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

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The kinetics of redox reactions of the type $n_2\ Ox_1 + n_1\ Red_2 \rightarrow n_1\ Ox_2 + n_2\ Red_1$ proceeding *via* electrode processes was studied on seven practical examples. The reaction time was measured as function of experimental parameters (resistance, concentration, volume of solution, electrode surface area), and the theoretical equation for the reaction time was verified.

Our preceding work[1] dealt with the derivation of theoretical equations expressing the reaction time for a redox reaction proceeding in a short-circuited galvanic cell as function of the concentrations, cell resistance, reaction volume, electrode surface area, and other parameters. The aim of the present work is to verify the theory on several practical examples.

EXPERIMENTAL

The measuring apparatus consisted of two cyllindrical glass cells, N_1 and N_2 (Fig. 1) with a thermostated mantle-piece. Their holding capacity was 40 cm^3 and one of them was filled with a solus tion of the oxidant, the other with a solution of the reductant (volumes V_1 and V_2). The cell-were connected through a salt bridge KM filled with 4M-KCl, which in turn was connected with a saturated calomel electrode S.C.E. They were further provided with a Teflon stopper with inlets for dosing the solutions and the solvent, washing the cells with distilled water, sucking off of the solutions, and filling the cells with argon. The shafts of spiral-formed glass stirrers M were inserted through the middle orifice. The working cyllindrical electrodes Pt_1 and Pt_2 were made of a 0·1 mm thick platinum foil with a Pt wire of 0·5 mm diameter serving as current lead. They could be short-circuited either directly or through a variable resistance R_v. The internal cell resistance R_i was measured with a conductance meter Konduktoskop (Laboratorní Přístroje, Prague).

The potentials of the platinum electrodes, E_{1e} and E_{2e}, against S.C.E. and their difference $\Delta E_{ext} = E_{1e} - E_{2e}$ were measured with three emitor followers of the type MOSFET (Tesla Rožnov) of $10^{11}\ \Omega$ input impedance. Potential–time curves were recorded on a six-channel pen-recorder (Rikadenki Kogyo, Japan).

The potential distribution in the measuring apparatus is shown schematically in Fig. 2. Owing to a potential drop, IR, the measured potentials are not equal to those entering the kinetic equa-

tions. These were calculated as

$$E_1(0) = E_{1e}(0) + 0{\cdot}5\,\Delta E_{ext} R_i/R_v\,,$$

$$E_2(0) = E_{2e}(0) - 0{\cdot}5\,\Delta E_{ext} R_i/R_v\,,$$

TABLE I

Redox systems and media used

Redox system	Oxidant	Medium	Reductant	Medium
1	$Fe(CN)_6^{3-}$	1M-NaOH	Ti^{3+}	0·5M-HCl
2	VO_3^-	1M-H_2SO_4	Ti^{3+}	0·5M-HCl
3	Fe^{3+}	0·1M-HCl 0·005M-KSCN	Ti^{3+}	0·5M-HCl
4	Ce^{4+}	1M-H_2SO_4	Fe^{2+}	1M-H_2SO_4
5	Ce^{4+}	1M-H_2SO_4	Ti^{3+}	0·5M-H_2SO_4
6	Ce^{4+}	1M-H_2SO_4	$Fe(CN)_6^{4-}$	1M-H_2SO_4
7	Ce^{4+}	1M-H_2SO_4	I^-	0·5M-H_2SO_4

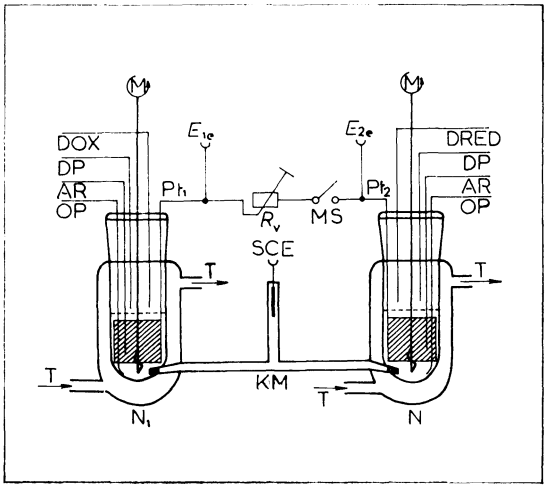


FIG. 1

Scheme of experimental setup. N_L, N_2 cells with termostated mantle-piece; Pt_1, Pt_2 platinum electrodes; KM salt bridge; M stirrer; R_v external resistance; MS mechanical switch; AR argon inlet; T thermostat; DOX capillary dosing of oxidant; DRED capillary dosing of reductant; DP inlet for dosing of reaction medium; OP tube for flushing with distilled water and sucking off of solution; E_{1e}. E_{2e} electrode potentials; S.C.E. saturated calomel electrode

TABLE II

Stock solutions and their standardization

Compound conc.	Base electrolyte	Standardization
		by potentiometry
0·01M-$Ce(SO_4)_2$	1M-H_2SO_4	ferrometrically
0·01M-$K_3Fe(CN)_6$	—	iodometrically
0·005M-$FeCl_3$	0·1M-HCl	titanometrically
0·01M-NH_4VO_3	1M-H_2SO_4	ferrometrically
0·01M-$Fe(NH_4)_2(SO_4)_2$	1M-H_2SO_4	cerrimetrically
0·01M-KI	0·5-HCl	cerrimetrically
0·01M-$TiCl_3$	0·5M-HCl	with $[Fe(CN)_6]^{-3}$
0·01 $K_4Fe(CN)_6$	0·2 g/l Na_2CO_3 as stabiliser	cerrimetrically

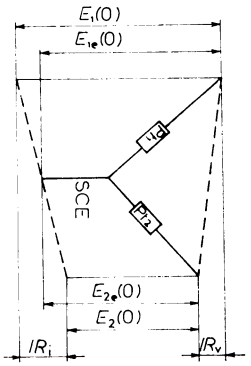


FIG. 2

Scheme of potential distribution in measuring cells. $E_{1e}(0)$, $E_{2e}(0)$ measured potential values; $E_1(0)$, $E_2(0)$ true potential values; Pt_1, Pt_2 platinum electrodes; S.C.E. saturated calomel electrode; IR_v potential drop on external resistance; IR_i potential drop on internal resistance

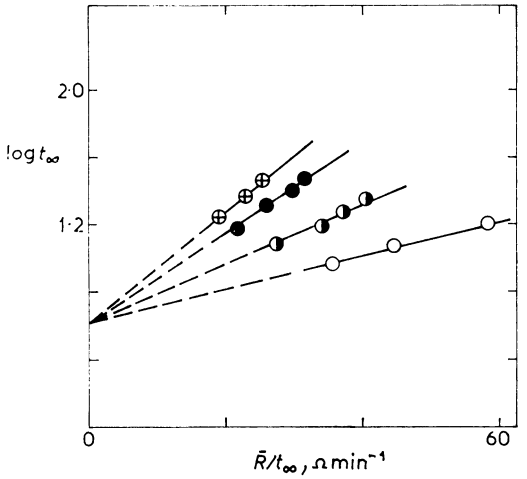


FIG. 3

Verification of Eq. (*14*)[1] with variable resistance and four values of $a_1 = [K_3Fe.(CN)_6]$ in redox system 1. $V_1 = V_2 = 25$ cm^3; $A_1 = A_2 = 32$ cm^2; $R_i = 330\ \Omega$; $a_1/b_2 = 0{\cdot}199$; $T = 314$ K; $R = 330$, 530, 730, and 930 Ω; $a_1^{(1)} = 1{\cdot}5 \cdot 10^{-4}$ mol/dm^3 (○); $a_1^{(2)} = 2{\cdot}4 \cdot 10^{-4}$ mol/dm^3 (◐); $a_1^{(3)} = 3{\cdot}2 \cdot 10^{-4}$ mol/dm^3 (●); $a_1^{(4)} = 4{\cdot}8 \cdot 10^{-4}$ mol : dm^3 (④)

where ΔE_{ext} denotes the external voltage drop. The values of $E_{1e}(0)$ and $E_{2e}(0)$ were determined from the initial course of the potential–time curves. The reaction time t_∞ was determined in 1/4 of the height of the E_{1e}–t curve.

TABLE III

Theoretical A and measured B ratios of the slopes of $\log t_\infty - R/t_\infty$ dependences

Redox system	Analysis	$a_1^{(4)}/a_1^{(1)}$	$a_1^{(3)}/a_1^{(1)}$	$a_1^{(2)}/a_1^{(1)}$	$a_1^{(4)}/a_1^{(3)}$	$a_1^{(4)}/a_1^{(2)}$	$a_1^{(3)}/a_1^{(2)}$
1	*A*	3·00	2·00	1·50	1·50	2·00	1·33
	B	3·52	2·21	1·52	1·51	2·31	1·45
2	*A*	—	2·00	1·50	—	—	1·33
	B		2·07	1·56			1·33
3	*A*	4·00	3·00	2·00	1·33	2·00	1·50
	B	3·76	2·82	1·97	1·33	1·91	1·43
4	*A*	4·00	2·00	1·50	2·00	2·67	1·33
	B	4·28	2·17	1·57	1·97	2·73	1·38
5	*A*	3·00	2·00	1·50	1·50	2·00	1·33
	B	3·61	2·24	1·48	1·61	2·44	1·51
6	*A*	4·00	3·00	2·00	1·33	2·00	1·50
	B	3·83	2·93	1·97	1·31	1·95	1·49
7	*A*	2·50	2·00	1·50	1·25	1·67	1·33
	B	2·61	1·97	1·48	1·32	1·76	1·33

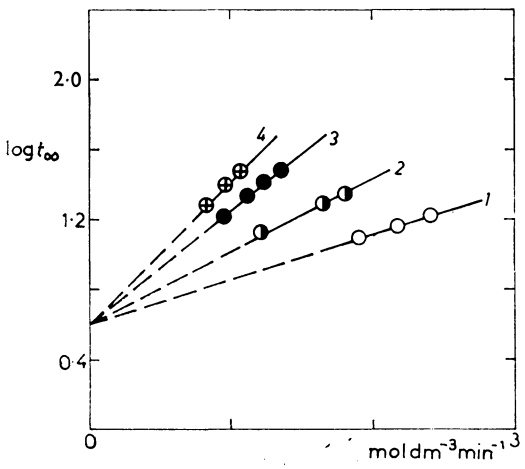


FIG. 4

Verification of Eq. (*14*)[1] with variable $a_1 = [K_3Fe(CN)_6]$ and four values of resistance in redox system 1. $V_1 = V_2 = 25$ cm^3; $A_1 = A_2 = 32$ cm^2; $R_1 = 300\ \Omega$; $a_1/b_2 = 0{\cdot}214$ $T = 314$ K; $a_1 = 1{\cdot}6 \cdot 10^{-4}$, $2{\cdot}4 \cdot 10^{-4}$ $3{\cdot}2 \cdot 10^{-4}$, and $4 \cdot 10^{-4}$ mol/dm^3; resistance: *1* 300 Ω; *2* 500 Ω; *3* 700 Ω; *4* 900 Ω

Prior to the measurement, the reaction solutions were tempered and bubbled with argon. After the potentials of both Pt electrodes had been established, the circuit was closed through a variable resistance R_v and the potential–time curves were recorded. Data about the solutions used are given in Tables I and II.

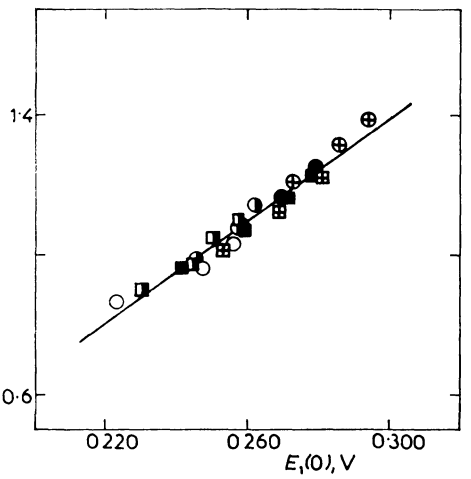
TABLE IV

Theoretical A and measured B ratios of the slopes of $\log t_\infty - a_1/t_\infty$ dependences

Redox system	Analysis	R_4/R_1	R_3/R_1	R_2/R_1	R_4/R_3	R_4/R_2	R_3/R_2
1	*A*	3·00	2·33	1·67	1·29	1·80	1·40
	B	2·96	2·43	1·66	1·22	1·78	1·46
2	*A*	—	1·90	1·35	—	—	1·31
	B		2·00	1·68			1·20
3	*A*	1·75	1·50	1·25	1·17	1·40	1·20
	B	1·80	1·52	1·17	1·19	1·54	1·29
4	*A*	10·38	7·25	4·13	2·52	1·76	1·43
	B	10·90	7·31	3·82	2·85	1·91	1·49
5	*A*	2·65	1·83	1·41	1·45	1·88	1·29
	B	3·03	2·19	1·52	1·38	1·99	1·44
6	*A*	—	2·02	1·34	—	—	1·51
	B	—	2·00	1·35			1·48
7	*A*	—	2·11	1·51	—	—	1·40
	B		2·14	1·52			1·41

FIG. 5

Verification of Eq. (9)[1] for $\log t_\infty$ as function of initial electrode potential $E_1(0, R)$ for redox system 1. $V_1 = V_2 = 25\ cm^3$; $A_1 = A_2 = 32\ cm^2$; $T = 314$ K; dependence $t_\infty = f(R)$: initial concentration $a_1^{(1)} = 9{\cdot}94 \cdot 10^{-5}$ mol/dm^3 (○); $a_1^{(2)} = 1{\cdot}49 \cdot 10^{-4}$ mol/dm^3 (◑); $a_1^{(3)} = 1{\cdot}99 \cdot 10^{-4}$ mol/dm^3 (●); $a_1^{(4)} = 2{\cdot}98 \cdot 10^{-4}$ mol/dm^3 (⊕); $R_i = 310\ \Omega$; $a_1/b_2 = 0{\cdot}109$; $R = 310$, 510, 710, and 910 Ω: dependence $t_\infty = f(a_1)$: $R_1 = 500\ \Omega$ (◨); $R_2 = 700\ \Omega$ (■); $R_3 = 900\ \Omega$ (⊞); (□); $R_i = 300\ \Omega$; $a_1/b_2 = 0{\cdot}110$; $a_1 = 9{\cdot}94 \cdot 10^{-5}$, $14{\cdot}92 \cdot 10^{-5}$, $1{\cdot}99 \cdot 10^{-4}$, and $2{\cdot}49 \cdot 10^{-4}$ mol/dm^3



RESULTS AND DISCUSSION

With regard to the theoretical Eq. (*14*) in ref.[1], the dependences of log t_∞ on R/t_∞ and a_1/t_∞ were plotted for seven redox systems (Table I), other parameters being kept constant. The slopes of the resulting straight lines and their ratios were evaluated (Figs 3 and 4, Tables III and IV). The relation between the reaction time t_∞ and the initial potential $E_1(0, R)$ was also verified (Eq. (*9*) in ref.[1]); a plot of log t_∞ against $E_1(0, R)$ is indeed a straight line (Fig. 5). Its slope and abscissa on the coordinate axis enables us to evaluate the electrochemical parameters α_1 and k_1^0 (Table V). All measurements were carried out at a temperature of 314 K.

The relation between the reaction time and the volumes of the two reaction solutions, which were equal to each other, is linear in the coordinates $t_\infty - V$ (Fig. 6)

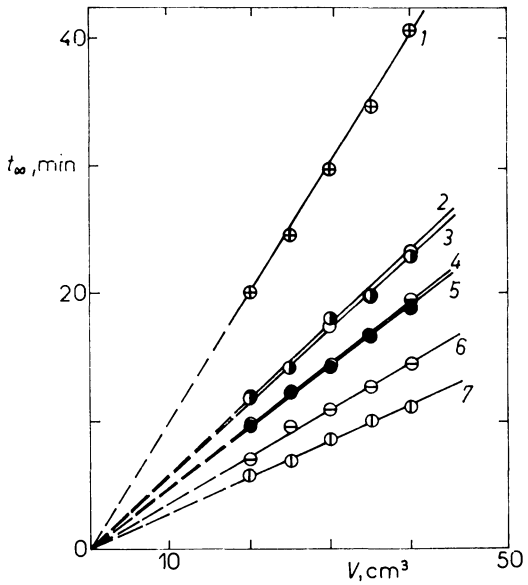


FIG. 6

Verification of the dependence of reaction time on solution volume for $V_1 = V_2$. *1* VO_3^-/Ti^{3+}; *2* Fe^{3+}/Ti^{3+}; *3* Ce^{3+}/I^-; *4* $Fe(CN)_6^{3-}/Ti^{3+}$; *5* $Ce^{4+}/Fe(CN)_6^{4-}$; *6* Ce^{4+}/Ti^{3+}; *7* Ce^{4+}/Fe^{3+}

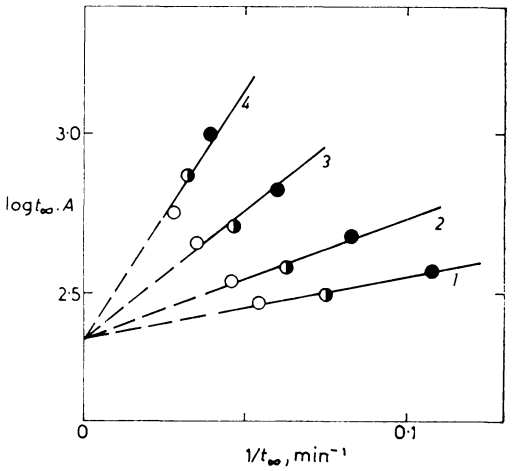


FIG. 7

Verification of Eq. (*14*)[1] for the reaction time as function of electrode surface area for $A_1 = A_2 = A$. Redox system Ce^{4+} : : Fe^{2+} in 1M-H_2SO_4; $V_1 = V_2 = 25$ cm³; $R = 385\ \Omega$; $a_i/b_2 = 0{\cdot}231$; $T = 314$ K; initial concentration *1* $a_1^{(1)} = 9{\cdot}24 \cdot 10^{-5}$ mol : : dm³- *2* $a_1^{(2)} = 2a_1^{(1)}$; *3* $a_1^{(3)} = 4a_1^{(1)}$; *4* $a_1^{(4)} = 8a_1^{(1)}$; $A_1 = A_2 = 16$, 24, and 40 cm²

passing through the origin of coordinates, which is in agreement with the theory (Eq. (*14*) in ref.[1]). The linear dependence of $\log(At_\infty)$ on $1/t_\infty$ for equal electrode surface areas ($A_1 = A_2 = A$) was verified in the case of the redox system Ce^{4+}/Fe^{2+} in 1M-H_2SO_4 (Fig. 7, Table VI).

It can be concluded that the experimentally found dependences of t_∞ on the cell parameters are in accord with the theoretical kinetic equations for the discharge

TABLE V

Experimental electrochemical parameters and correlation coefficients of linear dependences

Redox system	Dependence	Correlation coeff.	α_1	k_1^0, cm s^{-1}
$Fe(CN)_6^{3-} + Ti^{3+}$	$t_\infty = f(a_1)$	0·979	0·456	$1{\cdot}10 \cdot 10^{-3}$
	$t_\infty = f(R)$			
$VO_3^- + Ti^{3+}$	$t_\infty = f(a_1)$	0·994	0·166	$9{\cdot}30 \cdot 10^{-5}$
	$t_\infty = f(R)$			
$Fe^{3+} + Ti^{3+}$	$t_\infty = f(a_1)$	0·980	0·462	$2{\cdot}81 \cdot 10^{-4}$
	$t_\infty = f(R)$	0·975	0·471	$9{\cdot}02 \cdot 10^{-4}$
$Ce^{4+} + Fe^{2+}$	$t_\infty = f(a_1)$	0·964	0·175	$2{\cdot}11 \cdot 10^{-4}$
	$t_\infty = f(R)$	0·973	0·154	$4{\cdot}13 \cdot 10^{-4}$
$Ce^{4+} + Ti^{3+}$	$t_\infty = f(a_1)$	0·984	0·117	$6{\cdot}30 \cdot 10^{-4}$
	$t_\infty = f(R)$			
$Ce^{4+} + Fe(CN)_6^{4-}$	$t_\infty = f(a_1)$	0·981	0·121	$5{\cdot}19 \cdot 10^{-4}$
	$t_\infty = f(R)$			
$Ce^{4+} + I^-$	$t_\infty = f(a_1)$	0·966	0·151	$3{\cdot}28 \cdot 10^{-4}$
	$t_\infty = f(R)$			

TABLE VI

Theoretical and found slopes of $\log(At_\infty) - 1/t_\infty$ dependences

Ratio	R, Ω	$a_1^{(4)}/a_1^{(1)}$	$a_1^{(3)}/a_1^{(1)}$	$a_1^{(2)}/a_1^{(1)}$	$a_1^{(4)}/a_1^{(3)}$	$a_1^{(4)}/a_1^{(2)}$	$a_1^{(3)}/a_1^{(2)}$
Theory	385	8·00	4·00	2·00	2·00	4·00	2·00
Experiment		8·00	4·00	2·00	2·00	4·00	2·00
Theory	585	8·00	4·00	2·00	2·00	4·00	2·00
Experiment		8·47	4·20	1·80	2·02	4·70	2·33

curve of a short-circuited galvanic cell. Our results can be made use of in studies of certain industrial processes, *e.g.* in testing graphite materials used in amalgam decomposition, *etc.*

REFERENCES

1. Tockstein A., Macenauer J.: This Journal, in press.
2. Číhalík J.: *Potenciometrie.* Published by Nakladatelství ČSAV, Prague 1961.

Translated by K. Micka.