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Various relaxation techniques are used for studying the kinetics of processes which are limited by diffusion. Among these techniques there is, in particular, the temperature jump method which usually serves to determine the rate constants of fast reactions (proton or electron transfer, hydrolysis, complex formation, etc.). Heating of $0.1 \cdot 10^6$ within 10^{-4} – 10^{-8} sec is achieved with the aid of pulse lamps, microwave generators, or lasers. The relaxation is followed by means of spectrophotometry or conductometry [1].

Presently the possibility of using the temperature-jump method in electrochemical systems is studied. It was already reported [2, 3] that a current arises in the circuit of an electrochemical cell when the working electrode is irradiated with pulses of polychromatic light with a wavelength exceeding the red limit of photoemission ($\lambda > 540 \text{ m}\mu$). In the present work, the heating was achieved by pulse (IFK-2000 lamp with an energy of 700 J and a pulse duration of 3×10^{-4} sec) or intermittent (DRSh-1000 lamp, modulation frequency $f = 22 \text{ Hz}$) irradiation of a mercury drop electrode. The measuring equipment has been described before [2, 4]. In the pulse regime, the signal $V(t) = RI(t)$ is traced with an oscilloscope using a measuring resistance R placed in series with the cell. The recording circuit during modulated irradiation enables one directly to measure the average heating current, and consists of narrow-band signal amplifier tuned to the modulation frequency and of a following synchronous detector.

The heating current is independent of wavelength and proportional to the light intensity. The peak value of the signal, V_{max} , is shown as a function of electrode potential, φ_M , in Fig. 1. The signal, which is zero at the point of zero charge (pzc) of the metal, φ_0 , increases with the distance from the pzc. It is cathodic at $\varphi_M > \varphi_0$ and anodic at $\varphi_M < \varphi_0$. Near the pzc the $V_{\text{max}}(\varphi_M)$ relation is linear. The magnitude of the effect is independent of electrolyte concentration from 1 to 10^{-3} M but decreases with further dilution. In water with a conductivity of $10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$ the effect is practically absent. With pulse irradiation one can study the kinetics (Fig. 2) of the relaxation process. With a practically linear front the rise of the signal occurs within 2×10^{-4} sec, i.e., stops already during the life of the flash. The angle between pulse front and time axis increases with the distance from the point of zero charge. The peak value of the signal at a given electrode potential is independent of R between 1 k Ω and 1 M Ω . The highest signal for ideally polarizable electrodes is about 1 mV. With R of about 1 k Ω , the decay occurs within 1.2 msec and is exponential. With R of about 1 M Ω , the decay is protracted, and this part of the curve becomes linear when represented as V against $t^{-1/2}$. During modulated irradiation a signal is observed which corresponds to an average heating current of 0.05 μA .

We use a nonstationary modification of the Gouy-Stern theory to explain the kinetic curves and the dependence of signal size V_{max} on electrode potential as shown in Figs. 1 and 2. In this theory, the distribution of ionic concentrations, flows, electric field strength, and potential is described by a self-consistent system of nonlinear differential equations in partial derivatives with the corresponding initial and boundary conditions (see, for example, [5, 6]). In [6] a method has been developed by which one can reduce the study of transient phenomena in electrochemical systems at small times to the examination of one ordinary nonlinear differential equation. With insignificant changes it can be translated to the case of temperature perturbation considered here.

Consider a closed electrical circuit consisting of an electrochemical cell (an ideally polarizable spherical electrode in the solution of a binary 1-1 electrolyte), a measuring resistance R , and an external emf source E . Let the temperature of the system begin to change according to the law $T = T(t)$ at time $t = 0$. We shall assume the

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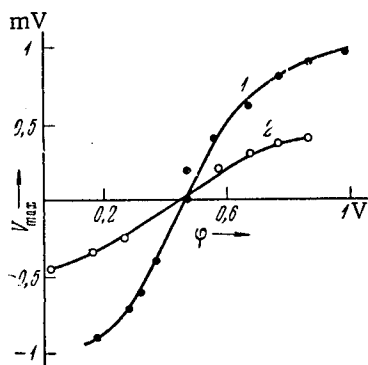


Fig. 1

Fig. 1. Dependence of $V_{\max}$ on electrode potential with $C_{H_2SO_4}$ of 0.1 (1) and $5 \cdot 10^{-5}$ N (2).

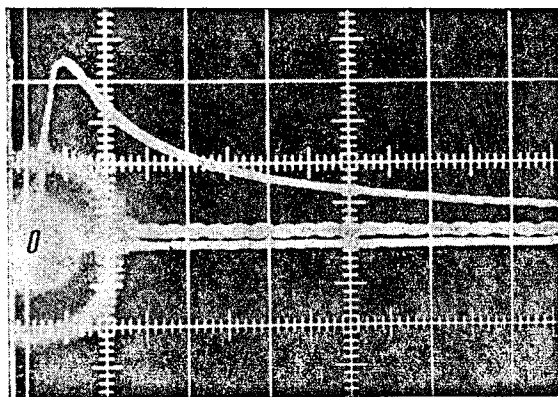


Fig. 2

Fig. 2. Oscillographic trace of the heating currents during pulse irradiation (0.1 N $HClO_4$); $\varphi = 0.0$ V (nce); horizontal scale resolution 200 $\mu\text{sec}/\text{cm}$; vertical scale resolution 500 $\mu\text{V}/\text{cm}$.

temperature field to be homogeneous; consideration in support of this approximation will be cited below. We shall examine the behavior of the system only during a time interval $t \sim L_d r_0 / (D_+ D_-)^{1/2}$, where $L_d = \epsilon_0 (kT/4\pi^2 N_0)^{1/2}$ is the Gouy length, r_0 is the electrode radius, D_+ and D_- are the ionic diffusion coefficients. It was shown in [6] that reorganization of the double layer occurs in this time interval while changes in the bulk of the solution due to diffusion and migration processes can be neglected.

Having taken advantage of the method of [6], one can readily obtain the differential equation for the total current $I(t)$:

$$(R + R_0) \frac{dI}{dt} + \left[\frac{1}{C_d} + \frac{1}{C_H} + \frac{\partial R_0}{\partial T} \dot{T} + (R + R_0) \frac{1}{\epsilon_H} \frac{\partial \epsilon_H}{\partial T} \dot{T} \right] I = \left[\frac{1}{\epsilon_H} \frac{\partial \epsilon_H}{\partial T} \varphi_{M,0} + \left(\frac{1}{\epsilon_0} \frac{\partial \epsilon_0}{\partial T} - \frac{1}{\epsilon_H} \frac{\partial \epsilon_H}{\partial T} \right) \tilde{\varphi} + \frac{k}{e} \left(1 + \frac{T}{\epsilon_0} \frac{\partial \epsilon_0}{\partial T} \right) \left(\text{th} \frac{e\tilde{\varphi}}{2kT} - \frac{e\tilde{\varphi}}{kT} \right) \right] \dot{T}, \quad (1)$$

$$I(0) = 0, \quad (2)$$

where R_0 is the resistance of the bulk solution, capacities ϵ_0 and ϵ_H are the differential and $C_d \cdot C_H$, and dielectric permittivities of the diffuse and compact part of the double layer, respectively. For a spherical electrode

$$R_0 = kT / [4\pi r_0 e^2 (D_+ + D_-) N_0], \quad (3)$$

$$C_d = L_d^{-1} r_0^2 2^{1/2} \epsilon_0 \text{ch}(e\tilde{\varphi}/2kT), \quad C_H = \epsilon_H r_0^2 / d_H, \quad (4)$$

where N_0 is the bulk electrolyte concentration, e is the electronic charge ($e > 0$), d_H is the Helmholtz layer thickness. The function of the boundary layer $\tilde{\varphi}$ in (1) and (4) is defined by the transcendental equation

$$e\tilde{\varphi}/kT + 2^{1/2} (\epsilon_0 d_H / \epsilon_H L_d) \text{sh}(e\tilde{\varphi}/2kT) + e(R + R_0)I/kT = e\varphi_{M,0}/kT, \quad (5)$$

where $\varphi_{M,0}$ is the electrode potential at $t < 0$ relative to the point of zero charge.

In deriving Eqs. (1)-(5) the simplest model was assumed for the compact part of the double layer, with linear potential profile; it was also assumed that specific adsorption is absent and that dielectric saturation can be neglected. Equations (1)-(5) describe the relaxation of the current in the time interval $t \sim L_d r_0 / (D_+ D_-)^{1/2}$, or practically in the interval $t \sim (R + R_0)C$, so long as $(R + R_0)C \ll r_0^2 / (D_+ D_-)^{1/2}$; time limitations linked to the assumption of a homogeneous temperature field can be disregarded as will be shown with the estimates cited below.

The examination of Eqs. (1)-(5) is substantially simplified when it is taken into account that the relative change in temperature is small, and the time of irradiation according to the experimental conditions is much shorter than the characteristic time $(R + R_0)C$:

$$\Delta T / T_0 \equiv [T(t) - T(0)] / T(0) \ll 1, \quad t_{\text{pulse}} \ll (R + R_0)C. \quad (6)$$

Consider the limiting cases of large and small departures of the metal potential $\varphi_{M,0}$ from the point of zero charge $\varphi_{M,0} = 0$. Let $(e|\varphi_{M,0}|/kT_0) \ll 1$, i.e., at $t < 0$ the system is close to the point of zero charge. In this case one can obtain an expression for the current from (1), (2), and (5) with (6):

$$I(t) \simeq (R + R_0)^{-1} \Omega_1(T_0) \varphi_{M,0} \exp[-t / (R + R_0)C] \Delta T(t), \quad (7)$$

where

$$C = C_d C_H / (C_d + C_H), \quad (8)$$

$$\Omega_1(T_0) = \left(1 + 2^{-1/2} \frac{\varepsilon_H L_d}{\varepsilon_0 d_H}\right)^{-1} \left[\frac{1}{\varepsilon_H} \frac{\partial \varepsilon_H}{\partial T} + 2^{-1/2} \frac{\varepsilon_H L_d}{\varepsilon_0 d_H} \left(\frac{1}{\varepsilon_0} \frac{\partial \varepsilon_0}{\partial T} - \frac{1}{T_0} \right) \right], \quad (9)$$

and where, in (7)-(9), all values depending on T are taken at $T = T_0$, while the capacity C_d is defined by (4) at $\tilde{\varphi} = 0$.

Far from the point of zero charge $(e|\varphi_{M,0}|/kT_0 \gg 1)$, it follows from (5) and the first inequality of (6) that $\tilde{\varphi}$ depends little on I and t . Therefore, the parameters R_0 , C_d , C_H , $\tilde{\varphi}$, and T in Eq. (1) can be taken as constant, while only terms with T are retained; Eq. (1) itself then linearizes, and its solution has the form

$$I(t) \simeq (R + R_0)^{-1} \Omega_2(T_0, \varphi_{M,0}) \varphi_{M,0} \exp[-t / (R + R_0)C_H] \Delta T(t), \quad (10)$$

where

$$\Omega_2(T_0, \varphi_{M,0}) = \left[\frac{1}{\varepsilon_H} \frac{\partial \varepsilon_H}{\partial T} + \frac{k}{e \varphi_{M,0}} \left(1 + \frac{T_0}{\varepsilon_0} \frac{\partial \varepsilon_0}{\partial T} \right) - \frac{2k}{e|\varphi_{M,0}|} \left(1 + \frac{T_0}{\varepsilon_H} \frac{\partial \varepsilon_H}{\partial T} \right) \ln \left(\frac{\varepsilon_H L_d e|\varphi_{M,0}|}{\varepsilon_0 d_H k T_0} \right) \right], \quad (11)$$

and where, as in (7)-(9), all quantities depending on T are taken at $T = T_0$. Since the temperature maximum is reached at $0 < t < t_{\text{pulse}}$, one can assume with a sufficient degree of accuracy that

$$I_{\text{max}} \simeq \begin{cases} (R + R_0)^{-1} \Omega_1 \varphi_{M,0} \Delta T_{\text{max}}, & \text{at } e|\varphi_{M,0}|/kT_0 \ll 1, \\ (R + R_0)^{-1} \Omega_2 \varphi_{M,0} \Delta T_{\text{max}}, & \text{at } e|\varphi_{M,0}|/kT_0 \gg 1. \end{cases} \quad (12)$$

In deducing Eq. (1) for the current $I(t)$, the temperature field was assumed to be homogeneous. One must examine the subsidiary problem of thermal conductivity in order to justify such a simplifying assumption. Two cases were considered, because we do not know the distribution of heat sources: 1) the heat sources are localized at the surface of the working electrode, 2) the heat sources are distributed uniformly throughout a certain volume of solution around the electrode. In the first case one can assume the temperature field to be homogeneous in a spherical layer with a thickness of about L_d near the electrode surface during the time interval $L_d^2/a_1^2 \ll t \ll r_0^2/a_2^2$ (where a_1^2 and a_2^2 are the coefficients of thermal conductivity of solution and metal, respectively), and the curvature of the electrode surface can be neglected in the calculations. In the second case the limitation $t \gg L_d^2/a_1^2$ is lifted. With $a_1^2 \sim 10^{-3} \text{ cm}^2/\text{sec}$, $a_2^2 \sim 4 \times 10^{-2} \text{ cm}^2/\text{sec}$, $r_0 \sim 10^{-1} \text{ cm}$, and $L_d \sim 10^{-6} \text{ cm}$, we obtain a numerical estimate of $10^{-9} \text{ sec} \ll t \ll 10^{-1} \text{ sec}$. On the other hand, a detailed analysis of the initial partial differential shows that the effect discussed is produced by a change in temperature only in the space-charge region. The temperature distribution outside the double layer, therefore, has no great importance.

It can readily be verified that the theory presented qualitatively explains the complex of experimental facts. In fact, the dependence of $V_{\text{max}} = RI_{\text{max}}$ on $\varphi_{M,0}$ according to (12) coincides with that shown in Fig. 1. The kinetic curves (7) and (9) correspond to Fig. 2. With $R \gg R_0 \sim 10^{-2} - 1 \text{ kohm}$ and $N_0 \sim 1 \times 10^{-3} \text{ M}$, the magnitude of the signal $V(t)$ does not depend on R according to (7) and (9), i.e., the cell works as a voltage generator. An explanation is obtained for the dependence of the asymptotic behavior of $I(t)$ on the measuring resistance R . With $R \approx 1 \text{ k}\Omega$ and $C \approx 7 \mu\text{F}$ we have $(R + R_0)C \approx 10^{-3} \text{ sec}$; according to (7) and (9), the asymptotic behavior of $I(t)$ must be exponential. With $R \approx 1 \text{ M}\Omega$, the characteristic time $(R + R_0)C \approx 1 \text{ sec}$, i.e., the asymptotic behavior of the function $I(t)$ must coincide with that of $\Delta T(t)$. Within the double layer, the latter is of the form: $\Delta T(t) \sim t^{-1/2}$ at $t \gg t_{\text{pulse}}$. Finally, Eq. (12) correctly describes the concentration dependence of the magnitude of the effect, which is easy to see upon exposing the dependence of R_0 , Ω_1 , and Ω_2 on N_0 . For a quantitative comparison between

theory and experiment one must know $\frac{1}{\varepsilon_H} \frac{\partial \varepsilon_H}{\partial T}$ and $\frac{1}{\varepsilon_0} \frac{\partial \varepsilon_0}{\partial T}$; according to the experimental data of Grahame [7, 8],

$\epsilon_0=80$, $\epsilon_2=15$, $\partial\epsilon_0/\partial T \approx \partial\epsilon_H/\partial T \approx 0.3$, which leads to a peak value of signal magnitude (in the voltage-generator regime) of $V_{\max} \approx 1$ mV at $\varphi_{M,0} \sim 100$ mV and $\Delta T_{\max} \sim 1^\circ\text{C}$ (which corresponds to the energy of irradiated light absorbed by the electrode).

In conclusion we remark that the theory developed above can directly be translated to the case of a working electrode of arbitrary shape; one must only make the corresponding changes in the values of R_0 , C_d , and C_H in Eqs. (1)-(4).

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