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KINETIC PARAMETERS OF ELECTRODE REACTIONS*

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Abstract—Kinetic parameters of electrode réactions are collected from the literature and tabulated.

Résumé—Les paramètes cinétiques des reactions d'électrodes ont été assemblés à partir des données de la littérature et sont présentés sous forme de tableaux.

Zusammenfassung—Die kinetischen Parameter von Elektroden reaktionen sind an Hand der Literatur zusammengestellt und tabelliert wurden.

INTRODUCTION

RECENTLY, both the theory and the experimental method on electrode reactions have made great progress, and many data on the kinetic parameters, such as the rate constant and the transfer coefficient, of electrode reactions have been published in the literature. Needless to say, these data play an important role in the discussion of the mechanism of electrode kinetics. Some instructive information on this subject can be found in the recent monograph by K. J. Vetter.[96] From the practical standpoint also, these data are very valuable, because the degree of "reversibility" of the polarographic current/potential curve and the favourable conditions for the electrochemical separation of components can be predicted from the kinetic parameters.

Unfortunately, there has been no compilation of kinetic parameters, and this has compelled the authors to undertake the compilation of all available kinetic parameters of electrode reactions. A large number of data on the hydrogen and the oxygen overpotentials and also some on the electrode reactions of organic substances which have been published, however, are not included in the compilation.

A preliminary draft‡ was sent for comments to the researchers whose results were referred in the table, and also to members of the Commission on Electrochemical Data and the Commission on Electrochemistry, IUPAC. The present compilation, which is a revision of the preliminary draft, is being published on the recommendation of the Commission on Electrochemistry, IUPAC, at its London meeting in July 1963. The compilation is yet almost uncritical, and therefore it is being presented for comments, criticism and additions.

The most serious problem which we met during the compilation arose from the fact that the presentation of the kinetic parameters differed from author to author. For example, some investigators present the rate of the electrode reaction in terms of the exchange current and others in terms of the standard rate constant. There is also an ambiguity in the transfer coefficient; some values correspond to the cathodic transfer coefficient and others to the anodic one. Such a situation often discourages us from comparing the data on the same system obtained by different investigators. Furthermore, it is evident from the theoretical standpoint that the analysis of the electrode kinetics requires at least both the rate constant and the transfer coefficient. As seen in the table, there are still many systems for which one of these parameters has not been obtained. This seems to be mainly due to the experimental difficulties.

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‡ This was first presented at the Montreal meeting of the Commission on Electrochemical Data, Analytical Chemistry Section, IUPAC, in August 1961.

It is highly desirable, however, that if possible both of these parameters are presented in future literature. In order to make kinetic data more useful to the further discussion of electrode kinetics, we suggest that clear description should be given on the following items:

(1) The electrode/solution system.

(2) The experimental methods and conditions.

(3) The rate constant of the electrode reaction. The standard rate constant, k_s, in cm/s or the standard exchange current density, $^\circ i$, are preferable to the exchange current density, i_0. When $^\circ i$ is used, the standard of the concentration unit must be clearly mentioned. If k_s cannot be determined, as in the case of the totally irreversible systems whose standard potentials are unknown, the rate constant, k_c° or k_a°, at the potential where the electrode potential equals zero against a reference electrode may be useful. In this case, the reference electrode should be mentioned, because the values of k° are dependent on the nature of the reference electrode used.

(4) In the presentation of the transfer coefficient, it must be made clear whether the value corresponds to the cathodic or the anodic one.

(5) Although the apparent heat of activation of the electrode reaction usually is not identical with the true heat of activation, its value seems to be useful in electrode kinetics. It is very important, however, to present clearly the assumptions under which the apparent heat of activation is calculated.

Finally, the authors wish to express their sincere thanks to many electrochemists who provided valuable information on their researches and their helpful comments and advice on the preliminary draft. They are also very grateful to Professor P. Van Rysselberghe, Professor H. Fischer and Dr. T. P. Hoar and also members of the Commission on Electrochemistry, IUPAC, for facilitating the publication of this report.

A NOTE ON ELECTRODE KINETICS

The over-all electrode reaction,

$$O + ne \rightleftharpoons R, \tag{1}$$

is generally considered to consist of the following processes: (i) the electron-transfer process at the electrode surface,

$$X + ne \rightleftharpoons Y, \tag{2}$$

(ii) the processes at the electrode surface which are accompanied by the electron-transfer process,

$$O \rightleftharpoons X \tag{3}$$

$$Y \rightleftharpoons R, \tag{4}$$

where O and R are the oxidant and the reductant, respectively, in the bulk of the solution, and (iii) the mass-transfer processes, such as diffusion and convection, of the reacting species between the electrode surface and the bulk of the solution. If it is assumed that both of the processes (i) and (ii) are of the first or the pseudo-first order with respect to X, Y and O, the over-all faradaic current density, i, is given by the equations

$$i = |i_c - i_a|, \tag{5}$$

$$i_c = nFC_O k_c, \tag{6}$$

$$i_a = nFC_R k_a, \tag{7}$$

where n is the number of electrons involved in the electron-transfer process,† F the faraday, and C_O and C_R are the concentrations of O and R, respectively, at the electrode surface. The rate constant of the reduction process of O, k_c, and that of the oxidation process of R, k_a, can be represented by

$$k_c = k_c^\circ \exp(-\alpha nFE/RT), \qquad (8)$$
$$k_a = k_a^\circ \exp(\beta nFE/RT),$$

where E is the electrode potential measured against a suitable reference electrode in the European convention, α and β are the cathodic and the anodic transfer coefficient, respectively, and k°'s the rate constants at $E = 0$. In (8), the effect of the diffuse double layer is neglected as the first approximation; most of the kinetic parameters which have been reported so far are determined with this approximation.

At the equilibrium potential of the system, E_e, the over-all faradaic current is equal to zero, and the concentrations of the reacting species at the electrode surface, C, are equal to those in the bulk of the solution, C°. Under these conditions, i_c and i_a are given by the relation

$$i_c = i_a = i_0 = nFC_O^\circ k_c^\circ \exp(-\alpha nFE_e/RT)$$
$$= nFC_R^\circ k_a^\circ \exp(\beta nFE_e/RT), \qquad (9)$$

where i_0 is the exchange current density of the system. At the standard potential, E_e°, both of k_c and k_a are equal to the standard rate constant, k_s, which is represented by

$$k_s = k_c^\circ \exp(-\alpha nFE_e^\circ/RT) = k_a^\circ \exp(\beta nFE_e^\circ/RT). \qquad (10)‡$$

The standard exchange current density, $^\circ i$, which corresponds to the exchange current density at the standard equilibrium conditions, *ie* $C_O^\circ = C_R^\circ = C^\circ = 1$ M,§ is also defined by

$$^\circ i = nFC^\circ k_s. \qquad (11)$$

By assuming that $\alpha + \beta = 1$, the following equation for i_0 is derived from eqns. (9) and (10),

$$i_0 = nFk_s(C_O^\circ)^\beta (C_R^\circ)^\alpha. \qquad (12)$$

The apparent heat of activation of the reduction process, $(\Delta H_c^*)_E$, can be determined by the relation

$$(\partial \ln k_c/\partial T)_E = (\Delta H_c^*)_E/RT^2. \qquad (13)$$

The value of $(\Delta H_c^*)_E$ is dependent on the nature of the reference electrode used, and it cannot be considered to be characteristic of the reduction process concerned. The apparent heat of activation at the standard potential, ΔH_s^*, is defined as

$$\Delta H_s^* = RT^2(\partial \ln k_s/\partial T), \qquad (14)$$

and is a characteristic constant of the system. However, ΔH_s^* is by no means identical with the "true" heat of activation of the corresponding process.††

† For the sake of simplicity, it is assumed that the number of electrons involved in the electron-transfer process is equal to that in the over-all electrode reaction.

‡ The apparent standard rate constant, k_a°, and the apparent transfer coefficient, α°, that are defined by Delahay correspond to k_s and α, respectively, in this report.

§ For the sake of simplicity, concentration is used instead of activity.

†† Because it refers to the value at the standard potential on the hydrogen scale, the true "thermal" heat of activation (and the true free energy of activation), containing no "electrochemical" contribution, is that obtaining at zero absolute potential difference between the electrode and the solution —*Ed.*

NOTATION AND ABBREVIATIONS

Notation

a activity

α transfer coefficient of the reduction process (cathodic transfer coefficient)

β transfer coefficient of the oxidation process (anodic transfer coefficient)

C molar concentration at the electrode surface, unless otherwise stated

C° molar concentration in the bulk of the solution, unless otherwise stated

D diffusion coefficient, cm^2/s

ΔG^* free energy of activation, Kcal/mole

$(\Delta H_a^*)_E$ apparent heat of activation of the oxidation (anodic) process, Kcal/mole, at the constant electrode potential E

$(\Delta H_c^*)_E$ apparent heat of activation of the reduction (cathodic) process, Kcal/mole, at the constant electrode potential E

ΔH_s^* apparent heat of activation, Kcal/mole, at the standard potential

ΔS_s^* apparent entropy of activation at the standard potential

E electrode potential measured against a suitable reference electrode in the European convention

E_e equilibrium potential

E_e° standard potential

$E_{1/2}$ half-wave potential

F Faraday constant

i over-all current density

i_a anodic current density

i_c cathodic current density

i_0 exchange current density, A/cm^2, unless otherwise stated

$^\circ i$ standard exchange current density, A/cm^2, unless otherwise stated.

k_a rate constant of the oxidation process, cm/s, unless otherwise stated

k_a° k_a at $E = 0$

k_c rate constant of the reduction process in cm/s, unless otherwise stated

k_c° k_c at $E = 0$

$k_{1/2}$ k_c at $E = E_{1/2}$

k_s standard rate constant, cm/s, unless otherwise stated

μ ionic strength

n number of electrons concerning the electron-transfer process

R gas constant

t time

T absolute temperature

Abbreviations

Ac acetate

ach alternating current harmonics method

acp alternating current polarography

ccs cyclic current step method

cp	current/potential curve
cps	cyclic potential step method
cr	coulostatic relaxation method
cs	current step method
CTAB	cetyl trimethyl ammonium bromide
dcp	direct current polarography
DME	dropping mercury electrode
dp	double pulse method
en	ethylenediamine
fi	faradaic impedance method
Fo	formate
fr	faradaic rectification method
Fu	fumarate
gel	gelatin
gs	galvanostatic method
LEO	polyoxyethylene lauryl ether
Ma	maleate
MC	methyl cellulose
NHE	normal hydrogen electrode
O	oxidant
op	oscillographic polarography
Ox	oxalate
Po	propionate
ps	potentiostatic method
pt	potential/time curve
R	reductant
rev	reversible
rt	radio-tracer method
SDS	sodium dodecyl sulphate
vs	voltage step method

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
Ag/1 mM and 0·1 M Ag^+	1 N $HClO_4$	—	$\beta = 0{\cdot}74 \pm 0{\cdot}02$	$^{\circ}i = 24 \pm 5$	—	dp	30
Ag/Ag^+(10 g $AgNO_3$/ 100 cm^3 H_2O	—	—	—	$i_0 = 1{\cdot}1 \times 10^{-2}$	—	fi	10
Bi/Bi(III)	Fused KCl–LiCl	450	$\alpha = 0{\cdot}48 \pm 0{\cdot}08$	$k_s = 0{\cdot}0009$ $i_0 = 8 \pm 3^a$	—	vs	55
Bi–Hg/Bi(III)	1 M $HClO_4$	20	—	$k_s = 3{\cdot}0 \times 10^{-4}$	$\Delta H_s^* = 10{\cdot}0$	fi	80
	1 M HCl	20	—	$k_s > 1$	—	fi	80
DME/Bi(III)	1 M $HClO_4$	25 ± 0·1	—	$k_s = 3 \times 10^{-4}$	—	acp	49
DME/5 × 10^{-3} N Bi(III)	1 N $HClO_4$	26 ± 0·5	—	$k_s = 0{\cdot}37 \times 10^{-3}$	—	fi	67
DME/2 × 10^{-3} N Bi(III)	0·8 N $HClO_4$ + 0·2 N HNO_3	26 ± 0·5	—	$k_s = (1{\cdot}0–1{\cdot}3) \times 10^{-3}$	—	fi	67
	0·6 N $HClO_4$ + 0·4 N HNO_3	26 ± 0·5	—	$k_s = (1{\cdot}7–1{\cdot}8) \times 10^{-3}$	—	fi	67
	0·4 N $HClO_4$ + 0·6 N HNO_3	26 ± 0·5	—	$k_s = (2{\cdot}2–2{\cdot}8) \times 10^{-3}$	—	fi	67
DME/(1–3) × 10^{-3} N Bi(III)	1 N HNO_3	26 ± 0·5	—	$k_s = (2{\cdot}8–4{\cdot}2) \times 10^{-3}$	—	fi	67
DME/1·9 × 10^{-3} N Bi(III)	1 N H_2SO_4	26 ± 0·5	—	$k_s = (1{\cdot}7–1{\cdot}9) \times 10^{-3}$	—	fi	67
DME/(1–3) × 10^{-3} N Bi(III)	1 N $HClO_4$ + 10^{-3} N HCl	26 ± 0·5	—	$k_s = (2{\cdot}4–3{\cdot}0) \times 10^{-3}$	—	fi	67
DME/5 × 10^{-5} N Bi(III)	1 N HCl	26 ± 0·5	—	$k_s = 1{\cdot}2–3{\cdot}6$	—	fi	67
Cd/2 N Cd(II)	—	20 ± 1	$\alpha = 0{\cdot}50 \pm 0{\cdot}05$	—	—	pt	56
Cd/Cd^{2+}(15 g $CdSO_4$/ 100 cm^3 H_2O)	—	—	—	$i_0 = 1{\cdot}4 \times 10^{-2}$	—	fi	10
Cd/1 × 10^{-2} N Cd(II)	0·8 N K_2SO_4	20 ± 1	$\alpha = 0{\cdot}45 \pm 0{\cdot}03$	$i_0 = 1{\cdot}5 \times 10^{-3}$	—	pt	56
Cd/Cd(II)	Fused KCl–LiCl	450	$\alpha = 0{\cdot}13 \pm 0{\cdot}05$	$k_s = 0{\cdot}4$ $i_0 = 210 \pm 50^a$	—	dp	55
	Fused KCl–LiCl	450	$\alpha = 0{\cdot}13 \pm 0{\cdot}05$	$k_s = 0{\cdot}4$ $i_0 = 210 \pm 50^a$	—	vs	55
$Cd–Hg/Cd^{2+}$	1 M $NaClO_4$	0	—	$i_0 = 40^b$	—	gs	68
Cd–Hg/Cd(II)	1 M KNO_3	20	—	$k_s = \sim 0{\cdot}6$	$\Delta H_s^* = \sim 5$	fi	80
Drop. Cd–Hg (1·22 mM Cd)	1 M KNO_3	25	—	$k_s = \sim 1{\cdot}0$	—	acp	7
Drop. Cd–Hg (1·5 mM Cd)	1 M KNO_3	25	—	$k_s = \sim 1{\cdot}0$	—	acp	7
Cd–Hg/Cd(II)	0·5 M Na_2SO_4	20	$\alpha = 0{\cdot}25$	$k_s = 2{\cdot}6 \times 10^{-2}$	—	vs	97
	0·5 M Na_2SO_4	—	$\alpha = 0{\cdot}12$	$k_s = 0{\cdot}085$	—	fi	77

[a] Exchange current at a metal–ion concentration of one mole per litre.
[b] $C_R = C_O = 1$ M.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
	0·5 M Na_2SO_4	20	$\alpha = 0{\cdot}17$	$k_s = 4{\cdot}2 \times 10^{-2}$	—	fi	26, 97
	0·5 M Na_2SO_4	20	$\alpha = 0{\cdot}22$	$k_s = 4{\cdot}5 \times 10^{-2}$	—	cs	26, 97
	0·5 M K_2SO_4	0	—	$i_0 = 5{\cdot}5$[a]	—	gs	68
Drop. Cd–Hg/Cd(II)	1 M K_2SO_4	0	—	$k_s = \sim 0{\cdot}2$ ($t = 0$)[b]	—	fi	13, 18
Cd–Hg/Cd(II)	1 M K_2SO_4	0	—	$k_s = 0{\cdot}037$ ($t = 20$)[b]	—	fi	13, 18
	1 M K_2SO_4	0	—	$k_s = 0{\cdot}016$ ($t = 40$)[b]	—	fi	13, 18
	1 M K_2SO_4	0	—	$k_s = 0{\cdot}0065$ ($t = 80$)[b]	—	fi	13, 18
	1 M K_2SO_4	0	—	$k_s = 0{\cdot}0038$ ($t = 120$)[b]	—	fi	13, 18
	1 M KCl	—	$\alpha = \sim 0{\cdot}7$	$k_s \simeq 5$	—	fi	77
DME/Cd(II)	1 M $NaClO_4$ (pH 2)[c]	22	$\alpha = 0{\cdot}07$	$k_s = 2{\cdot}3$	—	fr	4
DME/2 × 10^{-5} M Cd(II)	1 M $NaClO_4$ (pH 2)	22	$\alpha = 0{\cdot}13$	$k_{1/2} \simeq 0{\cdot}43$	—	fr	3
	1 M KNO_3 (pH 2)	22	$\alpha = 0{\cdot}12$	$k_{1/2} < 6{\cdot}4$(?)	—	fr	3
DME/Cd(II)	1 M KNO_3 (pH 2)[c]	22	$\alpha = 0{\cdot}15$	$k_s = 6{\cdot}3$	—	fr	4
	1 M KNO_3	25 ± 0·1	—	$k_s = 0{\cdot}6$	—	acp	49
DME/1·08 mM Cd(II)	1 M KNO_3	25	—	$k_s = \sim 0{\cdot}4$	—	acp	7
DME/Cd(II)	0·5 M Na_2SO_4	25	$\alpha = 0{\cdot}38$	—	—	acp	6
DME/0·5 mM Cd(II)	0·5 M Na_2SO_4	25	—	$k_s = 0{\cdot}25$	—	acp	7
DME/0·2 mM Cd(II)	1 M Na_2SO_4	25	—	$k_s = \sim 0{\cdot}3$	—	acp	7
DME/1 mM Cd(II)	1 M Na_2SO_4	25	—	$k_s = \sim 0{\cdot}1$	—	acp	7
DME/Cd(II)	1 M Na_2SO_4	25	$\alpha = 0{\cdot}37$	—	—	acp	6
	0·5 M K_2SO_4	22	$\alpha = 0{\cdot}08$	$k_s = 0{\cdot}08$	—	fr	4
DME/2 × 10^{-5} M Cd(II)	0·5 M K_2SO_4 (pH 2)	22	$\alpha = (0{\cdot}08)$	$k_{1/2} \simeq 0{\cdot}08$	—	fr	3
	1 M KF	22	$\alpha \simeq 0{\cdot}15$	$k_{1/2} \simeq 0{\cdot}25$	—	fr	3
DME/Cd(II)	0·5 M HCl	23·7–25·4	$\alpha = 0{\cdot}41$	$k_s = 0{\cdot}165$	—	acp	6
DME/1·08 mM Cd(II)	0·5 M HCl	25	—	$k_s = \sim 0{\cdot}5$	—	acp	7
DME/1 mM Cd(II)	1 M HCl	25	—	$k_s = \sim 0{\cdot}6$	—	acp	7
Hg/Cd(II)	0·1 M KCl	—	$\alpha = 0{\cdot}50$	—	—	ach	95
DME/Cd(II)	0·1 M KCl	25	$\alpha = 0{\cdot}44$	—	—	acp	6
	0·5 M KCl	25	$\alpha = 0{\cdot}45$	—	—	acp	6
DME/0·5 mM Cd(II)	0·5 M KCl	25	—	$k_s = \sim 1{\cdot}5$	—	acp	7
DME/Cd(II)	1·0 M KCl	25	$\alpha = 0{\cdot}45$	—	—	acp	6
	1 M KCl (pH 2)[c]	22	$\alpha = 0{\cdot}78$	$k_s = 2{\cdot}9$	—	fr	4

[a] $C_R = C_O = 1$ M.
[b] The value of t is the time in minutes when k_s is determined, measured from the formation of the electrode. k_s at $t = 0$ was obtained by extrapolation.
[c] pH adjusted by the addition of $HClO_4$.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
DME/2 × 10^{-5} M Cd(II)	1 M KCl (pH 2)	22	$\alpha = (0{\cdot}78)$	$k_{1/2} > 2{\cdot}9$	—	fr	3
	1 M KBr (pH 2)	22	$\alpha \simeq 0{\cdot}95$	$k_{1/2} \gg 0{\cdot}2$	—	fr	3
	1 M KI (pH 2)	22	$\alpha \simeq 1{\cdot}0$	$k_{1/2} \gg 0{\cdot}2$	—	fr	3
DME/Cd(II)	1 M KI	25 ± 0·1	—	$k_s > 1$(?)	—	acp	49
DME/$CdSO_4$	sodium hexaphosphate[a]	32	$\alpha n =$ {0·56; 0·13}	$k_c°$(?) = {$6{\cdot}9 \times 10^{-9}$; $9{\cdot}1 \times 10^{-5}$}	— —	dcp	72
	sodium hexaphosphate[a]	42	$\alpha n =$ {0·54; 0·21}	$k_c°$(?) = {$8{\cdot}5 \times 10^{-9}$; $1{\cdot}1 \times 10^{-4}$}	— —	dcp	72
	sodium hexaphosphate[a]	52	$\alpha n =$ {0·57; 0·20}	$k_c°$(?) = {$1{\cdot}1 \times 10^{-8}$; $4{\cdot}0 \times 10^{-5}$}	— —	dcp	72
	sodium hexaphosphate[a]	62	$\alpha n =$ {0·50; 0·24}	$k_c°$(?) = {$1{\cdot}5 \times 10^{-5}$; $2{\cdot}2 \times 10^{-8}$}	— —	dcp	72
Pt/3·00 mM Ce(III), 3·00 mM Ce(IV)	3 M $HClO_4$	0	—	$i_0 = 2{\cdot}4 \times 10^{-5}$	—	fi	21
	3 M $HClO_4$	0	—	$i_0 = 6{\cdot}9_5 \times 10^{-5}$	—	rt	21, 22
	3 M $HClO_4$	20	—	$i_0 = 4{\cdot}8 \times 10^{-5}$	—	fi	21
Pt/6·00 mM Ce(III), 6·00 mM Ce(IV)	3 M $HClO_4$	0	—	$i_0 = 9{\cdot}6_5 \times 10^{-5}$	—	fi	21
	3 M $HClO_4$	0	—	$i_0 = 2{\cdot}8 \times 10^{-4}$	—	rt	21, 22
	3 M $HClO_4$	20	—	$i_0 = 1{\cdot}9 \times 10^{-4}$	—	fi	21
Pt/10 mM Ce(III), 10 mM Ce(IV)	1 N H_2SO_4	25	$\beta = 0{\cdot}75$	$\log i_0 = -4{\cdot}36$	—	cp	96
Pt/Ce(IV), Ce(III)	1 M H_2SO_4	25	$\alpha = 0{\cdot}21$	$k_s = 3{\cdot}7 \times 10^{-4}$	—	cp[b]	23
Carbon Paste/Ce(IV), Ce(III)	1 M H_2SO_4	25	$\alpha = 0{\cdot}28$	$k_s = 3{\cdot}8 \times 10^{-4}$	—	cp[b]	23
$Co/CoCl_2$(0·1 ~ 2 N)	—	—	$\alpha = 0{\cdot}5$	$i_0 = 8 \times 10^{-7}$	—	—	87
DME/Co(II)	1 M KCl	—	$\alpha n = 0{\cdot}38$	$\log k_c° = -9{\cdot}7$[c]	—	op	58
DME/$[Co(NH_3)_6]^{3+}$	0·14 M $HClO_4$ + 1·26 M $NaClO_4$	25(?)	$\alpha = 0{\cdot}67$	$k_c°/\sqrt{D} = 2{\cdot}1 \times 10^{-4}$	$(\Delta H_c^*)_{E=0} =$ 12·6	dcp	99
DME/$[Co(NH_3)_5H_2O]^{3+}$	0·14 M $HClO_4$ + 1·26 M $NaClO_4$	25(?)	$\alpha = 0{\cdot}56$	$k_c°/\sqrt{D} = 2{\cdot}6 \times 10^{-2}$	$(\Delta H_c^*)_{E=0} =$ 9·5	dcp	99

[a] The log-plot gave two intersecting straight lines.
[b] With rotating disk electrodes.
[c] $k_c°$ is the rate const. at $E = 0$ V *vs* 0·1 N calomel electrode.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
	1 M HNO_3 + $NaNO_3$ + Th^{4+}($\mu = 2$)[a]	0	—	$k^\circ = 4 \times 10^{-5}$ $_{Th}k^\circ = 6{\cdot}6 \times 10^{-5}$	— —	dcp dcp	100 100
DME/$[Co(NH_3)_5NO_3]^{2+}$	0·14 M $HClO_4$ + 1·26 M $NaClO_4$	25(?)	$\alpha = 0{\cdot}53$	$k_c^\circ/\sqrt{D} = 1{\cdot}7 \times 10^{-1}$	$(\Delta H_c^*)_{E=0}$ = 9·3	dcp	99
DME/$[Co(NH_3)_5NO_3]^{2+}$	0·14 M $HClO_4$ + 1·26 M $NaClO_4$	25(?)	$\alpha = 0{\cdot}59$	$k_c^\circ/\sqrt{D} = 1 \times 10^{-3}$	$(\Delta H_c^*)_{E=0}$ = 15·2	dcp	99
DME/$[Co(NH_3)_5F]^{2+}$	0·14 M $HClO_4$ + 1·26 M $NaClO_4$	25(?)	$\alpha = 0{\cdot}51$	$k_c^\circ/\sqrt{D} = 4{\cdot}2 \times 10^{-4}$ [b]	$(\Delta H_c^*)_{E=0}$ = 11·2	dcp	99
	1·4 M $HClO_4$	25(?)	$\alpha = 0{\cdot}51$	$k_c^\circ/\sqrt{D} = 1{\cdot}3 \times 10^{-3}$ [b]	$(\Delta H_c^*)_{E=0}$ = 6·8	dcp	99
	1 M HNO_3 + $NaNO_3$ + Th^{4+} or La^{3+} ($\mu = 2$)	0	—	$k^\circ = 1{\cdot}4 \times 10^{-6}$ [a] $_{Th}k^\circ = 9{\cdot}7 \times 10^{-3}$ [a] $_{La}k^\circ = 5{\cdot}7 \times 10^{-5}$ [a]	— — —	dcp dcp dcp	100 100 100
DME/$[Co(NH_3)_5Fo]^{2+}$	0·14 M $HClO_4$ + 1·26 M $NaClO_4$	25(?)	$\alpha = 0{\cdot}63$	$k_c^\circ/\sqrt{D} = 4{\cdot}8 \times 10^{-4}$ [b]	$(\Delta H_c^*)_{E=0}$ = 7·5	dcp	99
DME/$[Co(NH_3)_5Ac]^{2+}$	0·14 M $HClO_4$ + 1·26 M $NaClO_4$	25(?)	$\alpha = 0{\cdot}65$	$k_c^\circ/\sqrt{D} = 9{\cdot}5 \times 10^{-4}$ [b]	$(\Delta H_c^*)_{E=0}$ = 8·3	dcp	99
DME/$[Co(NH_3)_5Po]^{2+}$	0·14 M $HClO_4$ + 1·26 M $NaClO_4$	25(?)	$\alpha = 0{\cdot}64$	$k_c^\circ/\sqrt{D} = 9{\cdot}5 \times 10^{-4}$ [b]	$(\Delta H_c^*)_{E=0}$ = 8·5	dcp	99
DME/$[Co(NH_3)_5N_3]^{2+}$	0·14 M $HClO_4$ + 1·26 M $NaClO_4$	25(?)	$\alpha = 0{\cdot}55$	$k_c^\circ/\sqrt{D} = 1{\cdot}1 \times 10^{-1}$ [b]	$(\Delta H_c^*)_{E=0}$ = 10·5	dcp	99
DME/$[Co(NH_3)_5(ONO)]^{2+}$	0·14 M $HClO_4$ + 1·26 M $NaClO_4$	25(?)	$\alpha = 0{\cdot}5$	$k_c^\circ/\sqrt{D} = 7 \times 10^{-4}$ [b]	$(\Delta H_c^*)_{E=0}$ = 15	dcp	99
DME/$[Co(NH_3)_5(OxH)]^{2+}$	0·14 M $HClO_4$ + 1·26 M $NaClO_4$	25(?)	$\alpha = 0{\cdot}59$	$k_c^\circ/\sqrt{D} = 9{\cdot}2 \times 10^{-4}$ [b]	$(\Delta H_c^*)_{E=0}$ = 12·7	dcp	99
DME/$[Co(NH_3)_5(FuH)]^{2+}$	1·4 M $HClO_4$	25(?)	$\alpha = 0{\cdot}73$	$k_c^\circ/\sqrt{D} = 6{\cdot}7 \times 10^{-4}$ [b]	$(\Delta H_c^*)_{E=0}$ = 12·5	dcp	99
DME/$[Co(NH_3)_5(MaH)]^{2+}$	1·4 M $HClO_4$	25(?)	$\alpha = 0{\cdot}76$	$k_c^\circ/\sqrt{D} = 1{\cdot}3 \times 10^{-3}$ [b]	$(\Delta H_c^*)_{E=0}$ = 12·5	dcp	99
DME/$[Co(NH_3)_5(FuCH)_3]^{2+}$	1·4 M $HClO_4$	25(?)	$\alpha = 0{\cdot}71$	$k_c^\circ/\sqrt{D} = 6{\cdot}8 \times 10^{-4}$ [b]	$(\Delta H_c^*)_{E=0}$ = 12·0	dcp	99
DME/$[Co(NH_3)_5SO_4]^{+}$	0·14 M $HClO_4$ + 1·26 M $NaClO_4$	25(?)	$\alpha = 0{\cdot}49$	$k_c^\circ/\sqrt{D} = 3{\cdot}8 \times 10^{-3}$ [b]	$(\Delta H_c^*)_{E=0}$ = 9·3	dcp	99

[a] The cathodic rate const. in the presence of Th^{4+} and La^{3+} is represented by the equation $k = k^\circ + {}_Mk^\circ[M^{n+}]$, where k° is the rate const. in a solution without polyvalent cations. The rate consts. are related to the potential of 0·1 M calomel electrode at 0°C.

[b] k_c° is the rate const. at $E = 0$ V *vs* 0·1 N calomel electrode.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
	1 M HNO_3 + $NaNO_3$ + Th^{4+} or La^{3+} ($\mu = 2$)	0	—	$k^\circ = 9{\cdot}55 \times 10^{-6}$ [a] $_{Th}k^\circ = 5{\cdot}3 \times 10^{-4}$ [a] $_{La}k^\circ = 1{\cdot}06 \times 10^{-5}$ [a]	—	dcp	100
DME/*cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$	0·14 M $HClO_4$ + 1·26 M $NaClO_4$	25(?)	$\alpha = 0{\cdot}55$	$k_c^\circ/\sqrt{D} = 2{\cdot}8$ [b]	$(\Delta H_c^*)_{E=0} = 8{\cdot}0$	dcp	99
DME/*trans*-$[Co(NH_3)_4(H_2O)_2]^{3+}$	0·14 M $HClO_4$ + 1·26 M $NaClO_4$	25(?)	$\alpha = 0{\cdot}52$	$k_c^\circ/\sqrt{D} = 8{\cdot}5 \times 10^{-1}$ [b]	$(\Delta H_c^*)_{E=0} = 7{\cdot}5$	dcp	99
DME/*cis*-$[Co(NH_3)_4(NO_2)_2]^{+}$	0·14 M $HClO_4$ + 1·26 M $NaClO_4$	25(?)	$\alpha = 0{\cdot}54$	$k_c^\circ/\sqrt{D} = 2{\cdot}3 \times 10^{-2}$ [b]	$(\Delta H_c^*)_{E=0} = 14{\cdot}2$	dcp	99
DME/*trans*-$[Co(NH_3)_4(NO_2)_2]^{+}$	0·14 M $HClO_4$ + 1·26 M $NaClO_4$	25(?)	$\alpha = 0{\cdot}6$	$k_c^\circ/\sqrt{D} = 1{\cdot}9 \times 10^{-4}$ [b]	$(\Delta H_c^*)_{E=0} = 15{\cdot}5$	dcp	99
DME/*cis*-$[Co(NH_3)_4Ac_2]^{+}$	1·4 M $HClO_4$	25(?)	$\alpha = 0{\cdot}55$	$k_c^\circ/\sqrt{D} = 2{\cdot}5 \times 10^{-1}$ [b]	$(\Delta H_c^*)_{E=0} = 6{\cdot}0$	dcp	99
DME/*trans*-$[Co(NH_3)_4Ac_2]^{+}$	1·4 M $HClO_4$	25(?)	$\alpha = 0{\cdot}52$	$k_c^\circ/\sqrt{D} = 3{\cdot}3 \times 10^{-1}$ [b]	$(\Delta H_c^*)_{E=0} = 4{\cdot}8$	dcp	99
DME/Cr^{3+}, Cr^{2+}	0·1 M $HClO_4$ + 0·9 M $NaClO_4$	—	$\alpha = 0{\cdot}45$	$\log k_s = -5{\cdot}0$	—	dcp	78
Hg/Cr(II), Cr(III)	1 M KCl	20	—	$k_s = 1{\cdot}0 \times 10^{-5}$	—	fi	79
DME/Cr(III), Cr(II)	KCl	—	—	$8{\cdot}0 \times 10^{-7}$ cm/s	—	dcp	71
DME/Cr(III)	1 M KCl	—	$\alpha n = 0{\cdot}40$	$\log k_c^\circ = -7{\cdot}1$	—	op	58
DME/Cr(IV), Cr(III)	KCl	—	—	$5{\cdot}1 \times 10^{-4}$ cm/s	—	dcp	71
DME/Cr(VI), Cr(IV)	KCl	—	—	$2{\cdot}7 \times 10^{-6}$ cm/s	—	dcp	71
DME/1·0 mM chromate	0·10 F NaOH	25(?)	$\alpha n = 0{\cdot}35$	$k_c^\circ = 1{\cdot}2 \times 10^{-9}$	—	dcp	63
Hg/5 mM $Cr(CN)_6^{3-}$, 5 mM $Cr(CN)_6^{4-}$	0·1 M KCN	30	—	$k_s = 0{\cdot}018$	—	fi	14
	0·1 M KCN + 0·1 M KCl	30	—	$k_s = 0{\cdot}052$	—	fi	14
	0·1 M KCN + 0·3 M KCl	30	—	$k_s = 0{\cdot}14$	—	fi	14
	0·1 M KCN + 0·5 M KCl	30	—	$k_s = 0{\cdot}31$	—	fi	14
	0·1 M KCN + 0·7 M KCl	30	—	$k_s = 0{\cdot}91$	—	fi	14

[a] The cathodic rate const. in the presence of Th^{4+} and La^{3+} is represented by the equation $k = k^\circ + {}_M k^\circ[M^{n+}]$, where k° is the rate const. in a solution without polyvalent cations. The rate consts. are related to the potential of 0·1 M calomel electrode at 0°C.

[b] k_c° is the rate const. at $E = 0$ V *vs* 0·1 N calomel electrode.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
DME/$Cr(CN)_6^{4-}$, $Cr(CN)_6^{3-}$	0·2 M NaCN	30	$\alpha = 0{\cdot}67$	$i_0 = 3{\cdot}9 \times 10^{-3}$	—	fi	16
Hg/$Cr(CN)_6^{4-}$, $Cr(CN)_6^{3-}$	1 M KCN	20	—	$k_s = 2{\cdot}5 \times 10^{-1}$ [a]	ΔH_s^* small	fi	79
Hg/5 mM $K_3Cr(CN)_6$	0·5 M KCN + 3 M KCl	25	$\alpha = 0{\cdot}53$–$0{\cdot}54$	$k_s = 1{\cdot}5_8 - 1{\cdot}0_0$	—	fr	41
DME/1·00 mM $K_3Cr(CN)_6$	1·0 M KCN	30	$\alpha = 0{\cdot}45 \pm 0{\cdot}05$	$k_s = 0{\cdot}22$	—	acp	89, 90
Drop. Tl–Hg(10% Tl)/ $Cr(CN)_6^{4-}$,$Cr(CN)_6^{3-}$	0·2 M NaCN	30	—	$i_0 = 3{\cdot}45 \times 10^{-3}$	—	fi	16
Drop. Tl–Hg(31% Tl)/ $Cr(CN)_6^{4-}$, $Cr(CN)_6^{3-}$	0·2 M NaCN	30	$\alpha = 0{\cdot}73$	$i_0 = 4{\cdot}8 \times 10^{-3}$	—	fi	16
DME/5 mM $Cr(SCN)_6^{3-}$	7 M KSCN	—	—	$k_s = 0{\cdot}01$	—	dcp[b]	50
	3 M KSCN	—	—	$k_s = 0{\cdot}007$	—	dcp[b]	50
	1 M KSCN	—	—	$k_s = 0{\cdot}002$	—	dcp[b]	50
	0·3 M KSCN	—	—	$k_s = 0{\cdot}004$	—	dcp[b]	50
	0·1 M KSCN	—	—	$k_s = 0{\cdot}004$	—	dcp[b]	50
Hg/Cs^+	1 M $N(CH_3)_4OH$	20	—	$k_s = 0{\cdot}2$ [c]	—	fi	80
DME/0·026 M CuCl	1 M NH_4OH + 1 M NH_4NO_3 + sat. camphor	25(?)	$\alpha n = 0{\cdot}55$	$k_s = 9{\cdot}75 \times 10^{-5}$ [d]	—	dcp	54
DME/0·035 M CuCl	1 M NH_4OH + 1 M NH_4NO_3 + sat. camphor	25(?)	$\alpha n = 0{\cdot}10$	$k_s = 3{\cdot}64 \times 10^{-4}$ [e]	—	dcp	54
Cu/0·001 M $Cu(NO_3)_2$	—	20	$\alpha n = 0{\cdot}22$	$i_0 = 10^{-9}$ [f]	—	—	11, 74
Cu/0·01 M $Cu(NO_3)_2$	—	20	$\alpha n = 0{\cdot}55$	$i_0 = 10^{-11}$	$\Delta H_0^* = 20$ [g]	—	11, 74
Cu/0·1 M $Cu(NO_3)_2$	—	20	$\alpha n = 0{\cdot}62$	$i_0 = 10^{-11}$	$\Delta H_0^* = 30$ [g]	—	11, 74
Cu/1 M $Cu(NO_3)_2$	—	16	$\alpha n = 0{\cdot}69$	—		—	11, 74
	—	20	$\alpha n = 0{\cdot}76$	$i_0 = 10^{-10}$		—	11, 74
	—	27	$\alpha n = 0{\cdot}76$	—	$\Delta H_0^* = 36$ [g]	—	11, 74
	—	37	$\alpha n = 0{\cdot}84$	—		—	11, 74
	—	47	$\alpha n = 0{\cdot}94$	—		—	11, 74

[a] Measured at the half-wave potential in a solution containing 5 mM $K_3Cr(CN)_6$.
[b] Kalousek's method.
[c] k_s was determined at the potential where the impedance is minimum.
[d] Reduction of Cu(I) to Cu(Hg).
[e] Oxidation of Cu(I) to Cu(II).
[f] log i_0 is constant from 23–58°C.
[g] ΔH_0^* seems to be the heat of activation determined from the temperature dependence of i_0.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
Cu/1 M $CuSO_4$	—	room temp.	0·5	$\log i_0 = -4{\cdot}7$	—	—	73
Cu/Cu^{2+}_{aq}	0·1 N H_2SO_4	0	$\alpha = 0{\cdot}5$	$^{\circ}i = (2{\cdot}3 \pm 0{\cdot}6) \times 10^{-3}$		gs	35, 37
	0·1 N H_2SO_4	15	$\alpha = 0{\cdot}5$	$^{\circ}i = (1{\cdot}2 \pm 0{\cdot}3) \times 10^{-2}$	$\Delta H_a^* = 15{\cdot}2$	gs	35, 37
	0·1 N H_2SO_4	20	$\alpha = 0{\cdot}5$	$^{\circ}i = (23{\cdot}9 \pm 0{\cdot}9) \times 10^{-3}$	$(\Delta H_a^*)_{E=0}{}^a = 30{\cdot}6$	gs	35, 37
	0·1 N H_2SO_4	25	$\alpha = 0{\cdot}5$	$^{\circ}i = (80{\cdot}5 \pm 2{\cdot}1) \times 10^{-3}$	$(\Delta H_c^*)_{E=0}{}^a = -0{\cdot}2$	gs	35, 37
	0·1 N H_2SO_4	35	$\alpha = 0{\cdot}5$	$^{\circ}i = (5{\cdot}4 \pm 1{\cdot}4) \times 10^{-2}$	$\Delta S_a^* = -40$ cal/°K	gs	35, 37
	0·1 N H_2SO_4	45	$\alpha = 0{\cdot}5$	$^{\circ}i = (1{\cdot}4 \pm 0{\cdot}3) \times 10^{-1}$		gs	35, 37
Cu/0·01 M $CuSO_4$	M KNO_3 + 0·05 M H_2SO_4(I)	—	—	$i_0 = 2{\cdot}3$	—	fi	33
	(I) + 0·0025% gel	—	—	$i_0 = 2{\cdot}1$	—	fi	33
	(I) + 0·0125% gel	—	—	$i_0 = 2{\cdot}0$	—	fi	33
	(I) + 0·05% gel	—	—	$i_0 = 2{\cdot}0$	—	fi	33
Cu/0·025 M $CuSO_4$	(I)	—	—	$i_0 = 3{\cdot}2$	—	fi	33
	(I) + 0·0125% gel	—	—	$i_0 = 3{\cdot}8$	—	fi	33
	(I) + 0·025% gel	—	—	$i_0 = 3{\cdot}7$	—	fi	33
	(I) + 0·05% gel	—	—	$i_0 = (4{\cdot}6)$	—	fi	33
Cu/0·05 M $CuSO_4$	(I)	—	—	$i_0 = 3{\cdot}9$	—	fi	33
	(I) + 0·0125% gel	—	—	$i_0 = 3{\cdot}8$	—	fi	33
	(I) + 0·025% gel	—	—	$i_0 = 3{\cdot}2$	—	fi	33
	(I) + 0·05% gel	—	—	$i_0 = 3{\cdot}2$	—	fi	33
Cu/0·025 M $CuSO_4$	(I) + 0·0025% CTAB	—	—	$i_0 = 5{\cdot}2$	—	fi	33
	(I) + 0·0125% CTAB	—	—	$i_0 = (7{\cdot}6)$	—	fi	33
	(I) + 0·05% CTAB	—	—	$i_0 = 3{\cdot}5$	—	fi	33
	(I) + 0·0025% SDS	—	—	$i_0 = 10{\cdot}0$	—	fi	33
	(I) + 0·0125% SDS	—	—	$i_0 = (23)$	—	fi	33
Cu–Hg/Cu(II)	1 M KNO_3	20	—	$k_s = 4{\cdot}5 \times 10^{-2}$	$\Delta H_s^* = 9{\cdot}0$	fi	80
Cu–Hg/$Cu(NH_3)_2^+$	1 M NH_3 + 1 M NH_4Cl	20	—	$k_s = 1{\cdot}1 \times 10^{-2}$	$\Delta H_s^* = 5{\cdot}0$	fi	80
Cu–Hg/$Cu(en)_2^{2+}$	1 M enHCl + 1 M en	20	—	$k_s = 3{\cdot}7 \times 10^{-2}$	$\Delta H_s^* = 0{\cdot}0$	fi	80
DME/Cu(II)	0·1 M $HClO_4$ + 0·05% Triton X-100	25	$\alpha n = 0{\cdot}59$	$k_s = 4{\cdot}4 \times 10^{-9}$	—	dcp	51
	0·1 M $HClO_4$ + 0·05% dodecylamine	25	$\alpha n = 0{\cdot}54$	$k_s = 3{\cdot}6 \times 10^{-14}$	—	dcp	52
	1 M KNO_3	25 ± 0·1	—	$k_s = 4{\cdot}5 \times 10^{-2}$	—	acp	49
DME/0·010 M $CuSO_4$	1 M NH_4OH + 1 M HN_4Cl + sat. camphor	25(?)	$\alpha n = 0{\cdot}27$	$k_s = 1{\cdot}03 \times 10^{-6}$	—	dcp	54

[a] The electrode potential E is referred to the hydrogen scale.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
DME/0·025 M $CuSO_4$	1 M NH_4OH + 1 M NH_4NO_3 + sat. camphor	25(?)	$\alpha n = 0{\cdot}37$	$k_s = 2{\cdot}28 \times 10^{-6}$	—	dcp	54
DME/0·047 M $CuSO_4$	1 M KNO_3 + 1·0 M en + sat. camphor	25(?)	$\alpha n = 0{\cdot}92$	$k_s = 1{\cdot}12 \times 10^{-5}$	—	dcp	54
DME/0·046 M $CuSO_4$	1 M KNO_3 + 0·95 M propylenediamine + sat. camphor	25(?)	$\alpha n = 0{\cdot}93$	$k_s = 9{\cdot}44 \times 10^{-6}$	—	dcp	54
	0·10 M KCl + 0·10 M EDTA + sat. camphor	25(?)	$\alpha n = 0{\cdot}43$	$k_s = 1{\cdot}43 \times 10^{-9}$	—	dcp	54
DME/0·045 M $CuSO_4$	1 M NH_4OH + 1 M NH_4NO_3 + 0·71 M EDTA + sat. camphor	25(?)	$\alpha n = 0{\cdot}47$	$k_s = 8{\cdot}75 \times 10^{-3}$	—	dcp	54
Hg/Eu^{3+}, Eu^{2+}	0·026 M ClO_4^-	—	$\alpha n = 1{\cdot}0$ ($\beta = 0$)	—	—	fi	78
	1 M $HClO_4$	—	$\alpha n = 0{\cdot}62$–$0{\cdot}46$	—	—	dcp	78
DME/10^{-3} M Eu(III)	10^{-3} M $HClO_4$ + 0·03–1·00 M $NaClO_4$	25	$\alpha = 0{\cdot}49 \pm 0{\cdot}03$	$k_c^\circ = 1{\cdot}3 \times 10^{-6}$ [a] $k_s = 2 \times 10^{-5}$	—	dcp	31
Hg/Eu(II), Eu(III)	1 M KCl	20	—	$k_s = 2{\cdot}1 \times 10^{-4}$	$\Delta H_s^* = 9{\cdot}0$	fi	79
	1 M KI	20	—	$k_s = 1{\cdot}6 \times 10^{-3}$	$\Delta H_s^* = 9{\cdot}0$	fi	79
	1 M KSCN	20	—	$k_s = 8{\cdot}0 \times 10^{-3}$	$\Delta H_s^* = 7{\cdot}5$	fi	79
Fe/Fe(II)	—	—	—	$v_0 = 10^{-13}$ g-ion/s/cm^2 [b]	—	—	84
Fe/1 M $FeSO_4$	—	room temp.	$\alpha = 0{\cdot}5$	$\log i_0 = -8{\cdot}0$	—	—	73
Fe/Fe^{2+}_{aq}	—	0	$\alpha = 0{\cdot}5$	$\log {}^\circ i = 2{\cdot}342$	$\Delta H_s^* = 23$ $\Delta H(a^*)_{E=0}{}^c = 2$	gs	35, 36
	—	25	$\alpha = 0{\cdot}5$	$\log {}^\circ i = 4{\cdot}046$	$(\Delta H_c^*)_{E=0}{}^c = 44$ $\Delta S_s^* = +12$ cal/°K	gs	35, 36
	—	50	$\alpha = 0{\cdot}5$	$\log {}^\circ i = 4{\cdot}851$		gs	35, 36
Pt/Fe^{2+}_{aq}, Fe^{3+}_{aq}	1 M $HClO_4$	20	—	$k_s = 5 \times 10^{-3}$	$\Delta H_s^* = 9$	fi	79
	1 M $HClO_4$	25	$\alpha = 0{\cdot}63$	$k_s = 2{\cdot}2 \times 10^{-3}$	—	cp	44
Pt/Fe(III)	0·1 M $HClO_4$	25	$\alpha = 0{\cdot}78 \pm 0{\cdot}04$	$k_s = (1{\cdot}1 \pm 0{\cdot}2) \times 10^{-2}$	—	cp[d]	47
Pt/Fe(III), Fe(II)	0·1 M H_2SO_4	25	$\alpha = 0{\cdot}60$, $\beta = 0{\cdot}39$	$k_s = 4{\cdot}3 \times 10^{-3}$	—	cp[e]	23

[a] Rate constant at $\phi = 0$ where ϕ is the potential defined by $\phi = E_{SCE} + 0{\cdot}450$ V. E_{SCE} means the electrode potential in V *vs* SCE.
[b] v_0: Rate of ionization and discharge of Fe(II) at equilibrium. $v = v_0(e^{-\Delta\epsilon/b'} - e^{\Delta\epsilon/b'})$, $b' = RT/\alpha nF$, $\Delta\epsilon$ = polarization voltage.
[c] The electrode potential E is referred to the hydrogen scale.
[d] Hydrodynamic voltammetry.
[e] With rotating disk electrode.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
Pt/0·002 M Fe^{2+}, 0·002 M Fe^{3+}	1 N H_2SO_4	25	$\alpha = 0{\cdot}583$	$k_s = 0{\cdot}033$	$\Delta H_s^* = 5{\cdot}1$	fr	1
	1 N H_2SO_4	30	$\alpha = 0{\cdot}585$	$k_s = 0{\cdot}038$		fr	1
	1 N H_2SO_4	35	$\alpha = 0{\cdot}586$	$k_s = 0{\cdot}044$		fr	1
	1 N H_2SO_4	40	$\alpha = 0{\cdot}587$	$k_s = 0{\cdot}050$		fr	1
Pt/Fe(II), Fe(III)	1 M H_2SO_4	25	$\alpha = 0{\cdot}62$	$^{\circ}i = (4{\cdot}7_8 - 5{\cdot}0_5) \times 10^2$ A/cm²/mole	—	cps	101
	1 F H_2SO_4	25 ± 2	—	$k_s = 5{\cdot}3 \times 10^{-3}$	—	gs	2
	1 M H_2SO_4	25	$\alpha = 0{\cdot}61$	$^{\circ}i = 5{\cdot}26 \times 10^2$ A/cm²/mole	—	ccs	101
Pt/0·015 M Fe(II), 0·015 M Fe(III)	2 N H_2SO_4	—	$\beta = 0{\cdot}58$	$\log i_0 = -2{\cdot}3$	—	—	73, 96
Pt/Fe(III), Fe(II)	1 M H_2SO_4	25	$\alpha = 0{\cdot}46$ $\beta = 0{\cdot}53$	$k_s = 4{\cdot}3 \times 10^{-3}$	—	cp[a]	23
	4 M H_2SO_4	25	$\alpha = 0{\cdot}44$ $\beta = 0{\cdot}55$	$k_s = 3{\cdot}1 \times 10^{-3}$	—	cp[a]	23
	1 M H_2SO_4 + 2·8 M Na_2SO_4	25	$\alpha = 0{\cdot}55$ $\beta = 0{\cdot}45$	$k_s = 1{\cdot}4 \times 10^{-3}$	—	cp[a]	23
Carbon Paste/Fe(III), Fe(II)	1 M H_2SO_4	25	—	$k_s = 5{\cdot}4 \times 10^{-5}$	—	cp[a]	23
				$4{\cdot}5 \times 10^{-5}$	—	op	23
Pt/Fe(II), Fe(III)	1 F $NaHSO_4$	25 ± 2	—	$k_s = 2{\cdot}7 \times 10^{-3}$	—	gs	2
	1 F $NaHSO_4$ + 1 F Na_2SO_4	25 ± 2	—	$k_s = 1{\cdot}4 \times 10^{-3}$	—	gs	2
Carbon Paste/Fe(III), Fe(II)	0·1 N $NaClO_4$ + 0·1 M HCl	25	—	$k_s = 8{\cdot}5 \times 10^{-5}$	—	cp[a]	23
	3·9 M $NaClO_4$ + 0·1 M HCl	25	—	$k_s = 1{\cdot}41 \times 10^{-4}$	—	cp[a]	23
	3·9 M $NaClO_4$ + 0·09 M $HClO_4$ + 0·01 M HCl	25	—	$k_s = 1{\cdot}37 \times 10^{-4}$	—	cp[a]	23
	3·4 M $NaClO_4$ + 0·1 M HCl + 0·5 M NaCl	25	—	$k_s = 1{\cdot}41 \times 10^{-4}$	—	cp[a]	23
	3·8 M KCl + 0·1 M HCl	25	—	$k_s = 2{\cdot}29 \times 10^{-4}$	—	cp[a]	23
	3·9 M LiCl + 0·1 M HCl	25	—	$k_s = 2{\cdot}19 \times 10^{-4}$	—	cp[a]	23
	0·1 M HCl	25	—	$k_s = (7{\cdot}4\text{–}10) \times 10^{-5}$	—	cp[a]	23

[a] With rotating disk electrodes.

System	Medium	Temperature °C	Transfer coefficient	Rate of constant	Heat of activation	Method	Ref.
Graphite/$Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$	—	20	$\alpha = 0{\cdot}50 \pm 0{\cdot}05$	$k_s = (6 \pm 1) \times 10^{-3}$ $^{\circ}i = 5{\cdot}8 \times 10^{-1}$	—	cp	82
$Pt/Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$	0·5 M K_2SO_4	20	—	$k_s = 13 \times 10^{-3}$	$\Delta H_s^* = 4$	fi	79
	0·5 M K_2SO_4	25	$\alpha = 0{\cdot}56$	$k_s = 7{\cdot}3 \times 10^{-2}$	—	cp	44
	1 M KCl	20	—	$k_s = 9 \times 10^{-2}$	$\Delta H_s^* = 4$	fi	79
	1 M KCl	25	$\alpha = 0{\cdot}61$	$k_s = 5{\cdot}2 \times 10^{-2}$	—	cp	44
	1 M KCl	25	$\alpha = 0{\cdot}45$	$^{\circ}i = 0{\cdot}92 \times 10^{-4}$ A/cm²/mole	—	cps	101
	1 M KCl	25	$\alpha = 0{\cdot}50$	$^{\circ}i = 1{\cdot}0 \times 10^{4}$ A/cm²/mole	—	ccs	101
$Pt/Fe(CN)_6^{3-}$	1 M KCl	25	—	$k_s = 0{\cdot}08 \pm 0{\cdot}01$	—	cp[a]	47
Carbon Paste/$Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$	0·1 M KCl	25	—	$k_s = 1{\cdot}48 \times 10^{-3}$	—	cp[b]	23
	0·3 M KCl	25	—	$k_s = 2{\cdot}65 \times 10^{-3}$	—	cp[b]	23
	1 M KCl	25	—	$k_s = 7{\cdot}08 \times 10^{-3}$	—	cp[b]	23
	1 M LiCl	25	—	$k_s = 1{\cdot}06 \times 10^{-3}$	—	cp[b]	23
$Pt/FeOx_3^{4-}$, $FeOx_3^{3-}$	0·5 M K_2Ox	20	—	$k_s = 9 \times 10^{-3}$	$\Delta H_s^* = 3$	fi	79
$Hg/FeOx_3^{4-}$, $FeOx_3^{3-}$	0·5 M K_2Ox	20	—	$k_s > 1$	—	fi	79
$Ag/FeOx_3^{4-}$, $FeOx_3^{3-}$	0·5 M K_2Ox	20	—	$k_s = 1 \times 10^{-3}$	—	fi	79
$Au/FeOx_3^{4-}$, $FeOx_3^{3-}$	0·5 M K_2Ox	20	—	$k_s = 5 \times 10^{-3}$	—	fi	79
Hg/Hg_2^{2+}	1 M $HClO_4$	0	$\alpha = 0{\cdot}4 \pm 0{\cdot}1$	$k_s > 1{\cdot}5$	$\Delta H_s^* = 10 \pm 1$	ps	29
Hg/1 mM Hg_2^{2+}	0·98 M $HClO_4$	25	$\alpha = 0{\cdot}24$	$i_0 = 0{\cdot}248$	—	dp	62
Hg/1 mM $Hg_2(NO_3)_2$	2 N $HClO_4$	room temp.	$\beta = 0{\cdot}6$	$\log i_0 = -0{\cdot}7$	—	—	73
$Hg(L)/Hg_2^{2+}$	1 M $HClO_4$	0	$\beta = 0{\cdot}7 \pm 0{\cdot}03$	$^{\circ}i = 14 \pm 1$	$\Delta H_s^* = 2 \pm 0{\cdot}5$ (0–45°)	dp	28
	1 M $HClO_4$	25	$\beta = 0{\cdot}7 \pm 0{\cdot}03$	$^{\circ}i = 16{\cdot}5 \pm 1{\cdot}5$	—	dp	28
	45% $HClO_4$	− 38·8	$\beta = 0{\cdot}7 \pm 0{\cdot}03$	$^{\circ}i = 10 \pm 1$	—	dp	28
$Hg(S)/Hg_2^{2+}$	45% $HClO_4$	− 38·8	$\beta = 0{\cdot}7 \pm 0{\cdot}03$	$^{\circ}i = 8{\cdot}5 \pm 1$	—	dp	28
DME/Hg(I)	0·1 M $HClO_4$	24 ± 2	$\alpha = 0{\cdot}28$	$k_s = 0{\cdot}28$	—	fr	42
	0·2 M $HClO_4$	24 ± 2	$\alpha = 0{\cdot}28$	$k_s = 0{\cdot}35$	—	fr	42
	1·1 M $HClO_4$	24 ± 2	$\alpha = 0{\cdot}28$	$k_s = 1{\cdot}3$	—	fr	42
Pt/I^-	0·1 M $HClO_4$	25	—	$k_s = (3 \pm 1) \times 10^{-2}$ cm⁴/s/mole[c]	—	cp[a]	45, 46

[a] Hydrodynamic voltammetry.
[b] With rotating disk electrodes.
[c] Second-order rate constant obtained from the electro-oxidation of iodide.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
	0·1 M $HClO_4$	25	$1 - \alpha = 0{\cdot}83 \pm 0{\cdot}08$	$(k''_{ox})^\circ = (1{\cdot}5 \pm 0{\cdot}8) \times 10^{-2}$ [b]	—	cp[a]	47
Pt/I_2	0·1 M $HClO_4$	25	$\alpha = 0{\cdot}17 \pm 0{\cdot}08$	$k_s = 60 \pm 20$	—	cp[a]	45, 46
Hg/0·1 mM IO_3^-	0·1 M KCl + acetate buff. (pH = 4·72)	25	$\alpha n = 0{\cdot}39$	—	—	cp	19
	0·1 M KCl + phosphate buff. (pH = 7·21)	25	$\alpha n = 0{\cdot}26$	—	—	cp	19
	0·1 M KCl + phosphate buff. (pH = 12·3)	25	$\alpha n = 0{\cdot}69$	—	—	cp	19
DME/1 mM KIO_3	$HClO_4$ (pH 0·94) + 0·01% gel	30	$(\alpha n = 1{\cdot}13)$	—	$\Delta G^* = 34{\cdot}6$	dcp	17
	Britton–Robinson buff. (pH 1·91) + 0·01% gel.	30	$\alpha n = 0{\cdot}59$	—	$\Delta G^* = 25{\cdot}3$	dcp	17
	Britton–Robinson buff. (pH 4·06) + 0·01% gel.	30	$\alpha n = 0{\cdot}53$	—	$\Delta G^* = 25{\cdot}4$	dcp	17
	Britton–Robinson buff. (pH 6·03) + 0·01% gel.	30	$\alpha n = 0{\cdot}28$	—	$\Delta G^* = 21{\cdot}4$	dcp	17
	Britton–Robinson buff. (pH 7·82) + 0·01% gel.	30	$\alpha n = 0{\cdot}31$	—	$\Delta G^* = 23{\cdot}5$	dcp	17
	Britton–Robinson buff. (pH 9·69) + 0·01% gel.	30	$\alpha n = 0{\cdot}61$	—	$\Delta G^* = 33{\cdot}1$	dcp	17
	Britton–Robinson buff. (pH 11·6) + 0·01% gel.	30	$\alpha n = 0{\cdot}63$	—	$\Delta G^* = 32{\cdot}7$	dcp	17
	KOH (pH 13·7) + 0·01% gel.	30	$\alpha n = 0{\cdot}61$	—	$\Delta G^* = 31{\cdot}0$	dcp	17
	KOH (pH 13·7) + 0·001% gel.	30	$\alpha n = 0{\cdot}89$	—	$\Delta G^* = 36{\cdot}6$	dcp	17
	KOH (pH 13·7) + 0·005% gel.	30	$\alpha n = 0{\cdot}76$	—	$\Delta G^* = 34{\cdot}0$	dcp	17

[a] Hydrodynamic voltammetry.
[b] Rate const. of the reaction $2I^- \rightarrow I_2 + 2e$ at the standard potential.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
	KOH (pH 13·7) + 1·0% gel.	30	$\alpha n = 0{\cdot}60$	—	$\Delta G^{*} = 31{\cdot}7$	dcp	17
In–Hg/In(III)	sulphate solns. (pH 2·5)	—	$\alpha = 0{\cdot}83$[a]	—	—	gs	57
DME/In(III)	0·48 M $HClO_4$	25	$\alpha n = 0{\cdot}66$	$k_e^{\circ} = 4{\cdot}4 \times 10^{-9}$[b]	—	dcp	39
	0·86 M H_3PO_4	25	$\alpha n = 0{\cdot}60$	$k_e^{\circ} = 6{\cdot}6 \times 10^{-11}$[b]	—	dcp	39
	0·5 M ClO_4^-	20	$\alpha n = 0{\cdot}66$	$k_e^{\circ} = 2{\cdot}2 \times 10^{-12}$[b]		dcp	43
	0·5 M ClO_4^-	26·5	$\alpha n = 0{\cdot}66$	$k_e^{\circ} = 4{\cdot}7 \times 10^{-12}$[b]	$(\Delta H_e^{*})_{E=0} = 21{\cdot}1$	dcp	43
	0·5 M ClO_4^-	30	$\alpha n = 0{\cdot}65$	$k_e^{\circ} = 7{\cdot}3 \times 10^{-12}$[b]		dcp	43
Hg/K^+	1 M $N(CH_3)_4OH$	20	—	$k_s \sim 0{\cdot}1$[c]	—	fi	80
Pt/0·01 M Mn(II), 0·01 M Mn(III)	15 N H_2SO_4	25	$\beta = 0{\cdot}72$	$\log i_0 = -5{\cdot}0$	—	—	73, 96
Carbon Paste/MnO_4^-, MnO_4^{2-}	0·9 M NaOH	25	—	$k_s = 1{\cdot}45 \times 10^{-2}$	—	cp[d]	23
	0·9 M LiOH	25	—	$k_s = 6{\cdot}92 \times 10^{-3}$	—	cp[d]	23
Hg/Mn(II)	0·1 M KCl	—	$\alpha = 0{\cdot}97$	—	—	ach	95
DME/Mn(II)	1 M KCl	—	$\alpha n = 1{\cdot}0$	$\log k_s = -2{\cdot}4$	—	op	58
Hg/Na^+	1 M $N(CH_3)_4OH$	20	—	$k_s \sim 0{\cdot}4$[c]	—	fi	80
Ni/1 M $NiSO_4$	—	room temp.	$\beta = 0{\cdot}5$	$\log i_0 = -8{\cdot}7$	—	—	73
Ni/0·01 N $NiSO_4$	2·0 N H_2SO_4 (pH $0{\cdot}0_0$)	—	$\beta = 0{\cdot}35$–$0{\cdot}40$	$i_0 = 8{\cdot}3 \times 10^{-10}$	—	cp	34
	0·2 N H_2SO_4 (pH $0{\cdot}8_3$)	—	$\beta = 0{\cdot}35$–$0{\cdot}40$	$i_0 = 2{\cdot}4 \times 10^{-9}$	—	cp	34
	2·0 N Na_2SO_4 (pH $5{\cdot}8_6$)	—	84 mV[e]	$i_0 = 4{\cdot}2 \times 10^{-8}$	—	cp	34
Ni/0·5 M $NiSO_4$	acetate buff. (pH 2·3)	20	$\alpha n = 0{\cdot}52$	$i_0 = 10^{-6}$	—	—	11, 86
	acetate buff. (pH 4·4)	20	$\alpha n = 0{\cdot}72$	$i_0 = 10^{-6}$	—	—	11, 86
	acetate buff. (pH 5·5)	20	$\alpha n = 0{\cdot}89$	$i_0 = 10^{-7}$	—	—	11, 86
	acetate buff. (pH 6·7)	20	$\alpha n = 0{\cdot}56$	$i_0 = 10^{-5}$	—	—	11, 86
	acetate buff. (pH 7·9)	20	$\alpha n = 0{\cdot}62$	$i_0 = 10^{-5}$	—	—	11, 86
Ni/0·01 M $NiCl_2$	2·0 N HCl (pH −0·28)	—	$\beta = 0{\cdot}35$–$0{\cdot}40$	$i_0 = 1{\cdot}1 \times 10^{-8}$	—	cp	34
	1·0 N HCl + 1·0 N KCl (pH $0{\cdot}0_1$)	—	$\beta = 0{\cdot}35$–$0{\cdot}40$	$i_0 = 6{\cdot}9 \times 10^{-9}$	—	cp	34

[a] Cathodic transfer coefficient of the reaction, $In^{3+} + e \rightleftharpoons In^{2+}$.
[b] Rate constant referred to 0 V *vs* NHE.
[c] k_s was determined at the potential where the impedance was minimum.
[d] With rotating disk electrodes.
[e] The value of dE/d log i for the anodic polarization curve.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
	0·2 N HCl + 1·5 N KCl (pH $0{\cdot}6_0$)	—	$\beta = 0{\cdot}35$–$0{\cdot}40$	$i_0 = 1{\cdot}7 \times 10^{-9}$	—	cp	34
	0·2 N HCl (pH 0·67)	—	$\beta = 0{\cdot}35$–$0{\cdot}40$	$i_0 = 3{\cdot}9 \times 10^{-9}$	—	cp	34
	2 N KCl (pH $5{\cdot}9_6$)	—	$\beta = 0{\cdot}35$–$0{\cdot}40$	$i_0 = 1{\cdot}0 \times 10^{-8}$	—	cp	34
Ni/Ni(II)	Fused KCl–LiCl	450	$\alpha = 0{\cdot}25 \pm 0{\cdot}06$	$k_s = 0{\cdot}1$ $i_0 = 110 \pm 20$[a]	—	dp	55
DME/Ni(II)	0·1 M $NaClO_4$ + 0·01% polyacrylamide	25	$\alpha n = 0{\cdot}65$	$k_s = 3{\cdot}3 \times 10^{-9}$	—	dcp	70
DME/0·0254 M $Ni(ClO_4)_2$							
($E = -0{\cdot}75$ to $-0{\cdot}86$)[b]	0·50 M $NaClO_4$	25(?)	$\alpha n = 0{\cdot}50$	$k_s = 5{\cdot}14 \times 10^{-9}$ [c]	—	dcp	54
($E = -0{\cdot}86$ to $-0{\cdot}99$)[b]	0·50 M $NaClO_4$	25(?)	$\alpha n = 0{\cdot}73$	$k_s = 7{\cdot}61 \times 10^{-10}$ [c]	—	dcp	54
($E = -0{\cdot}98$ to $-1{\cdot}06$)[b]	0·50 M $NaClO_4$ + $2{\cdot}0 \times 10^{-3}$ M *n*-octyl alcohol	25(?)	$\alpha n = 1{\cdot}15$	$k_s = 6{\cdot}06 \times 10^{-16}$ [c]	—	dcp	54
($E = -0{\cdot}75$ to $-0{\cdot}86$)[b]	0·10 M $NaClO_4$	25(?)	$\alpha n = 0{\cdot}63$	$k_s = 1{\cdot}22 \times 10^{-9}$ [c]	—	dcp	54
($E = -0{\cdot}86$ to $-0{\cdot}98$)[b]	0·10 M $NaClO_4$	25(?)	$\alpha n = 0{\cdot}77$	$k_s = 3{\cdot}02 \times 10^{-9}$ [c]	—	dcp	54
($E = -0{\cdot}97$ to $-1{\cdot}01$)[b]	0·10 M $NaClO_4$ + sat. β-naphthol	25(?)	$\alpha n = 0{\cdot}67$	$k_s = 7{\cdot}17 \times 10^{-12}$ [c]	—	dcp	54
($E = -1{\cdot}01$ to $-1{\cdot}09$)[b]	0·10 M $NaClO_4$ + sat. β-naphthol	25(?)	$\alpha n = 1{\cdot}18$	$k_s = 2{\cdot}92 \times 10^{-16}$ [c]	—	dcp	54
($E = -1{\cdot}26$ to $-1{\cdot}30$)[b]	0 10 M $NaClO_4$ + sat. camphor	25(?)	$\alpha n = 0{\cdot}70$	$k_s = 1{\cdot}09 \times 10^{-16}$ [c]	—	dcp	54
($E = -1{\cdot}31$ to $-1{\cdot}35$)[b]	0·10 M $NaClO_4$ + sat. camphor	25(?)	$\alpha n = 1{\cdot}20$	$k_s = 1{\cdot}18 \times 10^{-22}$ [c]	—	dcp	54
($E = -0{\cdot}730$ to $-0{\cdot}86$)[b]	—	25(?)	$\alpha n = 0{\cdot}57$	$k_s = 3{\cdot}18 \times 10^{-9}$ [c]	—	dcp	54
($E = -0{\cdot}86$ to $-0{\cdot}98$)[b]	—	25(?)	$\alpha n = 0{\cdot}73$	$k_s = 3{\cdot}44 \times 10^{-10}$ [c]	—	dcp	54
($E = -0{\cdot}74$ to $-0{\cdot}86$)[b]	1·00 M $NaClO_4$	25(?)	$\alpha n = 0{\cdot}46$	$k_s = 8{\cdot}05 \times 10^{-9}$ [c]	—	dcp	54
($E = -0{\cdot}86$ to $-1{\cdot}00$)[b]	1·00 M $NaClO_4$	25(?)	$\alpha n = 0{\cdot}70$	$k_s = 2{\cdot}41 \times 10^{-10}$ [c]	—	dcp	54
($E = -0{\cdot}74$ to $-0{\cdot}86$)[b]	2·00 M $NaClO_4$	25(?)	$\alpha n = 0{\cdot}39$	$k_s = 3{\cdot}53 \times 10^{-8}$ [c]	—	dcp	54
($E = -0{\cdot}86$ to $-0{\cdot}99$)[b]	2·00 M $NaClO_4$	25(?)	$\alpha n = 0{\cdot}64$	$k_s = 1{\cdot}03 \times 10^{-9}$ [c]	—	dcp	54
($E = -0{\cdot}71$ to $-0{\cdot}86$)[b]	3·00 M $NaClO_4$	25(?)	$\alpha n = 0{\cdot}47$	$k_s = 1{\cdot}69 \times 10^{-8}$ [c]	—	dcp	54
($E = -0{\cdot}86$ to $-0{\cdot}98$)[b]	3·00 M $NaClO_4$	25(?)	$\alpha n = 0{\cdot}64$	$k_s = 1{\cdot}56 \times 10^{-9}$ [c]	—	dcp	54
DME/Ni(II)	0·1 N KNO_3	25	$\alpha = 0{\cdot}4$	$\log k_c^\circ = -13{\cdot}7$[d] $\log k_s = (-10)$	—	dcp	66
DME/Ni(II)	0·1 M KNO_3 + 0·01% gel.	25	$\alpha = 0{\cdot}40$	$\log k_c^\circ = -13{\cdot}7$[d]	—	dcp	59, 64

[a] Exchange current at a metal-ion concentration of one mole per litre.
[b] Electrode potential in V *vs* SCE.
[c] Rate const. referred to standard potential rather than standard amalgam potential.
[d] Rate constant referred to 0 V *vs* NHE.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
	0·1 M KNO_3 + 4 μM LEO	25	$\alpha n = 0{\cdot}85$	$\log k_c^\circ = -13{\cdot}7^a$	—	dcp	69
	0·5 M KNO_3 + 4 μM LEO	25	$(\alpha n = 0{\cdot}78)$	$(\log k_c^\circ = -13{\cdot}4)^a$	—	dcp	69
Drop. Ni–Hg/Ni(II)	nitrate melt	140	—	$(k_s = 4{\cdot}2 \times 10^{-3})$	—	fi	81
DME/Ni(II)	nitrate melt	140	$\alpha = 0{\cdot}41$	$k_s = 6{\cdot}2 \times 10^{-3}$	—	fi	81
	0·12 M NaCl + 0·005% MC	25	$\alpha n = 0{\cdot}74$	$k_c^\circ = 1 \times 10^{-13\,a}$	—	dcp	39
	0·18 M NaCl + 0·005% MC	25	$\alpha n = 0{\cdot}69$	$k_c^\circ = 5 \times 10^{-13\,a}$	—	dcp	39
	0·24 M NaCl + 0·005 % MC	25	$\alpha n = 0{\cdot}63$	$k_c^\circ = 2{\cdot}7 \times 10^{-12\,a}$	—	dcp	39
	0·1 M KCl + 2 μM LEO	25	$\alpha n = 0{\cdot}84$	$\log k_c^\circ = -13{\cdot}5^a$	—	dcp	69
	0·12 M NaBr + 0·005% MC	25	$\alpha n = 0{\cdot}75$	$k_c^\circ - 1 \times 10^{-13\,a}$	—	dcp	39
	0·18 M NaBr + 0·005% MC	25	$\alpha n = 0{\cdot}69$	$k_c^\circ = 4 \times 10^{-13\,a}$	—	dcp	39
	0·24 M NaBr + 0·005% MC	25	$\alpha n = 0{\cdot}63$	$k_c^\circ = 2{\cdot}7 \times 10^{-12\,a}$	—	dcp	39
	0·18 M NaI + 0·005% MC	25	$\alpha n = 0{\cdot}69$	$k_c^\circ = 7 \times 10^{-13\,a}$	—	dcp	39
	0·24 M NaI + 0·005% MC	25	$\alpha n = 0{\cdot}61$	$k_c^\circ = 8 \times 10^{-12\,a}$	—	dcp	39
	0·1 M KI + 4 μM LEO	25	$(\alpha n = 0{\cdot}87)$	$(\log k_c^\circ = -14{\cdot}3)^a$	—	dcp	69
	0·4 M KI + 4 μM LEO	25	$(\alpha n = 0{\cdot}76)$	$(\log k_c^\circ = -13{\cdot}1)^a$	—	dcp	69
	0·1 N KNO_3 + 1 N NH_3	25	$\alpha = 0{\cdot}7$	$\log k_c^\circ = -16{\cdot}8^a$ $\log k_s = (-7{\cdot}0)$	—	dcp	66
	0·2–3 M NH_3 + 0·1 M KNO_3 + 0·01% gel.	25	$\alpha = 0{\cdot}71$	$\log k_c^\circ = -16{\cdot}8^a$	—	dcp	59, 64
	0·1 N KNO_3 + 1 M en + 0·02% gel.	25	$(\alpha = 0{\cdot}5)$	$\log k_c^\circ = -17{\cdot}6^a$ $\log k_s = (-6{\cdot}5)$	—	dcp	66
Pb/Pb(II)	Fused KCl–LiCl	450	$\alpha = 0{\cdot}38 \pm 0{\cdot}08$	$k_s = 0{\cdot}01$ $i_0 = 30 \pm 15^b$	—	dp	55

[a] Rate constant referred to 0 V *vs* NHE.
[b] Exchange current at a metal-ion concentration of one mole per litre.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
Pb–Hg/Pb(II)	1 M $HClO_4$	—	$\alpha = 0.5$	$k_s = 2.0$	—	fi	77
	1 M $HClO_4$	—	$\alpha = 0.55$	$k_s = 1.0$	—	fi	78
	1 M KNO_3	20	—	$k_s > 1$	—	fi	80
DME/Pb(II)	1 M $NaClO_4$ (pH 2)[a]	22	$\alpha = 0.60$	$k_s = 3.3$	—	fr	4
DME/2 × 10^{-5} M Pb(II)	1 M $NaClO_4$ (pH 2)	22	$(\alpha = 0.6)$	$k_{1/2}$ = slightly > 3·3	—	fr	3
DME/Pb(II)	1 M KNO_3 (pH 2)[a]	22	$\alpha = 0.81$	$k_s = 0.8$	—	fr	4
DME/2 × 10^{-5} M Pb(II)	1 M KNO_3 (pH 2)	22	$(\alpha = 0.81)$	$k_{1/2} > 0.8$	—	fr	3
DME/Pb(II)	1 M KNO_3	25 ± 0·1	—	$k_s > 1$	—	acp	49
DME/2 × 10^{-5} M Pb(II)	1 M KF (sat. PbF_2)	22	$\alpha = 0.5$	$k_{1/2} \simeq 5$	—	fr	3
Hg/Pb(II)	0·1 M KCl	—	$\alpha = 0.54$	—	—	ach	95
DME/Pb(II)	1 M KCl (pH 2)[a]	22	$\alpha = 0.94$	$k_s = 0.2$	—	fr	4
DME/2 × 10^{-5} M Pb(II)	1 M KCl (pH 2)	22	$(\alpha = 0.94)$	$k_{1/2} \geqslant 0.2$	—	fr	3
	1 M KBr (pH 2)	22	$\alpha \simeq 0.97$	$k_{1/2} \geqslant 0.2$	—	fr	3
	1 M KI (pH 2)	22	$\alpha \simeq 1.0$	$k_{1/2} \geqslant 0.2$	—	fr	3
DME/$Pb(NO_3)_2$	sodium hexaphosphate	27	$\alpha n = 0.37$	$k_c^\circ(?) = 2.0 \times 10^{-9}$		dcp	72
	sodium hexaphosphate	32	$\alpha n = 0.34$	$k_c^\circ(?) = 1.3 \times 10^{-8}$	$\Delta H_s^* = 38.1$	dcp	72
	sodium hexaphosphate	42	$\alpha n = 0.35$	$k_c^\circ(?) = 1.7 \times 10^{-8}$		dcp	72
	sodium hexaphosphate	52	$\alpha n = 0.26$	$k_c^\circ(?) = 2.2 \times 10^{-7}$		dcp	72
Pt/Pt(II)	Fused KCl–LiCl	450	$\alpha = 0.27 \pm 0.06$	$k_s = 0.03$ $i_0 = 40 \pm 10$[b]	—	dp	55
DME/Ti(IV), Ti(III)	0·23 M HCl + 0·005% gel.	16–17	$\alpha = 0.427 \pm 0.006$ $\beta = 0.558 \pm 0.015$	$^\circ i = 0.78$ mA/cm²/mM (at pH 0)	—	dcp	91
Hg/Ti(III), Ti(IV)	1 M tartaric acid	20	—	$k_s = 9.0 \times 10^{-3}$	$\Delta H_s^* = 7.0$	fi	79
DME/0·1–1 mM Ti(IV)	0·065 N H_2SO_4	25	$\alpha = 0.56$–0.67	—	—	dcp	93
DME/Ti(IV)	0·02 M HCl + 0·8 M NaCl + 0·002% Triton X — 305	25	$1 - \alpha = 0.41 \pm 0.063$	$k_c = 1.24$ ($E = -1.030$ V) $k_c = 3.20$ ($E = -1.090$ V)	—	dcp[c]	102
Tl–Hg/Tl(I)	1 M $HClO_4$	—	$\alpha = 0.52$	$k_s = 1.8$	—	fi	77
	1 M KNO_3	20	—	$k_s > 1$	—	fi	80
	0·33 M K_2SO_4 + 0·01 N H_2SO_4	25	α 0·18 ± 0·02	$k_s = 1.25 \pm 0.17$	$\Delta H_s^* = 1.9$	op	24
DME/Tl(I)	1 M $NaClO_4$ (pH 2)[a]	22	$\alpha = 0.69$	$k_s = 1.2$	—	fr	4
DME/10^{-4} M Tl(I)	1 M $NaClO_4$ (pH 2)	22	$(\alpha = 0.69)$	$k_{1/2} > 1.2$	—	fr	3

[a] pH adjusted by the addition of $HClO_4$.
[b] Exchange current at a metal-ion concentration of one mole per litre.
[c] From the dependence of polarographic current on drop time.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
DME/Tl(I)	1 M KNO_3 (pH 2)[a]	22	$\alpha = 0{\cdot}8$	$k_s = 0{\cdot}3$	—	fr	4
DME/10^{-4} M Tl(I)	1 M KNO_3 (pH 2)	22	$(\alpha = 0{\cdot}8)$	$k_{1/2} \gg 0{\cdot}3$	—	fr	3
DME/Tl(I)	0·5 M K_2SO_4	22	$\alpha = 0{\cdot}68$	$k_s = 3{\cdot}1$	—	fr	4
DME/10^{-4} M Tl(I)	0·5 M K_2SO_4 (pH 2)	22	$\alpha = 0{\cdot}68$	$k_{1/2} > 3{\cdot}1$	—	fr	3
	1 M KF	22	$\alpha = 0{\cdot}55$	$k_{1/2} \simeq 4{\cdot}1$	—	fr	3
DME/Tl(I)	1 M KCl (pH 2)[a]	22	$\alpha = 0{\cdot}9$	$k_s = 0{\cdot}15$	—	fr	4
DME/10^{-4} M Tl(I)	1 M KCl (pH 2)	22	$(\alpha = 0{\cdot}9)$	$k_{1/2} \gg 0{\cdot}15$	—	fr	3
Hg/UO_2^{2+}	1 N HCl	25	—	$k_s^{\circ}(?) = 2{\cdot}14 \times 10^{-2}$	—	op	32
Pt/V(III), V(II)	Fused KCl–LiCl	450	$\alpha = 0{\cdot}67 \pm 0{\cdot}05$	$k_s = 0{\cdot}3$ $i_0 = 30 \pm 2$[b]	$(2{\cdot}80 \pm 0{\cdot}4)$	vs	55
Hg/V(III), V(II)	1 M $HClO_4$	20	$\alpha = 0{\cdot}52$	$k_s = 3{\cdot}2 \times 10^{-3}$	$\Delta H_s^* = 7{\cdot}8$	fi	48
	1 M $HClO_4$	20	—	$k_s = 4{\cdot}0 \times 10^{-3}$	$\Delta H_s^* = 6{\cdot}5$	fi	79
DME (or Hg)/V(II), V(III)	1 M $HClO_4$	14·2	$\alpha = 0{\cdot}57$–$0{\cdot}49$	$k_s = 2{\cdot}20 \times 10^{-3}$	$\Delta H_s^* = 7{\cdot}6$	fi, dcp	76
	1 M $HClO_4$	25	$\alpha = 0{\cdot}57$–$0{\cdot}50$	$k_s = 3{\cdot}64 \times 10^{-3}$	—	fi, dcp	76
	1 M H_2SO_4	15·3	$\alpha = 0{\cdot}45_5$	$k_s = 1{\cdot}39 \times 10^{-3}$	—	fi, dcp	76
DME/V(III), V(II)	1 M H_2SO_4	15	$\alpha = 0{\cdot}455$	$k_s = 1{\cdot}03 \times 10^{-3}$	—	dcp	78
Hg/V(II), V(III)	0·5 M K_2Ox	20	—	$k_s = 1{\cdot}4 \times 10^{-3}$	$\Delta H_s^* = 5{\cdot}5$	fi	79
Zn/1 M $ZnSO_4$	—	room temp.	$\beta = 0{\cdot}5$	$\log i_0 = -4{\cdot}7$	—	—	73
Zn/0·5 N $ZnSO_4$	0·005 N H_2SO_4	—	—	$v_0 = 10^{-10}$ g.-ion/cm²/s[c]	—	—	85
$Zn/Zn^{2+}{}_{aq}$	3 M acid chloride soln.	20	$\alpha = 0{\cdot}5$?	$i_0 = 0{\cdot}7 \times a_{Zn^{2+}}$	$\Delta H_s^* = 25{\cdot}4$ $(\Delta H_s^*)_{E=0} = -11{\cdot}0$[d] $(\Delta H_s^*)_{E=0} = 61{\cdot}8$[d]	gs	38
Zn/Zn(II)	Fused KCl–LiCl	450	$\alpha = 0{\cdot}16 \pm 0{\cdot}05$	$k_s = 0{\cdot}3$ $i_0 = 150 \pm 30$[b]	(3 ± 1)	dp	55
	Fused KCl–LiCl	450	$\alpha = 0{\cdot}10 \pm 0{\cdot}05$	$k_s = 0{\cdot}4$ $i_0 = 150 \pm 20$[b]	(3 ± 1)	vs	55
Hg/Zn(II)	0·9 M $NaClO_4$	—	$\alpha = 0{\cdot}28 \pm 0{\cdot}03$	$i_0 = 1{\cdot}02 \times C_{Zn}^{0{\cdot}28} \times C_{Zn(II)}^{0{\cdot}72}$	$\Delta H_s^* = 9{\cdot}1 \pm 0{\cdot}3$ (15–38°C)	fi	25
Zn–Hg(1 mole%)/6 mM $Zn(ClO_4)_2$	1 M $NaClO_4$	0	$\alpha = 0{\cdot}3$	$i_0 = 2{\cdot}1 \times 10^{-3}$	—	ps	98
Zn–Hg(1 mole%)/0·02 M Zn(II)	1 M $NaClO_4$	0	$\alpha = 0{\cdot}25$	$i_0 = 5{\cdot}4 \times 10^{-3}$	—	gs	27
	1 M $NaClO_4$	0	$\alpha = 0{\cdot}25$	$i_0 = 5{\cdot}8 \times 10^{-3}$	—	ps	27
Zn–Hg/Zn(II)	1 M $NaClO_4$	0	—	$i_0 = 0{\cdot}1$[e]	—	gs	68

[a] pH adjusted by the addition of $HClO_4$.
[b] Exchange current at a metal-ion concentration of one mole per litre.
[c] v_0 : rate of ionization and discharge of Zn (II) at equilibrium.
$v = v_0 (e^{-\Delta\epsilon/b'} - e^{\Delta\epsilon/b'})$, $b' = RT/\alpha nF$, $\Delta\epsilon$ = polarization voltage.
[d] The electrode potential E is referred to the hydrogen scale.
[e] $C_R = C_O = 1$ M.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
	1 M $NaClO_4$ + 10^{-3} N $HClO_4$	25	$\alpha = 0{\cdot}29$	$k_s = 3{\cdot}26 \times 10^{-3} \pm 3{\cdot}6\%$	—	fi	88
	1 M KNO_3	20	—	$k_s = 3{\cdot}5 \times 10^{-3}$	$\Delta H_s^* = 8{\cdot}8$	fi	80
Zn–Hg/$ZnSO_4$	0·5 M Na_2SO_4	—	$\alpha = 0{\cdot}30$ $\beta = 0{\cdot}69$	$k_s(?) = 0{\cdot}208 \times 10^{-2}$	—	cp	5
Zn–Hg/Zn(II)	0·33 M K_2SO_4 + 0·01 N H_2SO_4	25	$\alpha n = 0{\cdot}46 \pm 0{\cdot}03$	$k_s = 4{\cdot}4 \times 10^{-3}$	—	op	24
	0·2 M KCl	—	—	$\log k_s = -0{\cdot}48$	—	fi	8
	1 M KCl	0	—	$i_0 = 0{\cdot}25^a$	—	gs	68
	1 M KCl	20	—	$i_0 = 0{\cdot}65^a$	—	gs	68
	1 M KCl	25	—	$i_0 = 0{\cdot}9^a$	—	gs	68
	1 M KCl	—	—	$\log k_s = -2{\cdot}03$	—	fi	8
	1 M KCl	20	—	$k_s = 4{\cdot}0 \times 10^{-3}$	$\Delta H_s^* = 8{\cdot}6$	fi	80
	1 M KCl	25	$\alpha n = 0{\cdot}88_4 \pm 0{\cdot}05$	$k_s = 1{\cdot}6 \times 10^{-2}$	—	op	24
	1 M KCl	25	—	$k_s = 6 \times 10^{-3}$	—	fi	75
	1 M KCl	25	$\alpha = 0{\cdot}30$	$k_s = (4{\cdot}1\text{–}4{\cdot}2) \times 10^{-3}$	—	cr	15
	1 M KBr	20	—	$k_s = 8{\cdot}0 \times 10^{-3}$	$\Delta H_s^* = 9{\cdot}3$	fi	80
	1 M KI	20	—	$k_s = 7{\cdot}0 \times 10^{-2}$	$\Delta H_s^* = 5{\cdot}6$	fi	80
	1 M KSCN	20	—	$k_s = 1{\cdot}7 \times 10^{-2}$	$\Delta H_s^* = 7{\cdot}0$	fi	80
Zn–Hg/0·01 M Zn(II)	1 M NaOH	20 ± 1	—	$\log k_s = -3{\cdot}61$	—	fi	8
DME/1 mM $Zn(NO_3)_2$	1 M $NaClO_4$ + 2 μM LEO	$0{\cdot}_2$	$\alpha = 0{\cdot}27$	$k_s = 0{\cdot}33 \times 10^{-3}$		dcp	94
	1 M $NaClO_4$ + 2 μM LEO	15	$\alpha = 0{\cdot}28$	$k_s = 1{\cdot}54 \times 10^{-3}$		dcp	94
	1 M $NaClO_4$ + 2 μM LEO	25	$\alpha = 0{\cdot}40$	$k_s = 4{\cdot}0_1 \times 10^{-3}$	$\Delta H_s^* \simeq 14$	dcp	94
	1 M $NaClO_4$ + 2 μM LEO	35	$\alpha = 0{\cdot}30$	$k_s = 5{\cdot}2_1 \times 10^{-3}$		dcp	94
DME/Zn(II)	0·1 N KNO_3 + 0·01% gel.	25	$\alpha n = 0{\cdot}87$	—	—	dcp	65
Hg/0·002 M $ZnCl_2$	0·1 M KNO_3	10·5	$\alpha n(?) = 0{\cdot}58$	$k_{1/2} = 1{\cdot}70 \times 10^{-2}$ [b]	—	cp	83
	0·1 M KNO_3	24	$\alpha n(?) = 0{\cdot}76$	$k_{1/2} = 1{\cdot}32 \times 10^{-2}$ [b]	—	cp	83
	0·1 M KNO_3	36·5	$\alpha n(?) = 1{\cdot}16$	$k_{1/2} = 2{\cdot}82 \times 10^{-2}$ [b]	—	cp	83
	0·1 M KNO_3	50	$\alpha n(?) = 1{\cdot}52$	$k_{1/2} = 3{\cdot}34 \times 10^{-2}$ [b]	—	cp	83
	1·0 M(?) KNO_3	21	$\alpha n(?) = 0{\cdot}46$	$k_{1/2} = 0{\cdot}40 \times 10^{-2}$ [b]	—	cp	83
	1·0 M(?) KNO_3	36	$\alpha n(?) = 0{\cdot}54$	$k_{1/2} = 0{\cdot}46 \times 10^{-2}$ [b]	—	cp	83
	1·0 M(?) KNO_3	54	$\alpha n(?) = 0{\cdot}80$	$k_{1/2} = 1{\cdot}20 \times 10^{-2}$ [b]	—	cp	83
DME/Zn(II)	1 M KNO_3	25 ± 0·1	—	$k_s = 3{\cdot}5 \times 10^{-3}$	—	acp	49

[a] $C_R = C_O = 1$ M.
[b] Rate constant at the theoretical half-wave potential.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
DME/1 mM $Zn(NO_3)_2$	1 M KNO_3 + 2 μM LEO	25	$\alpha = 0{\cdot}39$	$k_s = 5{\cdot}4_0 \times 10^{-3}$	—	dcp	94
DME/Zn(II)	0·1 M $NaNO_3$	22	$\alpha = 0{\cdot}24$–$0{\cdot}28$	$k_s = 5 \times 10^{-2}$	—	dcp	53
	0·25 M $NaNO_3$	22	—	$k_s = 2 \times 10^{-2}$	—	dcp	53
	0·50 M $NaNO_3$	22	—	$k_s = 5{\cdot}4 \times 10^{-3}$	—	dcp	53
	0·75 M $NaNO_3$	22	—	$k_s = 3{\cdot}3 \times 10^{-3}$	—	dcp	53
	1·0 M $NaNO_3$	22	—	$k_s = 2{\cdot}8 \times 10^{-3}$	—	dcp	53
	0·1 M $NaNO_3$ + 0·05 M $(CH_3)_4NCl$	22	—	$k_s = 1{\cdot}5 \times 10^{-3}$	—	dcp	53
	0·1 M $NaNO_3$ + 0·05 M $(C_2H_5)_4NCl$	22	—	$k_s = 1{\cdot}3 \times 10^{-5}$	—	dcp	53
	0·1 M $NaNO_3$ + 0·05 M $(C_4H_9)_4NCl$	22	—	$k_s = 1{\cdot}3 \times 10^{-8}$	—	dcp	53
	3 M KNO_3	25	$\alpha = 0{\cdot}57$ $\beta = 0{\cdot}59$	$k_s = 3{\cdot}0 \times 10^{-3}$ (cath) $k_s = 3{\cdot}5 \times 10^{-3}$ (anod)	—	op	39
	3 M KNO_3 + 0·002% gel.	25	$\alpha = 0{\cdot}59$ $\beta = 0{\cdot}54$	$k_s = 5{\cdot}8 \times 10^{-3}$ (cath) $k_s = 6{\cdot}2 \times 10^{-3}$ (anod)	—	op	39
	3 M KNO_3 + 0·004% gel.	25	$\alpha = 0{\cdot}59$ $\beta = 0{\cdot}50$	$k_s = 8{\cdot}7 \times 10^{-3}$ (cath) $k_s = 6{\cdot}2 \times 10^{-3}$ (anod)	—	op	39
	3 M KNO_3 + 0·006% gel.	25	$\alpha = 0{\cdot}59$ $\beta = 0{\cdot}45$	$k_s = 1{\cdot}1 \times 10^{-2}$ (cath) $k_s = 6{\cdot}2 \times 10^{-3}$ (anod)	—	op	39
	3 M KNO_3 + 0·008% gel.	25	$\alpha = 0{\cdot}59$ $\beta = 0{\cdot}36$	$k_s = 4{\cdot}6 \times 10^{-3}$ (cath) $k_s = 5{\cdot}5 \times 10^{-3}$ (anod)	—	op	39
	3 M KNO_3 + 0·01% gel.	25	$\alpha = 0{\cdot}59$ $\beta = 0{\cdot}31$	$k_s = 3{\cdot}0 \times 10^{-3}$ (cath) $k_s = 5{\cdot}5 \times 10^{-3}$ (anod)	—	op	39
	0·25 M Li_2SO_4	22	$\alpha = 0{\cdot}24$–$0{\cdot}28$	$k_s = 2{\cdot}4 \times 10^{-3}$	—	dcp	53
	0·25 M Na_2SO_4	22	—	$k_s = 2{\cdot}4 \times 10^{-3}$	—	dcp	53
	0·25 M K_2SO_4	22	—	$k_s = 1{\cdot}3 \times 10^{-3}$	—	dcp	53
	0·25 M Cs_2SO_4	22	—	$k_s = 4{\cdot}1 \times 10^{-4}$	—	dcp	53
Hg/0·002 M $ZnCl_2$	0·1 M KCl	1	$\alpha n(?) = 0{\cdot}66$	$k_{1/2} = 0{\cdot}52 \times 10^{-2}$ [a]	—	cp	83
	0·1 M KCl	23	$\alpha n(?) = 0{\cdot}80$	$k_{1/2} = 1{\cdot}23 \times 10^{-2}$ [a]		cp	83
	0·1 M KCl	38·5	$\alpha n(?) = 1{\cdot}40$	$k_{1/2} = 1{\cdot}55 \times 10^{-2}$ [a]		cp	83
	0·1 M KCl	50	$\alpha n(?) = 1{\cdot}46$	$k_{1/2} = 3{\cdot}24 \times 10^{-2}$ [a]	$\Delta H_s^* = 6$–8	cp	83
Hg/0·004 M $ZnCl_2$	0·1 M KCl	19	$\alpha n(?) = 0{\cdot}76$	$k_{1/2} = 1{\cdot}58 \times 10^{-2}$ [a]		cp	83
	0·1 M KCl	34	$\alpha n(?) = 1{\cdot}26$	$k_{1/2} = 1{\cdot}78 \times 10^{-2}$ [a]		cp	83
	0·1 M KCl	48	$\alpha n(?) = 1{\cdot}88$	$k_{1/2} = 3{\cdot}31 \times 10^{-2}$ [a]		cp	83
Hg/Zn(II)	1·0 M KCl [b]	15	$(\alpha n)_1 = 0{\cdot}88$ $(\alpha n)_2 = 0{\cdot}32$	$(k_{1/2})_1 = 0{\cdot}29 \times 10^{-2}$ [a] $(k_{1/2})_2 = 0{\cdot}42 \times 10^{-2}$ [a]	—	cp	83

[a] Rate constant at the theoretical half-wave potential.
[b] In 1 M KCl the log-plot gives two lines.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
	1·0 M KCl[a]	27·5	$(\alpha n)_1 = 1{\cdot}12$ $(\alpha n)_2 = 0{\cdot}38$	$(k_{1/2})_1 = 0{\cdot}34 \times 10^{-2}$ [b] $(k_{1/2})_2 = 0{\cdot}60 \times 10^{-2}$ [b]	—	cp	83
	1·0 M KCl[a]	37·5	$(\alpha n)_1 = 1{\cdot}48$ $(\alpha n)_2 = 0{\cdot}38$	$(k_{1/2})_1 = 0{\cdot}60 \times 10^{-2}$ [b] $(k_{1/2})_2 = 0{\cdot}93 \times 10^{-2}$ [b]	—	cp	83
	1·0 M KCl[a]	49·5	$(\alpha n)_1 = 1{\cdot}30$ $(\alpha n)_2 = 0{\cdot}46$	$(k_{1/2})_1 = 0{\cdot}83 \times 10^{-2}$ [b] $(k_{1/2})_2 = 1{\cdot}12 \times 10^{-2}$ [b]	—	cp	83
DME/Zn(II)	1 M KCl	—	$\alpha n = 0{\cdot}70$	$k_s = 3{\cdot}1_6 \times 10^{-3}$	—	op	58
	1 M KCl	25 ± 0·1	—	$k_s = 4{\cdot}0 \times 10^{-3}$	—	acp	49
	1 M KCl + 2 μM LEO	25	$\alpha = 0{\cdot}4$	$k_s = 3{\cdot}4 \times 10^{-3}$	—	fi	92
DME/1 mM $Zn(NO_3)_2$	1 M KCl + 2 μM LEO	25	$\alpha = 0{\cdot}31$	$k_s = 7{\cdot}0_9 \times 10^{-3}$	—	dcp	94
DME/Zn(II)	2 M KCl	25	$\alpha n = 1{\cdot}2$	—	—	dcp	20
	2 M NaCl	25	$\alpha n = 0{\cdot}7$	—	—	dcp	20
DME/1 mM $Zn(NO_3)_2$	0·01 M KCl + 0·99 M $NaClO_4$ + 2 μM LEO	25	$\alpha = 0{\cdot}31$	$k_s = 2{\cdot}8_2 \times 10^{-3}$	—	dcp	94
	0·10 M NaCl + 0·90 M $NaClO_4$ + 2 μM LEO	25	$\alpha = 0{\cdot}31$	$k_s = 3{\cdot}3_5 \times 10^{-3}$	—	dcp	94
	2·88 M KCl + 2 μM LEO	25	$\alpha = 0{\cdot}16$	$k_s = 4{\cdot}8_8 \times 10^{-3}$	—	dcp	94
	5·25 M $CaCl_2$ + 2 μM LEO	25	rev.	rev.	—	dcp	94
DME/Zn(II)	0·1 M $LaCl_3$	22	—	$k_s = 2{\cdot}5 \times 10^{-3}$	—	dcp	53
	1 M KBr	25 ± 0·1	—	$k_s = 8 \times 10^{-3}$	—	acp	49
DME/1 mM $Zn(NO_3)_2$	1 M KBr + 2 μM LEO	25	$\alpha = 0{\cdot}36$	$k_s = 10{\cdot}5 \times 10^{-3}$	—	dcp	94
DME/Zn(II)	1 M KI	25 ± 0·1	—	$k_s = 7 \times 10^{-3}$	—	acp	49
DME/1 mM $Zn(NO_3)_2$	1 M KI + 2 μM LEO	25	rev.	rev.	—	dcp	94
	0·01 M NaI + 0·99 M $NaClO_4$ + 2 μM LEO	25	$\alpha = 0{\cdot}28$	$k_s = 2{\cdot}7_8 \times 10^{-3}$	—	dcp	94
	0·10 M NaI + 0·90 M $NaClO_4$ + 2 μM LEO	25	$\alpha = 0{\cdot}25$	$k_s = 4{\cdot}7_6 \times 10^{-3}$	—	dcp	94
DME/Zn(II)	1 M KSCN	25 ± 0·1	—	$k_s = 1{\cdot}7 \times 10^{-2}$	—	acp	49
	1 M NaOH	20 ± 1	$\alpha = 0{\cdot}43$	$\log k_s = -3{\cdot}75$	—	dcp	8
	1 M NaOH	25 ± 0·1	—	$(k_s = 7{\cdot}4 \times 10^{-5})$	—	acp	49
	KCl + 0·1–1·8 M KOH ($\mu = 2$)	25	$\alpha = 0{\cdot}42 \pm 0{\cdot}02$	$\log (k_s)_B = -3{\cdot}3 \pm 0{\cdot}05$[c]	—	dcp	60
	2 M KOH	25	$\alpha n = 0{\cdot}4$	—	—	dcp	20
	2 M KOH + *ca* 0·01% gel.	25	$\alpha n = 0{\cdot}4$	—	—	dcp	20

[a] In 1 M KCl the log-plot gives two lines.
[b] Rate constant at the theoretical half-wave potential.
[c] Rate constant concerning the overall electrode reaction.

System	Medium	Temperature °C	Transfer coefficient	Rate constant	Heat of activation	Method	Ref.
	2 M NaOH	25	$\alpha n = 0{\cdot}8$	—	—	dcp	20
	2 M NaOH + *ca* 0·01% gel.	25	$\alpha n = 0{\cdot}5$	—	—	dcp	20
	0·25–2·8 M NH_3 + NH_4Cl	25	$\alpha = 0{\cdot}65 \pm 0{\cdot}02$	$\log (k_s)_B = -4{\cdot}9 \pm 0{\cdot}1$[a]	—	dcp	60
	1 N NH_3 + NH_4Cl	—	$\alpha n = 1$	—	—	op	12, 40
	1 N NH_3 + $(NH_4)_2SO_4$	—	$\alpha n = 1{\cdot}68$	$\log k_s = -4{\cdot}2$	—	op	40
	0·1 N KNO_3 + 1·185 N NH_3 + 0·01% gel.	25	$\alpha = 0{\cdot}77$	—	—	dcp	65
	0·1 N KNO_3 + 0·1–2·0 M en + 0·02% gel.	25	$\alpha = 0{\cdot}86$	$\log k_s = -4$ $\log k_c^\circ = -31{\cdot}2$[b]	—	dcp	66
	0·02–0·1 M $K_2C_2O_4$[c]	—	$\alpha = 0{\cdot}24$ $\beta = 0{\cdot}67$	—	—	dcp	8
DME/$ZnCl_2$	0·1–1·5 M tartrate + KCl	—	$\alpha = 0{\cdot}22$[d]	$(k_0)_B = 3{\cdot}4 \times 10^{-5}$ cm/s[e] $(k_2)_B = 3{\cdot}4 \times 10^{-4}$ (cm/s) × (mole/l)$^{-2}$ [f]	—	dcp	61

[a] Rate constant concerning the overall electrode reaction.
[b] Rate const. referred to 0 V *vs* NHE.
[c] The cathodic wave is composed of two overlapping waves. The value of α is that of the second wave. The slope of the first wave cannot be determined very accurately. The value of β was obtained from the slope of the anodic wave.
[d] In the concentration range of 0·09–1·5 M, α is independent of tartrate concentration.
[e] Rate constant of $Zn(tart)_0 + 2e \rightleftharpoons Zn(Hg)$ at the normal potential of the overall reaction.
[f] Rate constant of $Zn(tart)_2 + 2e \rightleftharpoons Zn(Hg) + 2(tart)$ at the normal potential of the overall reaction.

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