

CONTRIBUTION TO THE STUDY OF THE KINETICS
OF REDOX REACTIONS PROCEEDING *via* ELECTRODE PROCESSES:
REACTIONS WITH TWO-ELECTRON TRANSFER

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The author studied the kinetics of redox reactions of the type $n_2\text{Ox}_1 + n_1\text{Red}_2 \rightleftharpoons n_1\text{Ox}_2 + n_2\text{Red}_1$ proceeding *via* electrodes, for the case of two-electron redox systems. The dependence of the reaction time on experimental parameters (resistance, concentration, and volume of reactants) was studied on two model reactions, and the theory was verified.

A theoretical equation for the reaction time t_∞ of a redox reaction proceeding *via* electrode processes was derived in the preceding communication¹ in the form

$$t_\infty = \frac{V_1}{A_1 k_1^0 \kappa} \exp \left[\frac{\alpha_1 n_1 F}{RT} (E_1(0, R) - E_{01}) \right], \quad (1)$$

where V_1 denotes volume of solution containing the oxidant Ox_1 , A_1 is the surface area of a Pt electrode for reduction of Ox_1 , k_1^0 is the formal rate constant of the corresponding electrode reaction, κ a factor corresponding to ϱ_1 (for $R \leq 10 \Omega$ and $\alpha_1 < 0.3$, otherwise it is equal to 0.96), and $E_1(0, R)$ is the potential of the Pt electrode at the beginning of the reaction for $R > 0$. On introducing the proper expression for the value of $E_1(0, R)$, we obtain¹

$$\begin{aligned} \ln t_\infty = \ln \left[\frac{V_1 n_1 \kappa^{-1}}{(n_1 A_1 k_1^0)^{\varrho_2} (n_2 A_2 k_2^0)^{\varrho_1}} \left(\frac{a_1}{b_2} \right)^{\varrho_1} \right] + \frac{\alpha_1 n_1 F}{RT} \varrho_2 (E_{02} - E_{01}) + \\ + \frac{\alpha_1 n_1 F}{RT} \varrho_2 \frac{V_1 n_1 F a_1 R}{\kappa t_\infty}, \end{aligned} \quad (2)$$

where V_2 , A_2 and k_2^0 are analogous quantities for oxidation of Red_2 , a_1 is the starting concentration of Ox_1 , and b_2 is the starting concentration of Red_2 .

The aim of the present work is to verify the theoretical equations (1) and (2) for redox reactions with a two-electron transfer.

EXPERIMENTAL

The apparatus, evaluation and verification of the theory were described earlier². The following redox couples were chosen:

- a) $\text{Ce}^{4+}/\text{Ce}^{3+}$ in 1M H_2SO_4 and $\text{Sn}^{2+}/\text{Sn}^{4+}$ in 3.25M HCl
 b) $\text{Ti}^{3+}/\text{Ti}^{+}$ in 1M H_2SO_4 and $\text{Sn}^{2+}/\text{Sn}^{4+}$ in 3.25M HCl

All measurements were carried out at 314 K. Both Pt working electrodes had a geometrical surface area 32 cm^2 and the volume of the solutions was 25 cm^3 . Experimental conditions for redox system (a) are given in Figs 1 and 2; those for redox system (b) are as follows: Dependence $t_\infty = f(R) - a_1/b_2 = 0.246$; $R = 685, 885, 1085, 1285 \Omega$; $R_i = 485 \Omega$; $a_1^{(1)} = 1.07 \cdot 10^{-4} \text{ mol l}^{-1}$; $a_1^{(2)} = 1.60 \cdot 10^{-4} \text{ mol l}^{-1}$; $a_1^{(3)} = 2.13 \cdot 10^{-4} \text{ mol l}^{-1}$; $a_1^{(4)} = 2.67 \cdot 10^{-4} \text{ mol l}^{-1}$. Dependence $t_\infty = f(a_1) - a_1/b_2 = 0.166$; $a_1 = 7.1 \cdot 10^{-5}, 1.07 \cdot 10^{-4}, 1.42 \cdot 10^{-4}, 1.78 \cdot 10^{-4} \text{ mol l}^{-1}$; $R_1 = 675 \Omega$; $R_2 = 875 \Omega$; $R_3 = 1075 \Omega$; $R_4 = 1275 \Omega$; $R_i = 475 \Omega$.

Cerium(IV) sulphate of reagent grade was used as 0.01M solution in 1M H_2SO_4 and its concentration was determined by potentiometric (ferrometric) titration³. Thallium(III) sulphate of reagent grade was used in the form of a $2.5 \cdot 10^{-3} \text{ M}$ solution in 1M H_2SO_4 and its concentration was determined iodometrically³. The concentration of a solution of $5 \cdot 10^{-3} \text{ M}$ SnCl_2 in 3.25M HCl was determined by potentiometric titration with Ce(IV) ions³. Sulphuric and hydrochloric acids were of reagent grade. All chemicals were from Lachema Brno.

RESULTS AND DISCUSSION

Equation (2) was verified for both redox couples in the coordinates $\log t_\infty - R/t_\infty$

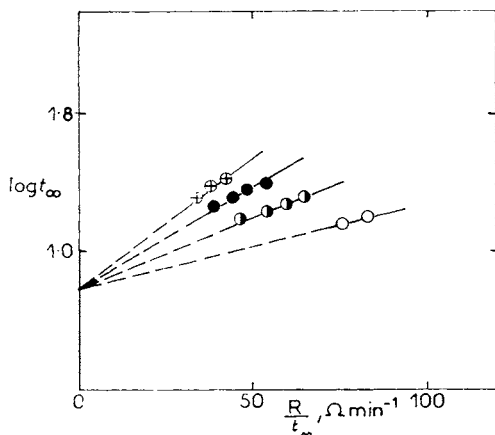


FIG. 1

Test of Equation (2) using system (a). Initial concentration a_1 of $\text{Ce}(\text{SO}_4)_2$: \circ 0.117; \bullet 0.175; \bullet 0.233; \oplus 0.292 mmol l^{-1} . Resistance $R = 720, 920, 1120, \text{ and } 1320 \Omega$; $R_i = 420 \Omega$; $V_1 = V_2 = 25 \text{ cm}^3$; $A_1 = A_2 = 32 \text{ cm}^2$; $a_1/b_2 = 0.244$; $T = 314 \text{ K}$

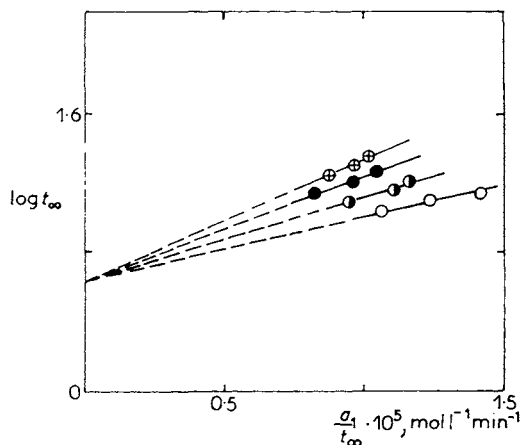


FIG. 2

Test of Equation (2) using system (a). Values of resistance R : \circ 620 Ω ; \bullet 820 Ω ; \bullet 1020 Ω ; \oplus 1220 Ω ; $R_i = 420 \Omega$; $V_1 = V_2 = 25 \text{ cm}^3$; $A_1 = A_2 = 32 \text{ cm}^2$; $a_1/b_1 = 0.165$; $a_1 = 0.117, 0.156, 0.194, \text{ and } 0.233 \text{ mmol l}^{-1}$; $T = 314 \text{ K}$

and $\log t_\infty - a_1/t_\infty$, other parameters being kept constant. The ratios of the slopes of the measured linear dependences (Figs 1 and 2) were compared with the theoretical

TABLE I
Comparison of theoretical and found ratios of the slopes of $\log t_\infty - R/t_\infty$ dependences

System	Concentration ratio of Ox form					
	$a_1^{(4)}/a_1^{(1)}$	$a_1^{(3)}/a_1^{(1)}$	$a_1^{(2)}/a_1^{(1)}$	$a_1^{(4)}/a_1^{(3)}$	$a_1^{(4)}/a_1^{(2)}$	$a_1^{(3)}/a_1^{(2)}$
a) Theory	2.50	1.99	1.50	1.25	1.67	1.33
Found	3.00	2.29	1.62	1.30	1.83	1.41
b) Theory	2.50	2.00	1.50	1.25	1.67	1.33
Found	2.79	2.04	1.43	1.35	1.84	1.42

TABLE II
Comparison of theoretical and found ratios of the slopes of $\log t_\infty - a_1/t_\infty$ dependences

System	Ratio of resistances					
	R_4/R_1	R_3/R_1	R_2/R_1	R_4/R_3	R_4/R_2	R_3/R_2
a) Theory	1.97	1.65	1.32	1.20	1.49	1.24
Found	1.90	1.63	1.30	1.17	1.47	1.26
b) Theory	1.89	1.59	1.30	1.19	1.46	1.23
Found	1.86	1.52	1.31	1.23	1.42	1.16

TABLE III
Experimental values of electrochemical parameters

Redox system	Dependence used	Correlation coefficient	α_1	k_1^0 [cm s ⁻¹]
Ce ⁴⁺ /Ce ³⁺	$t_\infty = f(a_1)$	0.956	0.117	$2.74 \cdot 10^{-4}$
	$t_\infty = f(R)$	0.982	0.085	$4.36 \cdot 10^{-4}$
Tl ³⁺ /Tl ⁺	$t_\infty = f(a_1)$	0.932	0.098	$1.81 \cdot 10^{-4}$
	$t_\infty = f(R)$	0.942	0.094	$2.46 \cdot 10^{-4}$

values (Tables I and II). A linear dependence of $\log t_\infty$ on $E_1(O, R)$ was found (Fig. 3) in accord with Eq. (1), and the parameters α_1 and k_1^0 for the redox systems $\text{Ce}^{4+}/\text{Ce}^{3+}$ and $\text{Tl}^{3+}/\text{Tl}^+$ were evaluated from the values of the slope and section on the coordinate axis (Table III).

The dependence of the reaction time on the volume of the solutions of both electrochemical systems for $V_1 = V_2 = V$ is linear in the coordinates $t_\infty - V$ (Fig. 4); the corresponding equations found by linear regression are $t_\infty = 0.558 V + 0.02$ (correlation coefficient $r = 0.999$) for system (a) and $t_\infty = 0.566 V + 0.08$ ($r = 0.992$) for system (b). The sections on the coordinate axis are close to zero in accord with the theory.

The electrochemical parameters α_1 and k_1^0 found for the system $\text{Ce}^{4+}/\text{Ce}^{3+}$ were compared with the literature data⁴ obtained from $i-E$ curves in the same reaction medium, but at 298 K: $\alpha_1 = 0.21$ and $k_1^0 = 3.7 \cdot 10^{-4} \text{ cm s}^{-1}$. The transfer coefficient given in Table III is somewhat lower, while the rate constant (average from two measurements) is nearly the same, $3.55 \cdot 10^{-4} \text{ cm s}^{-1}$. The values from the preceding work² (averages from eight measurements) are $\alpha_1 = 0.138$ and $k_1^0 = 4.47 \cdot 10^{-4} \text{ cm} \cdot \text{s}^{-1}$ at 314 K.

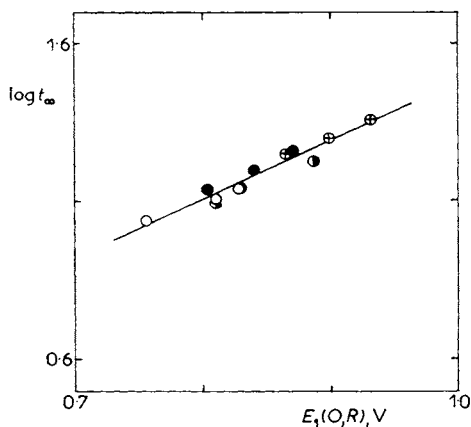


FIG. 3

Test of Equation (1) using system (a). Experimental conditions as in Fig. 2

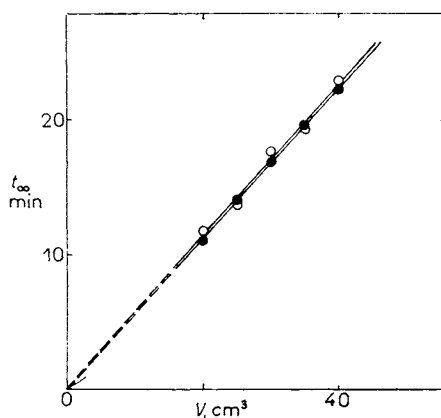


FIG. 4

Verification of the dependence of the reaction time on the solution volume for $V_1 = V_2 = V$. ● $\text{Ce}^{4+}-\text{Sn}^{2+}$: $A_1 = A_2 = 32 \text{ cm}^2$, $R_1 = 430 \Omega$, $a_1/b_2 = 0.233$, $a_1 = 0.194 \text{ mmol l}^{-1} \text{ Ce}(\text{SO}_4)_2$; ○ $\text{Tl}^{3+}-\text{Sn}^{2+}$: $A_1 = A_2 = 32 \text{ cm}^2$, $R_1 = 475 \Omega$, $a_1/b_2 = 0.199$, $a_1 = 0.178 \text{ mmol l}^{-1} \text{ TlCl}_3$; $T = 314 \text{ K}$

It should be noted that the purpose of our work was not an accurate determination of electrochemical parameters, but the verification of the theory based on simplified differential equations¹ describing the kinetics of the considered redox reactions. The results are evidence for the validity of the theoretical solution including redox reactions for which the number of exchanged electrons is different from 1. To determine the electrochemical parameters of a redox system, it would be necessary to evaluate statistically a number of measurements with a defined state of the surface of a platinum electrode, which is suitable for quantitative measurements thanks to its sensitivity.

REFERENCES

1. Tockstein A., Macenauer J.: *This Journal* **49**, 2857 (1984).
2. Macenauer J.: *This Journal* **49**, 2867 (1984).
3. Číhalík J.: *Potenciometrie*. Academia, Prague 1961.
4. Galus Z., Adams R. N.: *J. Phys. Chem.* **67**, 866 (1963).

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