CONTRIBUTION TO THE STUDY OF THE KINETICS OF REDOX REACTIONS PROCEEDING *via* ELECTRODE PROCESSES. THEORY OF THE METHOD

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A system of differential kinetic equations is derived for the redox reaction $n_2\ \mathrm{Ox}_1 + n_1\ \mathrm{Red}_2 \rightleftharpoons n_1\ \mathrm{Ox}_2 + n_2\ \mathrm{Red}_1$, proceeding only through electrode processes. Its numerical solution is compared with a simplified analytical solution which leads to linearization of the relations between measurable quantities and thus verification of the kinetic model used on real redox reactions.

If the electron exchange between species Ox_1 and Red_2 does not occur because they do not react chemically with each other or because they are in separate solutions connected by a salt bridge or diaphragm and provided with short-circuited platinum electrodes, the reaction between species Ox_1 and Red_2 can take place *via* electrode processes. The kinetics of similar processes is important, *e.g.*, in developing the latent image[1], in amalgam decomposition during manufacture of soda lye[2], in corrosion[3], and can serve as a model of certain enzymatic reactions[4].

The aim of the present work was to find an analytical expression for the reaction time in dependence on kinetic parameters of the electrode processes of both redox systems, concentrations, electrical resistance, and reactor parameters, and to use its linearized form as a testing criterion for the kinetics of the reaction.

THEORETICAL

If the reaction between two redox systems, $\mathrm{n_2Ox_1 + n_1Red_2 \rightarrow n_1Ox_2 + n_2Red_1}$, is realized by means of electrodes (Fig. 1), the increases and decreases of the reaction components are related to the current I_j equal to the net production of a positive charge per unit time, which is in turn equal to the difference between partial cathodic and anodic currents. For the positive electrode (potential E_1), the current I_j consists of the charging current necessary to change the electrode potential and the current, I, flowing through the outer circuit. For the negative electrode (potential E_2), the situation is analogous except for that the current I is reversed. By expressing the partial cathodic and anodic currents from the known equations of the theory of electrode processes[5], we obtain the kinetic equations of the considered process in the form $(j = 1, 2)$

$$I_j = (-1)^{j+1} I + A_j C_j \frac{dE_j}{dt} = -\frac{d[Ox_j]}{dt} V_j n_j F = \frac{d[Red_j]}{dt} V_j n_j F =$$

$$= A_j n_j F(k_{jRed}[Ox_j] - k_{jOx}[Red_j]) , \qquad (1a)$$

where

$$k_{jRed} = k_j^0 \exp\left[-(E_j - E_{0j}) \alpha_j n_j F/RT\right] ,$$

$$k_{jOx} = k_j^0 \exp\left[(E_j - E_{0j})(1 - \alpha_j) n_j F/RT\right] , \qquad (1b)$$

k_j^0 denotes formal rate constant of the electrode reaction for the j-th redox system, n_j the corresponding number of transferred electrons, α_j charge transfer coefficient, A_j surface area of electrode, C_j its specific capacity, and V_j volume of electrolyte in the electrode compartment. The concentrations $[Ox_j]$ and $[Red_j]$ at the electrode surface are on the assumption of an intense stirring equal to those in the bulk of the solution.

By expressing the actual concentrations as functions of the initial concentrations and their decrements

$$[Ox_1] = a_1 - x , \quad [Red_1] = b_1 + x , \quad [Ox_2] = a_2 + y , \quad [Red_2] = b_2 - y \qquad (2)$$

and considering Ohm's law, $I = (E_1 - E_2)/R$, where $R = R_v + R_i$ (Fig. 1) we obtain from $(1a)$ a system of four differential equations for the unknown electrode potentials E_1 and E_2 and the decrements x and y:

$$A_1 C_1 (dE_1/dt) = A_1 n_1 F[k_{1Red}(a_1 - x) - k_{1Ox}(b_1 + x)] - (E_1 - E_2)/R , \qquad (3a)$$

$$A_2 C_2 (dE_2/dt) = A_2 n_2 F[k_{2Red}(a_2 + y) - k_{2Ox}(b_2 - y)] + (E_1 - E_2)/R , \qquad (3b)$$

$$n_1 V_1 F(dx/dt) = A_1 n_1 F[k_{1Red}(a_1 - x) - k_{1Ox}(b_1 + x)] , \qquad (3c)$$

$$-n_2 V_2 F(dy/dt) = A_2 n_2 F[k_{2Red}(a_2 + y) - k_{2Ox}(b_2 - y)] . \qquad (3d)$$

Generally, this system cannot be solved in a closed form. It is of interest to find out the relation between the numerical solution for given parameter values and the analytical solution obtained under simplifying assumptions. The numerical solution was carried out by the Runge–Kutta method with variable step for 132 combinations of the parametrs $(R, a_1, a_1/b_2, V, A, \alpha_1, \alpha_2, k_1^0$, and $C)$ on a Hewlett-Packard 2116C computer. A set of E–t curves thus calculated for various ratios of the initial concentrations is shown in Fig. 2.

Analytical solution

The system of Eqs (*3a–d*) can be substantially simplified by setting the capacities C_j equal to zero; then Eqs (*3a,c*) and similarly (*3b,d*) become identical and the system is reduced to a single differential equation, *e.g.* (*3c*), where the coefficients $k_{1\mathrm{Red}}$ and $k_{1\mathrm{Ox}}$ are functions of the potential E_1. Further, since $I_1 = -I_2 = I$, we can express each actual concentration, *e.g.* $[\mathrm{Ox}_1]$, as function of the potentials E_1 and E_2

$$[\mathrm{Ox}_1] = \frac{n_1A_1k_{1\mathrm{Ox}}(a_1 + b_1) + n_2A_2[k_{2\mathrm{Ox}}(b_2 - a_1n_1V_1/n_2V_2) - k_{2\mathrm{Red}}(a_2 + a_1n_1V_1/n_2V_2)]}{n_1A_1(k_{1\mathrm{Ox}} + k_{1\mathrm{Red}}) - n_2A_2(n_1V_1/b_2V_2)(k_{2\mathrm{Ox}} + k_{2\mathrm{Red}})}\,. \tag{4}$$

On substituting this expression into Eq. (*3c*) we obtain a differential equation for E_1 and E_2, which together with Ohm's law $(E_1 - E_2)/R = I$ forms a system of two equations for two unknowns; however, the solution cannot be obtained in a closed form. The situation does not improve by setting $R = 0$, $E_1 = E_2$. A simplifying

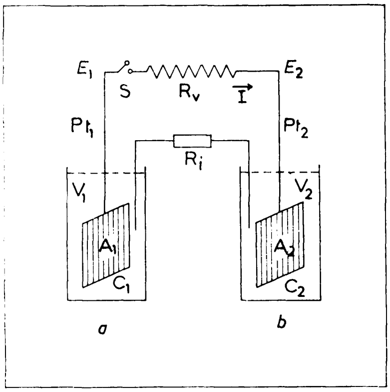

FIG. 1

Scheme of the model electrode system. E_1, E_2 potential; S switch; R_i internal resistance; R_v external resistance; I current; Pt_1, Pt_2 platinum electrodes of large surface area; A_1, A_2 electrode surface area; C_1, C_2 electrode capacity; V_1, V_2 solution volume $a\,\mathrm{Ox}_1 + n_1\,e^- \rightleftarrows \mathrm{Red}_1$, $b\,\mathrm{Red}_2 - n_2\,e^- \rightleftarrows \mathrm{Ox}_2$

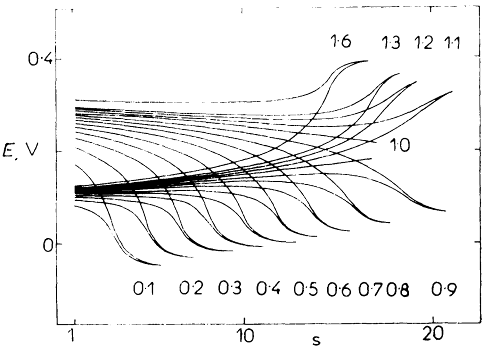

FIG. 2

Set of E–t curves with parameter a_1/b_2 obtained by solving the system of Eqs (*3a–d*). Numbers denote the values of a_1/b_2. Parameters: $C_1 = C_2 = 10^{-4}$ F; $R = 10\,\Omega$; $b_2 = 2 \cdot 10^{-7}$ mol cm^{-3}; $\alpha_1 = \alpha_2 = 0{\cdot}5$; $V_1 = V_2 = 10$ cm^3; $A_1 = A_2 = 100$ cm^2; $k_1^0 = k_2^0 = 10^{-3}$ cm s^{-1}; $E_{01} = 0{\cdot}4$ V; $E_{02} = 0{\cdot}0$ V; $T = 302$ K; $a_2 = b_1 = 0$. Decreasing curves corrrespond to E_1–t dependence, increasing to E_2–t

assumption is that the back reaction $n_2\,\mathrm{Red}_1 + n_1\,\mathrm{Ox}_2 \rightarrow n_2\,\mathrm{Ox}_1 + n_1\,\mathrm{Red}_2$ does not proceed, *i.e.* the terms containing $k_{1\mathrm{Ox}}$ and $k_{2\mathrm{Red}}$ are cancelled. Thus, Eq. (*4*) is simplified and Eq. (*3c*) takes the form

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \frac{RT}{F[\alpha_1 n_1 + (1 - \alpha_2)\, n_2]} \left(\frac{A_2}{V_2} k_{2\mathrm{Ox}} - \frac{A_1}{V_1} k_{1\mathrm{Red}} \right). \qquad (5a)$$

On substituting Eqs (*1b*) for $k_{2\mathrm{Ox}}$ and $k_{1\mathrm{Red}}$ and introducing the parameters

$$Q = \frac{RTA_2 \exp\left[-(1 - \alpha_2)\, n_2 FE_{02}/RT\right] k_2^0}{F[\alpha_1 n_1 + (1 - \alpha_2)\, n_2]\, V_2}, \quad W = \frac{RTA_1 \exp\left(\alpha_1 n_1 FE_{01}/RT\right) k_1^0}{F[\alpha_1 n_1 + (1 - \alpha_2)\, n_2]\, V_1}, \qquad (5b,c)$$

we can separate the variables in Eq. (*5a*) and integrate in a closed form on the assumption that $Fn_2(1 - \alpha_2)/RT = Fn_1\alpha_1/RT = m$. The solution with respect to the initial condition $t = 0$, $E = E(0)$ is

$$t = \frac{1}{2m\sqrt{(QW)}} \ln \left[\frac{-1 + \sqrt{(Q/W)} \exp(mE)}{-1 - \sqrt{(Q/W)} \exp(mE)} \cdot \frac{-1 - \sqrt{(Q/W)} \exp[mE(0)]}{-1 + \sqrt{(Q/W)} \exp[mE(0)]} \right]. \qquad (5d)$$

This is in substance the equation of the discharge curve in the simplified case.

It is interesting to determine the reaction time, t_∞, necessary for the defficient reaction component to be entirely exhausted. This time is, in contrast to homogeneoue reaction kinetics, not infinitely long, but corresponds to the value from Eq. (*5d*)

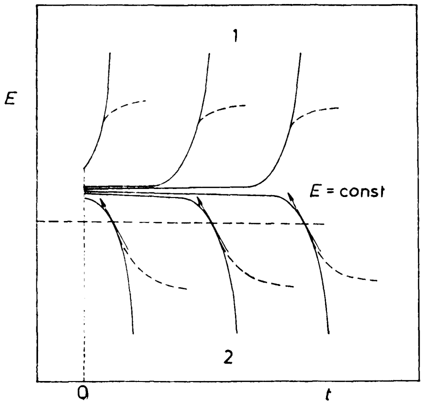

FIG. 3

Approximate course of E–t curves for various values of $E(0)$. Dashed curves were calculated with regard to back reactions for $E \to \infty$ (exhaustion of Red_2) or $E \to -\infty$ (exhaustion of Ox_1). Thus,

$$t_\infty = \frac{1}{2m\sqrt{(QW)}} \ln \left[\frac{-1 - \sqrt{(Q/W)} \exp\left[mE(0)\right]}{-1 + \sqrt{(Q/W)} \exp\left[mE(0)\right]} (\pm 1) \right] \qquad (6a)$$

and Eq. (*5d*) can be rewritten in the form

$$t_\infty - t = \frac{1}{2m\sqrt{(QW)}} \ln \left[\frac{-1 - \sqrt{(Q/W)} \exp(mE)}{-1 + \sqrt{(Q/W)} \exp(mE)} (\pm 1) \right]. \qquad (6b)$$

The positive sign applies to the decreasing E–t curve, negative for increasing. A set of E–t curves thus calculated is shown in Fig. 3. They can be brought to coincidence by shifting along the time axis: each shorter thus becomes a part of a longer one; its beginning corresponds to the value of $E(0)$, for which we obtain from Eq. (*1a*) (assuming $C_j = 0$, $R = 0$)

$$E(0) = \boldsymbol{F} \frac{\alpha_1 n_1 E_{01} + (1 - \alpha_2) n_2 E_{02}}{\boldsymbol{RT}\theta} + \frac{1}{\theta} \ln \frac{n_1 A_1 k_1^0 a_1}{n_2 A_2 k_2^0 b_2} = \frac{1}{\theta} \ln \frac{W n_1 V_1 a_1}{Q n_2 V_2 b_2}, \qquad (7a)$$

where $\theta = \boldsymbol{F}[\alpha_1 n_1 + (1 - \alpha_2) n_2]/\boldsymbol{RT}$. By introducing Eq. (*7a*) into (*6a*) we obtain the reaction time

$$t_\infty = \frac{\theta}{2m} \left(\frac{A_2 A_1}{V_2 V_1} k_2^0 k_1^0 \right)^{-m/\theta} \exp\left[E_{02} n_2 (1 - \alpha_2) + E_{01} \alpha_1 n_1\right] \frac{m}{\theta} \,.$$

$$. \ln \frac{1 + (n_1 V_1 a_1 / n_2 V_2 b_2)^{m/\theta}}{1 - (n_1 V_1 a_1 / n_2 V_2 b_2)^{m/\theta}} \,. \qquad (7b)$$

To generalize this result for the case $\alpha_1 n_1 \neq (1 - \alpha_2) n_2$, m must be chosen so as to obtain agreement with a special solution of Eq. (*5a*)* valid for any values of α_1 and α_2. If the form Red_2 is in excess, we choose $m = \alpha_1 n_1 \boldsymbol{F}/\boldsymbol{RT}$, and if the form Ox_1 is in excess, $m = n_2 (1 - \alpha_2) \boldsymbol{F}/\boldsymbol{RT}$. In the case where $n_1 V_1 a_1 / n_2 V_2 b_2 \ll 1$, or $n_2 V_2 b_2 / n_1 V_1 a_1 \ll 1$, the logarithmic term in Eq. (*7b*) can be expanded in series; we set $\varrho_1 = \alpha_1 n_1 / [\alpha_1 n_1 + (1 - \alpha_2) n_2]$, $\varrho_2 = (1 - \alpha_2) n_2 / [\alpha_1 n_1 + (1 - \alpha_2) n_2]$, and obtain respectively for the cases of decreasing and increasing E–t curve

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* Eq. (*5a*) can be rearranged by neglecting the back reaction and assuming $I_1 = -I_2$ to obtain $dE/dt = (k_{20x} A_2 / V_2 \theta)(1 - [Red_2]/[Ox_1])$ or analogously $dE/dt = (k_{1Red} A_1 / / V_1 \theta([Ox_1]/[Red_2] - 1)$. On the assumption that $[Ox_1]/[Red_2] \leqq a_1/b_2 \ll 1$ or $[Red_2]/[Ox_1] \leqq \leqq b_2/a_1 \ll 1$, the concentration ratio can be neglected against 1 and the equation can be integrated for any values of α_1 or α_2.

$$t_\infty = \frac{1}{\varrho_1}\exp\left[\left(E_{02} - E_{01}\right)\frac{\alpha_1 n_1 \varrho_2 F}{RT}\right]\left(\frac{A_2}{V_2}k_2^0\right)^{-\varrho_1}\left(\frac{A_1}{V_1}k_1^0\right)^{-\varrho_2}\left(\frac{n_1 V_1 a_1}{n_2 V_2 b_2}\right)^{\varrho_1} =$$

$$= \frac{V_1}{k_1^0 A_1 \varrho_1}\exp\left[\frac{\alpha_1 n_1 F}{RT}\left(E(0) - E_{01}\right)\right], \qquad (8a)$$

$$t_\infty = \frac{1}{\varrho_2}\exp\left[\left(E_{02} - E_{01}\right)\frac{\alpha_1 n_1 \varrho_2 F}{RT}\right]\left(\frac{A_2}{V_2}k_2^0\right)^{-\varrho_1}\left(\frac{A_1}{V_1}k_1^0\right)^{-\varrho_2}\left(\frac{n_2 V_2 b_2}{n_1 V_1 a_1}\right)^{\varrho_2} =$$

$$= \frac{V_2}{k_2^0 A_2 \varrho_2}\exp\left[-\frac{\left(1 - \alpha_2\right) n_2 F}{RT}\left(E(0) - E_{02}\right)\right]. \qquad (8b)$$

Reaction Time at Nonzero Resistance

It is seen from Eqs (*8a,b*) that many parameters influencing the value of t_∞ (*e.g.* starting concentration, standard redox potentials) are involved in a single quantity, *viz.* $E(0)$. Since the initial potential depends on the resistance, we may assume that the dependence of t_∞ on R will be involved in the quantity $E(0, R)$, *i.e.* in the initial potential at a given resistance. Since at nonzero resistance $E_1 \neq E_2$, we set $E(0) = E_1(0, R)$ in Eq. (*8a*) and $E(0) = E_2(0, R)$ in (*8b*). These assumptions were verified on theoretical E_1–t curves obtained by numerical solution of the system of Eqs (*3a–d*) at various resistances R, coefficients α, and initial concentrations; the values of $\log t_\infty$ and $E_1(0, R)$ so obtained and the values of $E_1(0, R)$ calculated from the approximate equations (Fig. 4) satisfy the linear relation corresponding to the equation

$$t_\infty = \frac{V_1}{A_1 k_1^0 \varkappa}\exp\left[\frac{\alpha_1 n_1 F}{RT}\left(E_1(0, R) - E_{01}\right)\right], \qquad (9)$$

which is analogous to (*8a*); the factor $\varkappa$ is equal to ϱ_1 only for low resistances ($R \leqq 10\,\Omega$) and low values of α_1($\alpha_1 < 0{\cdot}3$), otherwise $\varkappa = 0{\cdot}96$. This weak dependence of $\varkappa$ on α_1 and R in the region of low resistances causes deviations from the linear course, denoted by dashed curve in Fig. 4.

To obtain an analytical expression for $E_1(0, R)$ and $E_2(0, R)$, we use (for $C_j = 0$) the equality $I_1 = -I_2$ (see Eq. (*1a*)) for the initial concentrations and Ohm's law at the beginning of the reaction:

$$n_1 A_1 F k_1^0 \exp\left[-\frac{\alpha_1 n_1 F}{RT}\left(E_1(0, R) - E_{01}\right)\right] a_1 =$$

$$= n_2 A_2 F k_2^0 \exp\left[\left(1 - \alpha_2\right)\frac{n_2 F}{RT}\left(E_2(0, R) - E_{02}\right)\right] b_2 = I(0, R), \qquad (10a)$$

$$E_1(0, R) - E_2(0, R) = R \,.\, I(0, R)\,. \tag{10b}$$

The resistance R causes a shift of the initial potentials with respect to $E(0)$ towards the corresponding equilibrium values. Thus,

$$E_1(0, R) = E(0) + X\,, \quad E_2(0, R) = E(0) - Y\,. \tag{10c}$$

On introducing these relations into Eqs (*10a,b*) we obtain

$$n_1 A_1 F k_1^0 \exp\left[-\frac{\alpha_1 n_1 F}{RT}\left(E(0) - E_{01}\right)\right] \exp\left(-\frac{\alpha_1 n_1 F}{RT} X\right) a_1 =$$

$$= n_2 A_2 F k_2^0 \exp\left[\left(1 - \alpha_2\right)\frac{n_2 F}{RT}\left(E(0) - E_{02}\right)\right] b_2 \exp\left(-\frac{\left(1 - \alpha_2\right) n_2 F}{RT} Y\right), \tag{11a}$$

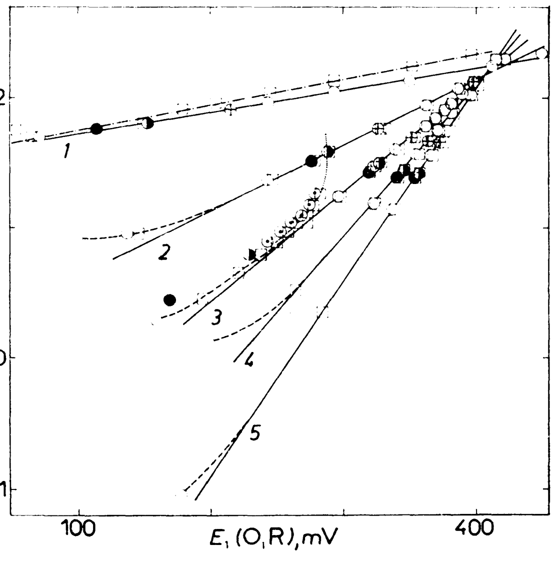

FIG. 4

Verification of the linear form of Eq. (*9*). Values of t_∞ were determined from E_1–t curves obtained by numerical integration of Eqs (*3a—d*); the point corresponding to 1/4 of the height of the E_1–t curve was used. Values of $E_1(0, R)$ were determined both from the E_1–t curves and from the solution of Eqs (*10a,b*) (points □). $R = 0, 10, 50, 100$—1 000 (at 100 Ω step), 1 500, and 2 000 Ω; $a_1 = 4 \,.\, 10^{-5}$ mol dm^{-3}, $a_1/b_2 = 0{\cdot}1$ (points ●), $a_1/b_2 = 0{\cdot}2$ (○), $a_1/b_2 = 0{\cdot}3$ (◑); $a_1 = 8 \,.\, 10^{-5}$ mol dm^{-3}, $a_1/b_2 = 0{\cdot}2$ (⊕); dotted line (⊙) $a_1 = 4 \,.\, 10^{-5}$ mol dm^{-3}, $a_1/b_2 = 0{\cdot}4$—$0{\cdot}9$ (at 0·1 step); parameter α: *1* 0·1; *2* 0·3; *3* 0·5; *4* 0·7; *5* 0·9. See Fig. 2 for other parameters

$$X + Y = Rn_1A_1\boldsymbol{F}k_1^0a_1 \exp\left[-\frac{\alpha_1n_1\boldsymbol{F}}{\boldsymbol{R}T}(E(0) - E_{01})\right] \exp\left(-\frac{\alpha_1n_1\boldsymbol{F}}{\boldsymbol{R}T}X\right). \quad (11b)$$

Since at zero resistance and capacity the initial concentrations must satisfy the condition $n_1A_1\boldsymbol{F}k_{1\mathrm{Red}}a_1 = n_2A_2\boldsymbol{F}k_{2\mathrm{Ox}}b_2$, Eq. (*11a*) is reduced to

$$\alpha_1n_1X = (1 - \alpha_2)\,n_2Y \quad (11c)$$

which together with Eq. (*11b*) forms a system of two equations for two unknowns, X and Y. On eliminating Y and introducing

$$\xi = XRa_1\mathfrak{R}_{1\mathrm{Red}}\varrho_2\,, \quad \eta = (\alpha_1n_1\boldsymbol{F}/\boldsymbol{R}T)\,\varrho_2\mathfrak{R}_{1\mathrm{Red}}a_1R\,, \quad \mathfrak{R}_{1\mathrm{Red}} = n_1A_1\boldsymbol{F}k_{1\mathrm{Red}}$$

we obtain

$$\xi = \exp(-\eta\xi)\,. \quad (12a)$$

Now, we define a new function $u = K(z)$ so that $K(z)$ is the solution of the equation $u = \exp(-zu)$. Thus,

$$\ln K(z) = -zK(z)\,. \quad (12b)$$

Eqs (*10c*) can hence be rewritten in the form

$$E_1(0, R) = E(0) - \frac{\boldsymbol{R}T}{\alpha_1n_1\boldsymbol{F}}\ln K(\eta)\,, \quad E_2(0, R) = E(0) + \frac{\boldsymbol{R}T}{(1 - \alpha_2)\,n_2\boldsymbol{F}}\ln K(\eta)\,, \quad (12c)$$

where use was made of the relation $\xi = K(\eta)$, and Eq. (*9*) for t_∞ can be rewritten as

$$t_\infty = \frac{V_1}{A_1k_1^0\varkappa}\exp\left[\frac{\alpha_1n_1\boldsymbol{F}}{\boldsymbol{R}T}(E(0) - E_{01})\right]\frac{1}{K(\eta)}\,, \quad (13a)$$

$$\ln t_\infty = \ln\frac{V_1}{A_1k_1^0\varkappa} + \frac{\alpha_1n_1\boldsymbol{F}}{\boldsymbol{R}T}(E(0) - E_{01}) + \eta\,K(\eta)\,. \quad (13b)$$

We can eliminate $K(\eta)$ from Eqs (*13a,b*), use the definition of η and Eq. (*7a*) to obtain

$$\ln t_\infty = \ln\left[\frac{V_1n_1\varkappa^{-1}}{(n_1A_1k_1^0)^{\varrho_2}\,(n_2A_2k_2^0)^{\varrho_1}}\left(\frac{a_1}{b_2}\right)^{\varrho_1}\right] + \frac{\alpha_1n_1\boldsymbol{F}}{\boldsymbol{R}T}\varrho_2(E_{02} - E_{01}) +$$

$$+ \frac{\alpha_1n_1\boldsymbol{F}}{\boldsymbol{R}T}\varrho_2\frac{V_1n_1\boldsymbol{F}}{\varkappa}\frac{a_1R}{t_\infty}\,. \quad (14)$$

Note: The factor $\varkappa$ can be interpreted as the ratio of the mean current $\bar{I}$ to its initial value $I(0, R)$. The latter is given as $I(0, R) = a_1 n_1 A_1 F k_1^0 \,.\, \exp\left[-\alpha_1 n_1 F(E(0) - E_{01})/RT\right] K(\eta)$, which follows from Eq. (*10a, 12a*). The mean value $\bar{I}$ is calculated from the total charge corresponding to the form Ox_1, $q = n_1 F a_1 V_1 = \bar{I} t_\infty$. From this and Eq. (*13a*) we obtain $\bar{I}/I(0, R) = \varkappa$.

TABLE I

Ratio of slopes of straight lines according to accurate (numerical) and approximate solutions

$\ln t_\infty \sim R/t_\infty$			$\ln t_\infty \sim a_1/t_\infty$		
Numerical solution					
4·00	2·00	2·00	2·00	1·33	1·50
Approximate solution					
4·00	2·00	2·00	2·00	1·33	1·51

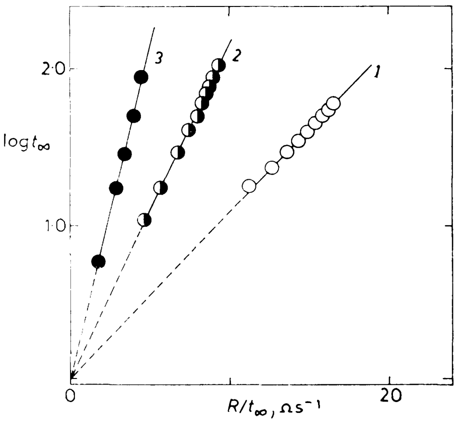

FIG. 5

Test of Eq. (*14*) with variable resistance. Value of R in the interval 50—1 000 Ω. Reaction time t_∞ was determined from E_1–t curves obtained by solving Eqs (*3a*—*d*) on a computer. Initial concentration of the oxidant a_1: *1* 2 . 10^{-5} mol dm^{-3}; *2* 4 . 10^{-5} mol dm^{-3}; *3* 8 . 10^{-5} mol dm^{-3}. Theoretical value of the abscissa −0·016; $C_1 = C_2 = 10^{-5}$ F. See Fig. 2 for other parameters

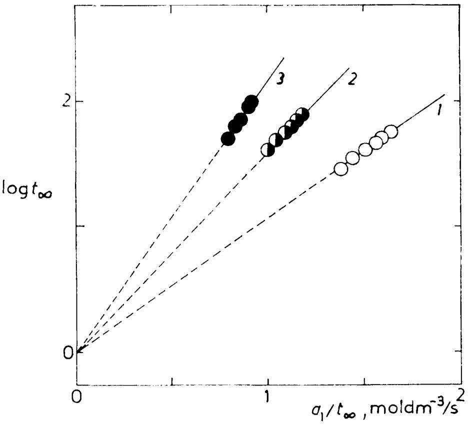

FIG. 6

Test of Eq. (*14*) with variable initial concentration of oxidant in the interval 4 . 10^{-5} to 9 . 10^{-5} mol dm^{-3}. Values of reaction time t_∞ were determined from E_1–t curves obtained by solving Eqs (3*a*—*d*) on a computer. Values of R: *1* 200 Ω; *2* 300 Ω; *3* 400 Ω. $C_1 = C_2 = 10^{-5}$ F, theoretical value of the abscissa −0·016, See Fig. 2 for other parameters

Equation (14) *as a Testing Criterion*

According to Eq. (*14*), a plot of ln t_∞ against R/t_∞ (at variable resistance) or ln t_∞ against a_1/t_∞ at variable initial concentration of Ox_1 and constant ratio of a_1/b_2 and other parameters should give a straight line provided that the simplifying assumptions are fulfilled, *i.e.* practically $n_1V_1a_1/n_2V_2b_2 \leqq 0{\cdot}5$. The specific capacity of the electrodes plays no role within the range of usual values. If the volume is the only variable, a plot of t_∞ against V_1 is according to Eq. (*13a*) a straight line passing through the origin of coordinates. The dependence of t_∞ on the electrode surface areas is more complicated. If $A_1 = A_2 = A$, which is variable, then a plot of ln $(t_\infty A)$ against $1/t_\infty$ should be a straight line. If only the surface area of one electrode changes, *e.g.* A_1, then a plot of ln $(t_\infty A_1)$ against $1/t_\infty$ should be a straight line.

These predictions, derived from the simplified kinetic equations, were tested on theoretical *E–t* curves calculated numerically from the nonsimplified system of equations (*3a–d*) with various parameter values. Illustrative results ar shown in Figs 5 and 6 and in Table I. Eq. (*14*) is in good agreement with the numerical solution of the mentioned system, hence it can be used in its linearized form as a testing criterion for the applicability of Eqs (*3a–d*) in the analysis of experimental data related to reactions in redox systems, as wll be shown in a subsequent communication.

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