 1 kHz), and the variable heat of the remaining mass of the solution does not arrive to the electrode.

To determine the sign of the heat effect, simultaneous oscillograms of the reaction current, I_r, and the vibrations of the electrode, v_r, are superposed on simultaneous oscillograms of the short-circuited current, I_h, and the corresponding vibrations of the electrode, v_h, in such a way that the vibrations of the electrode (v_r and v_h) will coincide in phase (Fig. 2c). In this case, the extrema of the sine curve of I_r are found to be located exactly opposite to zero and to the extrema of the sine curve of I_h, which has a twice greater period. To the short-circuited current, I_h, there corresponds a sinusoidal evolution of heat with a maximum rate at the extrema of I_h, regardless of their sign. In time, to these extrema there correspond maxima of the sine curve of I_r which, as established by measurement of the polarity, correspond to passage of the electrodes into the solution. Thus, reduction is accompanied by the evolution of heat, $Fe(CN)_6^{3-} + e \rightleftharpoons Fe(CN)_6^{4-} + 7.8$ kcal/F.

After the heat has been measured for one oxidation-reduction system in the required frequency range, this system can be used, by comparison, for determination of the heat in other systems. The measurements are made with an electrode located over the meniscus [2]; the electrode is made of a completely metallic plate. The distribution of the current in the electrode is not important since, with an identical arrangement of the electrodes, the distribution is identical in both systems. A system with a known heat of reaction also makes possible calibration in the investigation of the surface tension of solid electrodes [2].

With a given amplitude of the reaction current, an increase in the concentration leads to a decrease in the amplitude of the potential and, as a result, of the amplitude of the surface tension, γ [2]. In the system $K_3Fe(CN)_6/K_4Fe(CN)_6$, at concentrations of 0.30 M-0.15 M, the effect of γ is practically absent, and the whole effect is due only to the heat of reaction. This is confirmed by the lack of dependence on the concentration in the above-mentioned interval (Fig. 1). With further dilution, the amplitude of the tension $|\Delta\gamma|$ reaches a considerable level, and there is an anomalous increase in the vibration of the electrode, the more rapid the higher the frequency. Under these conditions, both effects combine. They can be separated, thanks to the rapid penetration of heat into the depths of the plate, as a result of which the phase difference between the vibrations of the electrode due to the heat and the stress, as well as the ratio of the amplitudes of the vibrations, depend on the thickness of the electrode and the frequency. The action of the thermal stresses can be expressed by an equivalent force, directed along the surface of the electrode and caused by the bending of the plate [3]

$$|\Delta\vartheta| = |\Delta\eta| P(\beta), \qquad |\Delta\eta| = \frac{\varkappa Y}{\zeta d} \frac{W}{1-\mu} \frac{|\Delta j|}{\omega},$$

where $\beta = \lambda\sqrt{\omega\zeta d / 8k}$, Δ is a symbol of the complex amplitude; ω is the angular frequency of a current with a density j; λ is the thickness of the plate of an electrode, for which: $\varkappa$ is the coefficient of linear expansion; Y is the elastic modulus; ξ is the heat capacity; d is the density; ω is the Poisson coefficient; k is the heat conductivity

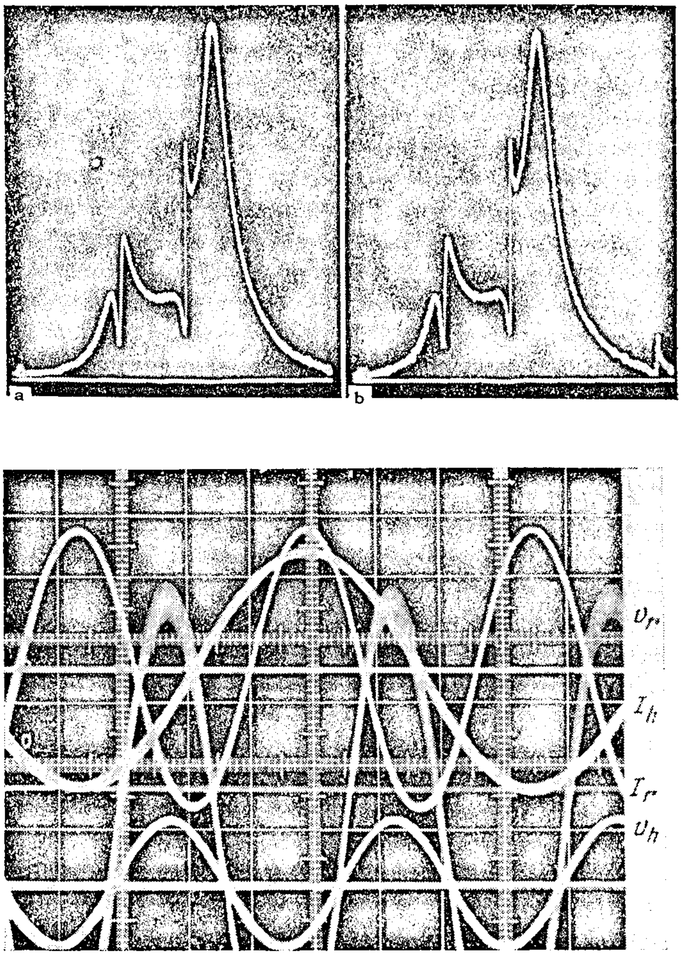

Fig. 2. Comparison of the vibrations of the electrode, v_r and v_h (frequency ν), brought about, respectively, by the reaction current, I_r, (frequency ν) and the short-circuited current, I_h (frequency $\nu/2$); a and b) resonance curves near the peak 660 Hz; a) dependence of $|\Delta v_r|$ on ν within the limits from 550 (left) to 724 Hz; b) dependence of $|\Delta v_h|$ on ν within the limits from 556 to 735 Hz; c) change in I_r, v_r, and v_h with time.

coefficient (for Pt at 20°C: $\varkappa = 0.9 \cdot 10^{-5}$ deg^{-2}; $Y = 1.7 \cdot 10^{12}$, dyn/cm; $\xi = 0.0320$, cal/(g)(deg); $d = 21.4$ g/cm^3; $\mu = 0.44$; $k = 0.165$ cal/cm · sec · deg). $P(\beta)$ is the relative level at which there is a decrease in the effect, $\Delta\vartheta$, due to propagation of heat inside the plate, $P(\infty) = 1$, $P(0) = 0$. Figure 3 gives the dependence of P on the angle (phase difference) α between the vectors $\Delta\vartheta$ and $\Delta\gamma$, the sum of which is recorded.

$$|\Delta\Theta(\beta)| = |\Delta\vartheta + \Delta\gamma| = \{|\eta|^2 P^2(\beta) + 2|\eta| P(\beta) \cos\alpha(\beta) + |\Delta\gamma|^2\}^{1/2}.$$

Measurements at two values of β (for example, in two electrodes of different thickness) are sufficient to determine the two unknowns: $\Delta\eta$ and $\Delta\gamma$.

With adsorption, $\Delta\gamma$ usually predominates over $\Delta\vartheta$; and the curve of $|\Delta\Theta| - \varphi_m$ is close to the curve of $|\Delta\gamma| - \varphi_m$, where φ_m is the mean potential of the electrode. Under these conditions, the minimum of $|\Delta\Theta|$ close to a zero value of $\Delta\gamma$ (the point at which $\Delta\gamma = 0$), is sufficiently sharp so that, in its neighborhood, it can be assumed that $\Delta\vartheta$ does not depend on φ_m. Then $|\Delta\Theta| = |\Delta\Theta| \sin\alpha$, that is, the height of the location of the minimum of the curve $|\Delta\Theta| - \varphi_m$ below the zero line is determined only by the heat.

By selection of the thickness of the electrode (the parameter β in Fig. 3) conditions can be created for measurement of the sum $\Delta\gamma + \Delta\vartheta$ or of one value of $\Delta\gamma$ only. A decrease of β weakens the effect of $\Delta\vartheta$, due to a decrease of P and an increase of the angle α between the vectors $\Delta\vartheta$ and $\Delta\gamma$. For example, $P = 0.209$ and $\alpha = 75°$ for Pt at a frequency of 1 kHz and a thickness $\lambda = 0.1$ mm ($\beta = 0.57$). For Pt in 1 N H_2SO_4, at potentials from +1.30 to 0, in normal hydrogen electrodes [2], the curve of $|\Delta\Theta| - \varphi_m$ under the above conditions may be identified with the curve of $|\Delta\gamma| - \varphi_m$, with an accuracy of 1% of the maximum value of $|\Delta\gamma|$.

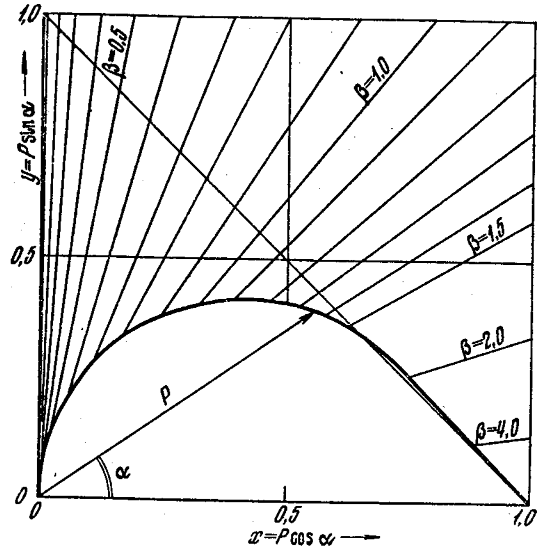

Fig. 3. Dependence of P(β) on α(β) in polar coordinates: $\beta = \lambda\sqrt{\omega\zeta d/8k}$; max $\{P \sin \alpha\} = 0{,}4172$ at $\beta = 1.13$.

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